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<tbody>
<tr>
<td>acac</td>
<td>Acetylacetonate</td>
</tr>
<tr>
<td>An</td>
<td>Actinide</td>
</tr>
<tr>
<td>&quot;^BuLi</td>
<td>n-Butyllithium</td>
</tr>
<tr>
<td>CCI</td>
<td>Cation-Cation Interaction</td>
</tr>
<tr>
<td>C₆D₆</td>
<td>Per-deuterated Benzene</td>
</tr>
<tr>
<td>CD₂Cl₂</td>
<td>Per-deuterated Dichloromethane</td>
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<tr>
<td>CDCl₃</td>
<td>Per-deuterated Chloroform</td>
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<td>CHCl₃</td>
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<tr>
<td>Cp</td>
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<tr>
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<tr>
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<td>Dimethylsulphoxide</td>
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<tr>
<td>DOSY</td>
<td>Diffusion-Ordered Spectroscopy</td>
</tr>
<tr>
<td>Et₂O</td>
<td>Diethyl ether</td>
</tr>
<tr>
<td>hfac</td>
<td>Hexafluoro-Acetylacetonate</td>
</tr>
<tr>
<td>HMDS</td>
<td>Hexamethyldisilazane</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-Red</td>
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<tr>
<td>LDA</td>
<td>Lithium di-iso-propylamine</td>
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<tr>
<td>LHMDS</td>
<td>Lithium Hexamethyldisilazane</td>
</tr>
<tr>
<td>LMCT</td>
<td>Ligand to Metal Charge Transfer</td>
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<tr>
<td>Ln</td>
<td>Lanthanide</td>
</tr>
<tr>
<td>MeCN</td>
<td>Acetonitrile</td>
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<td>d₃-MeCN</td>
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<td>MeOH</td>
<td>Methanol</td>
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<tr>
<td>NaHCO₃</td>
<td>Sodium hydrogen carbonate</td>
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<tr>
<td>nIR</td>
<td>Near Infra-Red</td>
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<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>ORTEP</td>
<td>Oak Ridge Thermal Ellipsoid Plot</td>
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<tr>
<td>OTf</td>
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<tr>
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<td>Ph₃PO</td>
<td>Triphenylphosphine oxide</td>
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<tr>
<td>¹PrOH</td>
<td>Propan-2-ol</td>
</tr>
<tr>
<td>py</td>
<td>Pyridine</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethylsilane</td>
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<tr>
<td>TPIP</td>
<td>Tetraphenylimidodiphosphinate</td>
</tr>
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<td>F-TPIP</td>
<td>Per-fluoro Tetraphenylimidodiphosphinate</td>
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<tr>
<td>TRES</td>
<td>Time resolved Emission Spectrum</td>
</tr>
<tr>
<td>tta</td>
<td>Thenoylfluoroacetonediyacetone</td>
</tr>
<tr>
<td>UV/ vis</td>
<td>Ultraviolet/ Visible</td>
</tr>
<tr>
<td>VT</td>
<td>Variable Temperature</td>
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<td>XRD</td>
<td>X-ray Diffraction</td>
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## List of Symbols and Units

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<td>Å</td>
<td>Angstroms</td>
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<tr>
<td>a.u.</td>
<td>Arbitrary Units</td>
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<tr>
<td>°C</td>
<td>Degrees Celsius</td>
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<tr>
<td>°</td>
<td>Degrees</td>
</tr>
<tr>
<td>cm⁻¹</td>
<td>Wavenumber</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion Coefficient</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical Shift</td>
</tr>
<tr>
<td>ε</td>
<td>Molar Extinction Coefficient</td>
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<tr>
<td>g</td>
<td>Gram</td>
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<tr>
<td>h.</td>
<td>Hour</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>J</td>
<td>Coupling constant</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>Kg</td>
<td>Kilogram</td>
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<tr>
<td>λ</td>
<td>Wavelength</td>
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<tr>
<td>M</td>
<td>Mol dm⁻³</td>
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<td>m</td>
<td>Metre</td>
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<td>MHz</td>
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<tr>
<td>mM</td>
<td>Millimolar</td>
</tr>
<tr>
<td>mN</td>
<td>Millinewtons</td>
</tr>
<tr>
<td>ms</td>
<td>Millisecond</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometre</td>
</tr>
<tr>
<td>ns</td>
<td>Nanosecond</td>
</tr>
<tr>
<td>η</td>
<td>Solvent Viscosity</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per Million</td>
</tr>
<tr>
<td>r_H</td>
<td>Hydrated Spherical Radius</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>τ</td>
<td>Emission Lifetime</td>
</tr>
<tr>
<td>ν</td>
<td>Vibrational Mode</td>
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<td>μM</td>
<td>Micromolar</td>
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<td>μs</td>
<td>Microsecond</td>
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X-Ray Crystal Structure Colour Code

Alkali metal (Sodium or Potassium)
Carbon
Fluorine
Iodine
Neptunium
Nitrogen
Oxygen
Phosphorus
Silicon
Sulphur
Uranium
Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

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‘You must have long term goals to keep you from being frustrated by short term failures’ Charles C. Noble

‘Uranium chemistry is just harder than organic chemistry’ Dr R.J. Baker, May 2011

Remember guys, a PhD is completed in several steps. Or moonwalks, robots, cha-cha slides and macarenas…
Abstract

Nuclear power currently plays a significant role in today’s balanced energy portfolio. However, with this expansion, comes the need for improved methods to characterise and manage radioactive wastes arising from fission activities throughout the fuel cycle, and the need for fundamental research into all aspects of the nuclear fuel cycle. Whilst the chemistry of actinides is enjoying a renaissance, in particular the study of unusual oxidation states which were previously unobtainable, many fundamental properties of the actinides remain unknown.

This thesis explores the coordination chemistry and emission spectroscopy of a selection of actinides (U to Cm) with a view to accessing the unstable \( f^1 \) oxidation states of uranium and neptunium. In particular, the role of cation-cation interactions (CCIs) on the stability, redox and spectroscopic properties has been addressed. Work on the luminescence of uranyl(VI) complexes has led to an increased understanding of the non-aqueous solution behaviour of the actinyl ion, in particular by fingerprinting/identifying complexes bearing cation-cation interactions. The uranyl(VI) LMCT emission profiles are observed to significantly red shift when CCIs are present, accompanied by a drastic reduction in the radiative lifetime. These observations have been supported by the increasingly effective diffusion-ordered nuclear magnetic resonance technique. This leads to the conclusion that uranyl(VI) cation-cation interactions unsupported by bridging ligands are unstable in solution.

Attempts to isolate stable uranyl(V) complexes of tetraphenylimidodiphosphinate (TPIP) and the fluorinated acacs have proved difficult. The TPIP ligand has shown an unprecedented preference to stabilise NpO\(_2\)(VI). From these observations, it has been possible to conclude that TPIP has a strong preference for the actinyl(VI) oxidation states.

A preliminary study on the minor actinides Am and Cm in the +III oxidation state has taken place and allowed preliminary comparisons between a novel series of bis-trialkylsilyl bipyridyl and phenanthroline ligands, which have been designed in an attempt to study the effect of steric bulk in supporting unusual oxidation states of the actinides. An initial study of these ligands with AnO\(_2\)(V) and AnO\(_2\)(VI) (An = U and Np) has also taken place.
Chapter 1

Introduction
1.1 Background

Human activity and its influence in climate change has led to the need for alternative energy supplies that can meet the current energy demand.\cite{1,2} With its low carbon footprint and high energy efficiency, nuclear power is seen as a viable alternative to traditional fossil fuels in a balanced mix of long-term energy strategies.\cite{1,2} However, the elements that form the energy source for nuclear power, the actinides, are a comparatively unknown group of elements, particularly with respect to their neighbouring lanthanides and the d-block transition metals. This is due to their infancy in the modern periodic table and the specialised techniques that are required to handle them.\cite{3}

1.1.1 A historical perspective

The actinide elements (denoted An) range from thorium to lawrencium (or from actinium under the IUPAC actinoid classification)\cite{4} and are situated beneath the lanthanide ‘rare earth’ series at the bottom of the modern periodic table (Fig. 1.01). Together they comprise the f-elements.

![Fig. 1.01 The modern periodic table. Taken from reference [5].](image-url)

The first of the f-elements to be discovered was uranium in 1789 by Martin Klaproth in the mineral pitchblende.\cite{3} The last of the naturally occurring elements (although non-primordial Np and Pu can be found by natural nuclear reactions in the Earth’s crust),\cite{3,6-8} uranium first found use intriguingly as a glass colourant by the Romans, unaware of the then undiscovered element it contained.\cite{9} It is also the element with which Becquerel discovered radioactive decay in the late 19th century.\cite{3} However, it is with the discovery of nuclear fission in 1939 that uranium has had such an impact on today’s society.\cite{10,11}
During the fission of $^{235}\text{U}$, atoms are converted into smaller fissile particles, resulting in the release of energy according to Equation 1.1.$^{[12]}$

$$E = Mc^2$$

Equation 1.1. $E =$ energy, $M =$ mass and $c =$ the speed of light.$^{[12]}

This meant uranium presented an energy source vastly more efficient than any before it, and by 1942 Fermi and his co-workers developed the means by which the energy might be harnessed when they constructed the first nuclear reactor in a squash court at The University of Chicago.$^{[13]}$ Further work headed by J. Oppenheimer in the Manhattan project led to the realisation of nuclear power when ‘little boy’ was dropped on Hiroshima on August 6th, 1945.$^{[14]}$ Soon after, the plutonium based ‘fat man’ was dropped on Nagasaki to similar devastating effect. After the Second World War, focus changed to the generation of electricity from nuclear energy, culminating in the construction of Calder Hall at Sellafield; the first power station in the world to produce electricity derived from nuclear energy on an industrial scale.$^{[15]}

1.1.2 The nuclear fuel cycle

The process of obtaining energy from radioactive materials has many steps, from mining the ore to disposing of the waste, briefly summarised in Fig. 1.02.$^{[16]}$ Of interest to actinide chemists are the reprocessing (coloured yellow) and disposal (blue) steps.

Reprocessing of materials involves the re-use of fissionable isotopes and processes involved are heavily dependant on the chemistry of the elements involved, particularly with respect to the different oxidation states of each actinide ion.$^{[17]}$ The PUREX process (Plutonium and Uranium Refinement by Extraction) is perhaps the most well established example.$^{[18]}$ Uranium and plutonium are selectively extracted from nitric acid into kerosene by tri-$n$-butylphosphate due to their preference for the $+VI$ and $+IV$ oxidation states respectively, a characteristic not shared by neptunium and other actinides.$^{[18]}$
The disposal of radioactive waste is a major issue in today’s society because of the severe damage that exposure to radioactive material can cause to the human body and the environment.\textsuperscript{[3,19-21]} The disposal of each of these products varies in detail, but the fundamental idea remains the same; deposition in an area which poses as a geological barrier and use of man-made barriers for extra protection.\textsuperscript{[13]} Immobilisation of higher level waste in a solid structure (e.g. ceramic material) followed by storage in a deep geological deposit is often seen as the most valid route for its disposal.\textsuperscript{[13]} An example of such a deposit is the Yucca mountain site in Nevada which was approved for the disposal of high level activity waste by the United States senate in 2002\textsuperscript{[25]} until the Obama administration rejected it in 2010.\textsuperscript{[26]}

1.1.3 Nuclear waste

Radioactive waste is classified as high, low or intermediate depending on the level of radioactivity. The disposal of each of these products varies in detail, but the fundamental idea remains the same; deposition in an area which poses as a geological barrier and use of man-made barriers for extra protection.\textsuperscript{[13]} Immobilisation of higher level waste in a solid structure (e.g. ceramic material) followed by storage in a deep geological deposit is often seen as the most valid route for its disposal.\textsuperscript{[13]} An example of such a deposit is the Yucca mountain site in Nevada which was approved for the disposal of high level activity waste by the United States senate in 2002\textsuperscript{[25]} until the Obama administration rejected it in 2010.\textsuperscript{[26]}

Fig. 1.02. A summary of the nuclear fuel cycle. Taken from reference [16].
One of the main concerns in the disposal of waste is that, despite intended natural and artificial protection, radioactive elements will still migrate away from the site.\textsuperscript{[13]} The main mechanism for this is through the action of water;\textsuperscript{[18,22]} uranium stored in solid phases is oxidised from the +4 oxidation state to the aquatically mobile +6 state by the action of groundwater.\textsuperscript{[18,22,27]} This migration will contribute to radioactive environmental pollution along with, for example, waste from mining operations,\textsuperscript{[28]} fallout from nuclear weapons testing\textsuperscript{[13,24]} and dispersed radiation arising from accidental release such as the Chernobyl\textsuperscript{[13]} and Fukushima incidents.\textsuperscript{[21]}

The study of the actinides is therefore an important issue. However, the wide range of oxidation states displayed by the actinides\textsuperscript{[29]} renders this a difficult task.

1.2 Actinide Oxidation States

1.2.1 Overview

When J. Gadolin discovered Yttria in 1794 he believed it to be the oxide of a new element.\textsuperscript{[29]} It transpired to consist of 10 new elements from the lanthanide group. The lanthanides are difficult to separate from one another\textsuperscript{[4]} due to their strong affinity for the +3 oxidation state and resulting reasonably similar chemistry.\textsuperscript{[29]} This arises from the fact that the $f$-orbitals lie buried within the core orbitals; once the 5$d$ and two 6$s$ electrons have been removed the $f$-orbitals are not usually accessible for the removal of a fourth electron.\textsuperscript{[4]} In contrast, the actinides can exist in a greater variety of oxidation states as depicted in Table 1.1. This is particularly true for the early actinides. Since the 5$f$ orbitals receive greater shielding from the nucleus (in comparison to the 4$f$ orbitals of the lanthanides), the energy separation between them and the 6$d$, 7$s$ and 7$p$ orbitals decreases and thus they are able to act as valence electrons.\textsuperscript{[4,30]} As the series is traversed, the orbital energy of the 5$f$ electrons decrease and consequently the electrons are less available for bonding, resulting in ‘lanthanide-like’ chemistry and also the ‘actinide contraction’.\textsuperscript{[4,30,31]}
Table 1.1. The oxidation states of the actinides.\textsuperscript{[4]} An denotes the most stable oxidation states of that element. *Taken from references [32-34]

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<th>An</th>
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| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

1.2.2 Relativity and covalency

Albert Einstein proposed his special theory of relativity in 1905.\textsuperscript{[35]} In the paper it is explained that it is impossible to accelerate a body beyond the speed of light and that as a body is accelerated, its mass increases (Equation 1.2).

\[ m = \frac{m_0}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} \]

Equation 1.2. A simplified expression of Einstein’s equation.\textsuperscript{[38]}

For smaller elements, the effects of this on electrons orbiting the nucleus are negligible. However, in larger nuclei the increased charge of the nucleus is such that it leads to an increase in velocity of the s electrons and subsequent contraction of the orbital radius. Whilst this has an energetically stabilising effect on the s electron, this in turn generates a destabilising effect on the d and f orbitals.\textsuperscript{[29,36]} The heavier actinides experience greater relativistic effects than their lanthanide counterparts (Fig. 1.03), which leads to a greater effect on the chemistry of the actinides. Fig. 1.04 depicts the orbital density distribution of Sm\textsuperscript{3+} and Pu\textsuperscript{3+} (as plots of radial distribution of electron density),\textsuperscript{[30]} exhibiting the increased contraction of the 7s orbital in plutonium compared to 6s in samarium alongside the increased extension of the comparative f orbitals. The contribution of relativistic effects on the increased bonding capabilities of f (and d) orbitals in the actinides is therefore quite significant.
Fig. 1.03 Ratio of the the radii (r) of the 6s electrons by relativistic (R) and non-relativistic calculations (NR) of the heavier elements in the periodic table. Adapted from reference [37].

Fig. 1.04 A comparison between orbital density distribution in Pu$^{3+}$ and Sm$^{3+}$. P is the radial probability of finding an electron at a given distance from the nucleus. Taken from reference [30].
The increased radial extension of the 5f orbitals to interact in chemical reactions gives the early actinides a degree of covalency in their bonding interactions\[4\] (with given ligands) and is responsible for their ability to exist in multiple oxidation states.

The ability of the actinides to form covalent bonds is crucial to their chemistry and understanding their roles in the nuclear fuel cycle. It is generally accepted that the heavier actinides (transplutonium) experience a significantly lower degree of covalent bonding.\[31,38,39\] The greater covalency of the actinides compared to the lanthanides is also key; with separation of the two thought to be of great importance in liquid-liquid reprocessing strategies.\[40\] The differences in their chemistry resulting from the actinides ability to form bonds of a more covalent nature are fundamental in attempts to perform separations, allowing ligand design which favours such interaction.\[41-43\] However, the presence and degree of covalency in metal-ligand bonds in transplutonium compounds and how this affects separations from trivalent lanthanides is still a matter of great debate.

1.2.3 Effect of oxidation state

The oxidation states of the actinides are fundamental to their chemical and physical properties. This is perhaps most noticeable in Fig. 1.05 where the colour of aqueous neptunium samples changes considerably upon alteration of oxidation state.\[44\] Different oxidation states of an actinide also bear different orbital energy levels in their electronic structures.\[45\]

![Fig.1.05 The change in oxidation state of an actinide affects the absorption spectrum considerably. Aqueous neptunium samples are displayed here. Taken from reference [44].](image-url)
Most actinides in higher oxidation states have a tendency to exist as a dioxo species; \( \text{AnO}_2^{n+} \) (\( n = 1-3 \)).\(^{[29]} \) These are known as actinyl ions, and are the dominant species of the actinides in non-reducing environment conditions.\(^{[13]} \)

1.3 Actinyl Ions

1.3.1 The linear nature of the actinyl moiety

In contrast to di-oxo species of the transition metals, which tend to exist in a cis arrangement,\(^{[29,46]} \) actinyl ions tend to exist in a linear O=An=O fashion,\(^{[29,45,47]} \) with the exception of the matrix-isolated cis \( \text{ThO}_2 \).\(^{[45]} \) The linear geometry is favoured due to the similar energy of the 5f orbital and the oxygen 2p orbital with which it bonds.\(^{[45]} \) A decrease in energy of the 2p orbital would lead to a bent geometry, however it is interaction of the uranium 6d orbital with the oxygen 2s and 2p orbitals that renders the oxygen 2p orbital of similar energy to the uranium 5f orbital.\(^{[45]} \) Of importance in the linearity of the actinyl ions is the inverse trans-influence; observed in studies on actinide mono-oxo species.\(^{[48-50]} \) Seen most simply in AnOX\(_5\) complexes (where X = F, Cl, Br or I), the halogen situated trans to the oxygen displays the strongest bond with the actinide, in comparison to the halogens located cis to the oxygen.\(^{[45,49]} \) The inverse trans-influence is said to play a role in strengthening the trans configuration of the actinyl oxygens.

Of all the early actinides that form actinyl ions in their higher oxidation states (U-Am), uranium is the least radioactive and therefore most widely studied. The uranyl ion has five known accessible oxidation states (see Table 1.1): +2 to +6. Uranyl species in the +3 and +4 oxidation state have been observed in low temperature inert element solid matrices by infra-red spectroscopy.\(^{[51,52]} \) These are the only examples, however, and only uranyl in higher oxidation states (+5, +6) are found in less enforced and specific conditions (such as in solution).\(^{[3,53]} \) Of these, uranyl(VI) is the most thermodynamically stable.

1.3.2 Uranyl(VI)

The molecular orbital diagram of the \( \text{UO}_2^{2+} \) moiety\(^{[45,47]} \) (Fig. 1.06) shows the contribution of the 5f and 6d orbitals to bonding with the oxygen 2p orbitals, giving uranyl(VI) (and other actinyl ions) a strong expression of covalent bonding between the uranium and oxygen.\(^{[30]} \) Uranyl(VI) has no f-electrons and so all electrons in the bonding come from the oxygen 2p orbitals; 6 electrons from each oxygen resulting in a formal triple bond. This is
evidenced by the short bond lengths usually found for uranyl (and actinyl) units (typically between 1.7 and 1.9 Å).\(^{[29]}\)

![Molecular orbital diagram of UO\(_2^{2+}\). Redrawn from references [45,47].](image)

The formal triple bond between the uranium and oxygen renders the uranyl bond very strong, with a bond dissociation energy of 701 kJmol\(^{-1}\) for UO\(_2^{2+}\) comparable to the strongest transition metal dioxides and CO\(_2\) (802 kJmol\(^{-1}\)).\(^{[45]}\) The U=O bond is reasonably kinetically inert under most conditions\(^{[54,55]}\) (with the exception of aggregated hydroxide species and highly acidic conditions)\(^{[3,55-57]}\) and is considered to be thermodynamically stable,\(^{[47]}\) with the uranyl moiety generally remaining preserved during chemical reactions.\(^{[53]}\) Indeed, one report that claimed to have synthesised a cis-uranyl complex by reacting a uranyl hydroxide complex with a ferrocene-based compound was subsequently questioned and dismissed due to questionable NMR and crystallographic data.\(^{[58,59]}\)

### 1.3.3 The other actinyl ions

It is reasonable to assume that uranyl(VI) may exhibit (one of) the strongest of the An=O bonds; subsequent actinyl groups will have 5\(f\) electrons to contribute to bonding (such as uranyl(V), neptunyl(VI)), which would result in a lower charge density of the metal ion and subsequent weaker interaction with the electronegative oxygen atoms. Indeed, longer bond lengths are exhibited by uranyl(V) compounds (vs. uranyl(VI))\(^{[60,61]}\) and also greater
kinetic lability of the uranyl oxygens in aqueous and acidic solutions\textsuperscript{[62]} would suggest a less inert actinyl moiety. A calculated molecular orbital diagram for neptunyl(VI) in [NpO\textsubscript{2}Cl\textsubscript{4}]\textsuperscript{2-} confirms the entry of an electron into a non-bonding orbital (Fig. 1.07).\textsuperscript{[63]} However, work on the comparative rates of oxo-atom exchange for uranyl(V), plutonyl(V) and neptunyl(V) indicate uranyl(V) to exhibit the most kinetically labile actinyl oxo-atoms of the trio,\textsuperscript{[64]} thus comparison between the actinyls by addition of electrons to non-bonding orbitals is perhaps not so straightforward, even taking into account the increase in charge density across the series.

![Fig. 1.07](image)

Fig. 1.07 The molecular orbital diagram of [NpO\textsubscript{2}Cl\textsubscript{4}]\textsuperscript{2-}. Redrawn from reference [63].

The molecular orbital diagram of [NpO\textsubscript{2}Cl\textsubscript{4}]\textsuperscript{2-} parallels that of UO\textsubscript{2}\textsuperscript{2+}, with the strong actinyl bond described by the filling of bonding orbitals from electrons in oxygen 2\textit{p} orbitals. The strength of the actinyl bonds are such that that the actinyl di-oxo species is the preferred configuration for all the early actinides (that are capable of forming di-oxo ions) except protactinium(V), which is more stable as a terminal mono-oxo than di-oxo species.\textsuperscript{[65]}

The strength of the actinyl bond, and full electronic configuration in molecular bonding orbitals, means that the majority of the coordination chemistry of actinyl ions occurs in the equatorial plane, coordinating in an electrostatic fashion (vs. the An=O bond). However,
the role of orbital overlap with the non-bonding orbitals in the molecular orbital diagram may be significant.\cite{30,47,53}

1.4 Actinyl Coordination Chemistry

1.4.1 The equatorial plane

Actinyl coordination chemistry typically observes a coordination number between 4 and 6 in the equatorial plane (Fig. 1.08)\cite{53} although 3 has been observed in the presence of sterically demanding ligands.\cite{66} The most common equatorial coordination number is 5, forming pentagonal bipyramidal complexes.\cite{3,53} with the coordination number and geometry determined by both steric and electronic effects.\cite{3}

![Fig. 1.08 Possible geometries of actinyl complexes determined by equatorial coordination number. Redrawn from references [53,66].](image)

Because of the more ionic nature of the equatorial bonds (compared to the An=O bond), ‘hard’ donors are preferred in the equatorial plane, such as oxygen and nitrogen donors and the lighter halides. Ligands with strong electron donation (such as hydroxides)\cite{67} in the equatorial plane have the effect of lengthening and weakening the actinyl An=O bonds.\cite{67,68} This is common in strong σ-donating ligands\cite{68,69} and in the case of uranyl(VI) can result in activation of the uranyl oxygen to interact with Lewis acids.\cite{68,69} This is presumably through the increase in electron density at the uranium centre resulting in an electronic repulsion towards the ‘yl’ oxygens,\cite{69} and a subsequent decrease in strength of the covalent uranyl bond.\cite{68}

1.4.2 Uranyl(VI) Lewis acid-base adducts and cation-cation interactions (CCIs)

The action of the uranyl oxygen as a Lewis base gives rise to uranyl chemistry that contradicts the convention of an inert uranyl moiety.\cite{53} This is demonstrated by the use of the ligand (SiMe₃N)₂CPh in work by Sarsfield (Scheme 1.1).\cite{70} The complex UO₂((SiMe₃N)₂CPh)₂THF was prepared by reaction of the ligand with uranyl chloride. The use of Raman spectroscopy highlights the lengthening and weakening of the uranyl bond
with the symmetric ($\nu_1$) stretch (see Section 1.8.1) recorded at 803 cm$^{-1}$ (c.f. 840 cm$^{-1}$ for the uranyl chloride reactant). This is then able to react with B($C_6F_5)_3$ to form a Lewis acid-base adduct between a uranyl oxygen and an electron deficient boron centre. The elongation of the uranyl bond is also apparent in the X-ray crystal structure; a significantly altered bond length of 1.898(3) Å is observed for the elongated bond, compared to 1.770(3) Å for the unperturbed bond.$^{[70]}

![Scheme. 1.1 The reaction of uranyl with B($C_6F_5)_3$ to form a Lewis acid-base interaction.$^{[70]}$](image)

In a similar reaction, uranyl in UO$_2$((SiMe$_3$N)$_2$CPh)$_2$THF is able to coordinate to a sodium cation by reaction of uranyl chloride with the sodium salt of the ligand, therefore the uranyl oxygen is interacting with a cation.$^{[71]}$ The Arnold group$^{[72]}$ have investigated the ability of the uranyl(VI) moiety to form intramolecular CCIs using an expanded porphyrin macrocycle, which contorts in such a fashion upon coordination to a uranyl(VI) cation that the resulting complex is referred to as ‘pacman’. Addition of a transition metal (Mn(II), Fe(II), Co(II)) results in the occupancy of said metal in the lower ‘jaw’ of the pacman complex. Both metals are held in close proximity to one another and the divalent transition metal interacts with the uranyl oxygen (Fig. 1.09), resulting in the first synthetic uranyl-transition metal interaction through the ‘yl’ oxygen (measured around 2.1 Å, depending on the metal). Further work has shown that this is not an anomalous occurrence,$^{[69]}$ such as the U=O-Zn-O=U bonds observed in the extended diphosphinate solid framework.$^{[73]}$ At an average of 2.274(11) Å, the Zn-O bonds are slightly longer than that seen for the intramolecular interactions in the ‘pacman’ complex.$^{[72,73]}$
Unsurprisingly, the basicity of the ‘yl’ oxygens are such that they can also act as hydrogen-bond acceptors, especially in extended solids.\(^{[69,74]}\)

Under certain conditions, and notably in the absence of other Lewis acids or cations, uranyl(VI) can coordinate to a neighbouring uranyl in a CCI. However, examples of such in discrete molecules are rare for uranyl(VI).\(^{[69]}\) One example is the trimetallic complex \([\text{UO}_2(\text{TPIP})_2]_3\) (TPIP = tetraphenylimidodiphosphinate)\(^{[75]}\) (see Chapter 2), where two terminal uranyl moieties are coordinated in the equatorial plane by three TPIP ligands (one terminal, two bridging) and a CCI from a bridging uranyl in a T-shaped CCI (Fig. 1.10). Examples in solution are rare,\(^{[69]}\) although one further example sees the formation of the tetrametallic \([\text{UO}_2(\text{OCH}[\text{Pr}_2])_2]_4\) from the reaction of uranyl chloride and the potassium alkoxide.\(^{[76]}\) The oligomer is assembled by T-shaped CCIs and bridging alkoxide interactions. The (U=O)-U bond length of 2.435(4) Å is longer than that seen for interaction of uranyl(VI) with a transition metal,\(^{[72,73]}\) representative of the larger uranium ion. The bond angle around the CCI is severely deviated from linearity at 116.7(2)°.\(^{[76]}\) More uranyl(VI) CCIs can be found in extended solids,\(^{[77-79]}\) with the uranyl moieties contributing in a T-shaped CCI, the dominant form of CCIs in uranyl(VI).\(^{[69]}\)

![Diagram](image)

**Fig. 1.09** The uranyl-transition metal interaction in the ‘pacman’ complex. Taken from reference [72].
1.4.3 Uranyl(V) CCIs

In contrast to uranyl(VI), uranyl(V) forms CCIs more readily and may not necessarily need strong σ-donating ligands in the equatorial plane. This is likely due to the extra electron located on the uranium, providing electronic repulsion to the oxygen. Work by the Mazzanti group has resulted in the elucidation of several uranyl(V) complexes that display both T-shaped and diamond CCIs (Fig. 1.10). In addition, many of the complexes that display T-shaped CCIs form a tetrameric array and the uranyl units are also coordinated to potassium cations (as a result of the synthetic procedure, Fig. 1.11). The solid state structures of many other uranyl(V) complexes elucidated display coordination to alkali metals, such as the one-dimensional coordination polymer $\{[\text{UO}_2(\text{py})_3][\text{KI}_2(\text{py})_2]\}_n$, where pentagonal bipyramidal $[\text{UO}_2(\text{py})_3]$ units are joined by bridging potassium ions, charge balanced by iodide (Fig. 1.11). Comparison of bond length data between these and analogous uranyl(VI) complexes reveals a significant lengthening of the uranyl bond for uranyl(V). For example, $\{[\text{UO}_2(\text{py})_3][\text{KI}_2(\text{py})_2]\}_n$ exhibits uranyl bond lengths of 1.834(2) and 1.836(2) Å, 0.08 Å longer than $[\text{UO}_2\text{I}_2(\text{py})_3]$. This elongation of the bond is indicative of a weaker uranyl U=O bond compared to uranyl(VI), and is implicative of its role in the more readily coordinative uranyl(V) oxygen.

Fig. 1.11 View of left the tetrameric uranyl(V) complex and right the one-dimensional uranyl-cation polymer. All equatorial geometry, solvent and counter ions omitted. Adapted from references [82,83].

1.4.4 Neptunyl(V/VI) CCIs

In applying similar anhydrous synthetic techniques to neptunyl(V) chemistry as used for uranyl(V), the Mazzanti group have been able to prepare neptunyl(V) complexes that are isostructural to their uranyl(V) analogues. The one-dimensional neptunyl(V) polymer $\{[\text{NpO}_2(\text{py})_3][\text{KI}_2(\text{py})_2]\}_n$ is similar in composition to $\{[\text{UO}_2(\text{py})_3][\text{KI}_2(\text{py})_2]\}_n$. 
incorporating neptunyl-potassium interactions. The tetrameric complex \([\{\text{NpO}_2(\text{salen})\}_4(\mu_8-\text{K})_2][\text{K}(18\text{C}6)(\text{py})_2]\) follows the geometry of the uranyl(V) tetramer in Fig. 1.11. The increased Np=O bond length for oxygen participation in CCIs is evident from the X-ray crystal structure of \([\{\text{NpO}_2(\text{salen})\}_4(\mu_8-\text{K})_2][\text{K}(18\text{C}6)(\text{py})_2]\), with average bond lengths of 1.877(2) and 1.830(2) Å for those participating in CCIs and those not respectively.

Other reports highlight the diversity of CCIs displayed by neptunyl(V) in the solid state, with approximate diamond shaped CCIs and T-shaped CCIs leading to extended (Fig. 1.12) one-, two- or three-dimensional structures.

![Fig. 1.12 Ribbon sheet neptunyl(V) CCIs. Adapted from reference [88].](image)

Similar to uranyl(VI/ V) chemistry, neptunyl(VI) does not display CCIs as readily as neptunyl(V). In fact, to date there is only one report of the solid state structure of a neptunyl(VI) oxygen participating in a CCI. Sheets of neptunyl(VI) borates, \(\text{Na}[(\text{NpO}_2)_2\text{B}_{15}\text{O}_{24}(\text{OH})_6(\text{H}_2\text{O})](\text{ClO}_4).0.75\text{H}_2\text{O}\), are joined by CCIs between neptunyl moieties in an approximate T-shaped geometry. Following on from the trend seen for uranyl(V/ VI) and neptunyl(V), the bond lengths for neptunyl(VI) moieties interacting in CCIs are measured at 1.87(1) Å, 0.07 Å longer than isolated Np=O bonds.

### 1.4.5 Transneptunium and mixed An CCIs

CCIs also exist for plutonyl(V) and americyl(V), however only one report of a structurally characterised plutonyl(V) CCI exists, with a further example assigned by comparison with a neptunyl analogue.
CCIs exist for americyl(V) interacting in aqueous solution with neptunyl(VI) and uranyl(VI), similarly for plutonyl(V) and uranyl(VI). Aqueous solutions of neptunyl(V) and uranyl(VI) also exhibit CCIs. Indeed, the 1962 report of neptunyl(V)-uranyl(VI) ‘specific interactions’ is the first report of CCIs, where Sullivan et al. determined a single neptunyl(V)-uranyl(VI) species in the reduction of neptunyl(VI) by uranium(IV), utilising NMR relaxation methods alongside potentiometric and spectrophotometric measurements to ascertain that the uranyl(VI) and neptunyl(V) centres directly communicate. The analytical nature of these investigations means there is yet to be a mixed actinyl CCI crystal structure elucidated, and at present the exact coordination geometry of the CCI is unknown, although it may be anticipated that a neptunyl(V) oxygen coordinates to the uranyl(VI) equatorial plane due to the high and low affinities for CCIs of neptunyl(V) and uranyl(VI) respectively.

### 1.4.6 Mixed oxidation state CCIs.

During work on the study of neptunyl(V)-uranyl(VI) CCIs, the formation of neptunyl(V)-neptunyl(VI) CCIs were also presented. Such an interaction has recently been structurally characterised in work by Cornet et al. The structure of \([\{\text{Np}^{VI}\text{O}_2\text{Cl}_2\}\{\text{Np}^{IV}\text{O}_2\text{Cl}^{(\text{THF})}_3\}]_2\) (Fig. 1.14) connects two neptunyl(V) centres to neptunyl(VI) via coordination of neptunyl(V) oxygens to the neptunyl(VI) equatorial plane in approximate T-shaped geometries.
The propensity of actinyl(V) ions to aggregate via CCIs is demonstrated in reports of compounds of mixed oxidation state NpO$_2$(V)-Np(IV)\textsuperscript{[99]} and UO$_2$(V)-U(IV).\textsuperscript{[100]} In the former a six-membered ring is constructed by neptunyl(V) CCIs and extended into a third dimension by coordination through an ‘yl’ oxygen to Np(IV) (Fig. 1.15).\textsuperscript{[99]} The latter features a one dimensional polymer of uranyl(V) units connected by U(IV) atoms between uranyl oxygens.\textsuperscript{[100]} Neither example can be classified as T or diamond shaped according to the nomenclature in Fig. 1.10 due to the spherical actinide(IV) cation, however the topology resembles an almost linear bond between (O=An=O)-An in each case.

Reports of complexes involving uranyl(V)-uranyl(VI) CCIs are rare.\textsuperscript{[101]} The complex \{[UO$_2$(salen)]\textsubscript{µ-K}(18C6)\}$_3$[UO$_2$(salen)]$_3$(µ$_8$-K)$_2$ consists of three uranyl(V) and one uranyl(VI) centre(s) arranged in a tetrameric manner, supported by interstitial potassium cations (Fig. 1.11). All four uranyl moieties donate an ‘yl’ oxygen to coordinate to a neighbouring uranium in a CCI, including that of uranyl(VI).\textsuperscript{[101]} The uranyl(VI) cation can be identified amongst the uranyl(V) by the shorter bond lengths; 1.804(12) and 1.862(14)
Å vs. 1.833(12) Å, 2.022(11) Å, 1.797(14) and 1.941(12) Å and 1.863(13) and 1.964(12) Å.\textsuperscript{[101]}

Overall, actinyl(V) is the dominant form of the actinyl ions that participate in CCIs, though an increasing number of actinyl(VI) CCIs are being discovered. Of particular importance is the potential role CCIs play in the disproportionation reaction of actinyl(V) chemistry.

1.5 The Disproportionation Reaction

The uranyl(V) cation is known to disproportionate into uranyl(VI) and uranium(IV), and is proposed to proceed by the presence of protons\textsuperscript{[102]} which coordinate to the ‘yl’ oxygens\textsuperscript{[103]} (Equation 1.3). This reaction is considered to be mediated by an ‘inner-sphere’ electron transfer between uranyl(V) centres joined by CCIs.\textsuperscript{[103]} the plutonyl(V) cation follows a similar reaction pathway,\textsuperscript{[102]} however the kinetics are more complex and Pu(III) is found as one of the disproportionation products alongside Pu(IV) and plutonyl(VI).\textsuperscript{[104]}

\[ 2\text{UO}_2^+ + 4\text{H}^+ \rightarrow \text{U}^{4+} + \text{UO}_2^{2+} + 2\text{H}_2\text{O} \]

\textit{Equation 1.3. The disproportionation reaction of uranyl(V).}\textsuperscript{[102]}

Conversely, neptunyl(V) does not follow this CCI orientated disproportionation pathway,\textsuperscript{[103]} and is stable in aqueous solutions except at low pH with high \([\text{Np}^{\text{V}}\text{O}_2]^3\)]\textsuperscript{[3]} with aqueous complexes of neptunyl(V) displaying comparatively stable CCIs.\textsuperscript{[105]} Neptunyl(V) is therefore generally considered to be more stable than its uranyl(V) and plutonyl(V) neighbours.\textsuperscript{[3]} Instead, neptunyl(V) disproportionates more readily in organic solvents (such as kerosene).\textsuperscript{[106]} Studies of americyl(V) complexes are rare, however disproportionation reactions of americium(IV), americyl(V) and americyl(VI) have been reported.\textsuperscript{[3]}

The disproportionation of uranyl(V) is rapid in aqueous solutions\textsuperscript{[107]} but being less radioactive than Np and Pu is still therefore subject to much study, despite this limitation.

1.6 Uranyl(V)

1.6.1 Occurrence

Uranyl(V) is unstable due to its propensity to disproportionate and also its facile oxidation to uranyl(VI).\textsuperscript{[61]} However, this instability has presented uranyl(V) as a key intermediate\textsuperscript{[108]} in the bioreduction of environmentally mobile uranyl(VI) to the immobile
uranium(IV); \textsuperscript{109} via the CCI mediated disproportionation of uranyl(V), \textsuperscript{108,110} which is formed from the one electron reduction of uranyl(VI). \textsuperscript{108} Studies of solid state structures have shown that uranyl(V) can be stabilised in extended solids in ceramics, \textsuperscript{111} minerals, \textsuperscript{112,113} and marine sediments. \textsuperscript{114} Therefore uranyl(V) presents an oxidation state of uranium of which little is known yet there is need for its comprehension.

Additionally, its use as a less radioactive surrogate for neptunyl(V) and plutonyl(V) is important due to the environmental significance of both of the transuranic actinyl(V) cations, \textsuperscript{115} including the bioreduction of plutonyl(VI) by the same or similar mechanisms as uranyl(VI). \textsuperscript{116} Neptunyl(VI) does not reduce to neptunium(IV) in the same manner (i.e. with the same bacteria) due to the aquatic stability of neptunyl(V) complexes with CCIs. \textsuperscript{108,116}

\textbf{1.6.2 Stabilising the uranyl(V) cation}

Whilst uranyl(V) has been stabilised previously in concentrated carbonate media (pH = 11.95), \textsuperscript{117} the study of uranyl(V) complexes only began in the early 21\textsuperscript{st} century by the fortuitous discovery of [UO$_{2}$(OPPh$_{3}$)$_{4}$](OTf). \textsuperscript{118} The complex was isolated under anaerobic conditions after standing in direct sunlight, and it is only in the absence of water and oxygen that uranyl(V) can be isolated. \textsuperscript{61} Several years later, the isolation of [{[UO$_{2}$(py)$_{5}$][KI$_{2}$(py)$_{2}$]}$_{n}$ (Fig. 1.16) by an overall two electron oxidation of UI$_{3}$(THF)$_{4}$ with pyridine-N-oxide and stoichiometric quantities of water represented the first reproducible synthesis of a stable uranyl(V) compound. \textsuperscript{83} This was immediately followed by the synthesis of the same compound by the reduction the one electron reduction of [UO$_{2}$I$_{2}$(THF)$_{3}$] with KC$_{5}$Me$_{5}$. \textsuperscript{119} This compound is poorly soluble in pyridine solution, and its ease of crystallisation is perhaps responsible for its unusual stability against the disproportionation reaction. The elongation of the bond lengths, discussed in Section 1.4.3, due to the +V oxidation state of the uranyl cation are represented by a lower energy symmetric stretching mode at 797 cm$^{-1}$. \textsuperscript{83}

Literature reports that followed have often attempted to obviate the formation of CCIs in order to stabilise the complexes against disproportionation. However, in non-protonic media it can not be assumed that the disproportionation of uranyl(V) follows the pathway in Equation 1.3.
The Hayton group reported the synthesis of uranyl(V) complexes by reduction of uranyl(VI) with Cp*₂Co. The stability of the complex is attributed to the use of the bulky ligand (2,6-iPr₂C₆H₃)NC(Me)CHC(Me)N(2,6-iPr₂C₆H₃), Ar₂nacnac, to produce uranyl(V) complexes (Fig. 1.17) that do not exhibit CCIs, with the orientation of the iso-propyl groups also surrounding the ‘yl’ oxygens. A crystallographic investigation revealed an increase in uranyl U=O bond lengths from 1.748(4) and 1.756(4) Å to 1.810(4) and 1.828(4) Å, consistent with elongation and subsequent weakening of the uranyl(V) U=O bond compared to uranyl(VI) (section 1.3.3). This is reflected by the shift of the asymmetric uranyl stretch in the IR spectrum from 918 to 800 cm⁻¹. The equatorial bond lengths also experience an increase (> 0.1 Å). The use of acetylacetonate (acac) based ligands alongside Ar₂nacnac provided further anaerobically stable uranyl(V) complexes with bulky ligands. Additionally, the choice of aryl group in Ar₂nacnac can be altered to allow coordination of one of the uranyl(VI) U=O oxygens to B(C₆F₅)₃. It is suggested that the resulting complex may be easier to reduce due to the weakened uranyl U=O bond.
The Arnold group have also taken advantage of reduction chemistry of uranyl(VI). Reductive coordinative silylation of the ‘pacman’ macrocyclic complex in Fig. 1.09\textsuperscript{60} leads to the elucidation of a uranyl(V) complex with the \textit{exo} U=O bond coordinated to a trialkyl-silyl group (Fig. 1.18).\textsuperscript{123} Similar to the work of Hayton \textit{et al.}, an elongation and weakening of the uranyl bond was observed upon reduction to uranyl(V), particularly for the \textit{exo} bond (1.993(4) Å).\textsuperscript{123} The reduction is facilitated by the activation of the uranyl bond due to its coordination to a transition metal.\textsuperscript{123,124} Replacement of said metal with lithium also promoted reduction of the uranyl(VI) centre in the ‘pacman’ complex (as long as an alternative C-H activation pathway was not presented).\textsuperscript{124}
Ephritikhine et al.\textsuperscript{[125]} follow on from the reduction of [UO$_2$I$_3$(THF)$_3$]\textsuperscript{[119]} to investigate the reduction of uranyl(VI) salts with a variety of reducing agents.\textsuperscript{[125]} The uranyl(V) complexes formed can be described in two categories; those that bear cation interactions (with a metal from the reducing agent used, Scheme 1.2) and those that are mononuclear complexes (Scheme 1.3).\textsuperscript{[125]} Both categories present complexes which are stable in spite of a lack of sterically bulky ligands and Ephritikhine attributes this stability to the lack of uranyl-uranyl CClIs.\textsuperscript{[125]} It is noted that the reduction is strongly dependent on the uranyl salt and the reducing agent, with the non-coordinating salt anions (I, OTf) providing uranyl(VI) salts that are more readily reduced, with other salts sometimes leading to incomplete reductions.\textsuperscript{[125]} It is proposed that many of the uranyl(V) salts could be used as starting reagents in uranyl(V) complex syntheses.

![Scheme 1.2](image-url)

Scheme 1.2 A summary of the uranyl(VI) salt reductions that produce cation-coordinated uranyl(V) complexes. Adapted from reference [125].
Scheme 1.3 A summary of mononuclear uranyl(V) complexes produced by reduction of uranyl(VI) salts. Adapted from reference [125].

The Mazzanti group have taken a different approach, utilising the uranyl(V) salt \([\{UO_2(py)_5\}[K_2(py)_2]_n]\) produced from \(U_3(THF)_4\) and reacting it with ligands to produce uranyl(V) complexes.\(^{81,82}\) Addition of the acac-based ligand dibenzoylmethanate (dbm) results in a tetrameric complex incorporating potassium cations (Fig. 1.11).\(^{81}\) The crystallographic information obtained shows the elongation of the uranyl bonds that are partaking in CCIs (1.923(10) and 1.934(8) Å vs. 1.828(10) and 1.811(9) Å).\(^{81}\) The choice of solvent proves to be important in the resulting uranyl(V) complex,\(^{82}\) and addition of 18-crown-6 alters the geometry of the complex to produce one that displays the rarer diamond-shaped CCI interaction between neighbouring uranyl cations (Fig. 1.10). The CCIs in the complexes can be disrupted by addition of a coordinating solvent such as DMSO, and Mazzanti reports that this leads to a more stable complex (stable after a month, compared to a matter of weeks for the complexes that display CCIs).\(^{82}\) This would suggest that obviation of CCIs is the key to stabilising uranyl(V). However, a later report concerning uranyl(V) salen complexes (Fig. 1.19) results in CCI-bearing complexes that are surprisingly stable with respect to disproportionation, even in the presence of stoichiometric amounts of water.\(^{101,126}\) The coordination to potassium also plays a role in the stability of the tetrameric complex; replacing the potassium for lithium results in disproportionation over a month.\(^{127}\) From these observations the role of CCIs in the disproportionation of uranyl(V) in anaerobic and aprotic media can not be clarified,
although prevention of protonation of the uranyl oxygen atoms clearly aids the stability of the complexes.

![Figure 1.19 Sketch of the uranyl(V) salen complex \([\{\text{UO}_2\text{(salen)}\}_4(\mu-\text{K})_2][\{\text{K(18C6)py}\}_2]\), represented by the terameric geometry of the uranyl cations and the salen ligand which is present in the equatorial plane of each. Adapted from reference [127].](image)

### 1.6.3 Reduction of uranyl(VI) as a route to the preparation of uranyl(V) complexes

Whilst the Mazzanti group have had success synthesising uranyl(V) complexes from the salt \([\{\text{UO}_2(\text{py})_5\}[\text{KI}_2(\text{py})_2]\]_n[^{80-82}] reduction of uranyl(VI) complexes is a more common route to synthesising uranyl(V) complexes in the literature. The one electron reducing agent \(\text{Cp}^*\text{Co}\) has found much use in reducing uranyl(VI) complexes, with the Mazzanti group also employing it in their work[^126-128] following the success of Hayton et al. with the reducing agent[^120-122,130] Subsequent work by the Hayton group[^131-133] has utilised the reductive silylation chemistry presented in the Arnold groups ‘pacman’ work[^121-124] Uranyl(VI) acnac complexes (acnac = \((3,5-\text{Bu}_2\text{C}_6\text{H}_3)\text{NC(ph)CHC(ph)O}\)) react with \(\text{Me}_3\text{SiI}\) to produce the uranyl(V) complex with \(\text{SiMe}_3\) coordinated to both the uranyl oxygens.[^131] Changing the silylating reagent (to \(\text{HSiEt}_3\)) still leads to reduction,[^132] whilst the addition of triphenylphosphine leads to loss of the acnac ligand.[^133] Attempts to coordinate other ligands (such as \(2,2'-\text{bipyridine}\) and \(1,10\)-phenanthroline) lead to reduction to uranium(IV).[^133]

The Arnold group took advantage of the unique topology of the ‘pacman’ complex to incorporate a divalent samarium or yttrium metal in the lower jaw of ‘pacman’, which instantly facilitates the reduction of the uranyl(VI) moiety to uranyl(V) and presents a uranyl(V) complex where two ‘pacman’ complexes are connected by a diamond shaped CCI between the \(\text{exo}\) oxygen atoms of the uranyl cations (Fig. 1.20).[^134]
Fig. 1.20 Schematic representation of [[\text{UO}_2\text{Sm(py)}_2(L)]]_2 (L = ‘pacman’ ligand, represented by the bold lines). Adapted from reference [134].

1.6.4 Chemistry of the uranyl(V) ion

Whilst the exact formula for the stabilisation of uranyl(V) complexes is uncertain, a sufficient number of anaerobically stable uranyl(V) complexes have been synthesised to allow study on their chemistry.

By generating a uranyl complex with one Ar\textsubscript{2}acnac ligand (Fig. 1.18), the Hayton group synthesised a uranyl(V) complex to which they could add further ligands.\textsuperscript{[130]} Addition of 2,2’-bipyridine, 1,10-phenanthroline, TMEDA (N,N,N’,N’-tetramethylethlenediamine) or 1-methylimidazole (Melm) resulted in a series of complexes of varying stability; ‘softer’ ligands, such as 1,10-phenanthroline and Melm were found to coordinate favourably over the other ligands used.\textsuperscript{[130]} This suggests the possibility of an increased degree of covalent interaction in the equatorial plane for uranyl(V) over uranyl(VI), a view supported by the work on uranyl(V) salen and salophen complexes.\textsuperscript{[128]} In these uranyl(V) salen and salophen complexes, the presence of the covalent bonding is said to stabilise the complexes against disproportionation, and so it could be hypothesised that the key to stabilising uranyl(V) complexes lies in the use of ‘softer’ donor ligands.\textsuperscript{[128]}

Work on the activation of the uranyl(V) moiety by Hayton \textit{et al.} showed an increased affinity for coordination through the ‘yl’ oxygens in uranyl(V), with both coordinating to a Lewis acid in the reaction of a uranyl(V) acnac complex with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}\textsuperscript{[135]} (compared to the coordination through one oxygen in uranyl(VI)).\textsuperscript{[122]} Attempts to reduce the activated complex to uranium(IV) were deemed successful by the paramagnetic shifts in the NMR spectrum and the lower energy asymmetric stretch of the U-O bond (679 cm\textsuperscript{-1}). However, elucidation of the reduced product was not achievable. By substituting smaller alkyl groups onto the acnac ligand (2,4,6-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{2} vs. 3,5-\textsuperscript{3}BuC\textsubscript{6}H\textsubscript{3}, Scheme 1.4), an analogous complex was crystallised and the uranium(IV)-oxygen bonds are assigned as single bonds (bond lengths of 2.029(6) and 2.025(6) Å with a deviated O-U-O angle of 153.3(2) °) from the X-ray crystal structure.\textsuperscript{[135]} The question of whether a uranyl(IV) complex can be
synthesised remains unanswered. The activation of the uranyl(V) centre was presented as the reason reduction was able to occur on the uranium,\[^{[135]}\] and activation of uranyl is therefore noticable in decreasing the reduction potential of uranium to facilitate reduction, with activation of uranyl(VI) by silyl groups said to be key in enabling reduction of uranyl(VI) in the work by Hayton\[^{[131]}\] and Arnold.\[^{[123,136]}\] Unusually, addition of one equivalent of $\text{B(C}_6\text{F}_5)_3$ to a uranyl(V) acnac complex results in disproportionation, whilst two equivalents is needed to yield a pure uranyl(V)-borane product. Hayton argues that this is due to a comproportionation reaction of uranium(IV) and uranyl(VI), evidenced by the stepwise addition of $\text{B(C}_6\text{F}_5)_3$ (Scheme 1.4).\[^{[135]}\]

![Scheme 1.4](image.png)

Scheme 1.4 The comproportionation reaction between uranium(IV) and uranyl(VI) acnac complexes to yield the uranyl(V) acnac – borane adducted complex. Redrawn from reference [135]. Ar = 3,5-$^1\text{Bu}_2\text{C}_6\text{H}_3$.

Work on the disproportionation reaction has confirmed the importance of the presence of protons, with reaction of $\{\text{[UO}_2\text{(py)}_3]\text{[KI}_2\text{(py)}_2]\}_n$ with benzoic acid (as the proton source) resulting in disproportionation.\[^{[137]}\] In this reaction, the disproportionation products have been characterised for the first time as $\text{[U}_6\text{O}_4\text{(OH)}_4\text{(PhCOO)}_{12}\text{(py)}_3]$ and
Reaction of the stable uranyl(V) complex [UO$_2$(Mesaldien)K]$_n$ with UI$_4$(Et$_2$O)$_2$ results in the formation of uranyl(V)-uranium(IV) CCIs and also the uranium(IV)-induced disproportionation of the uranyl(V) complex.$^{138}$ This result shows that it may not be necessary for CCIs to connect two uranyl(V) centres for disproportionation to occur; simply the one interaction between a uranyl and an adjacent uranium may be sufficient.$^{138}$ The role of protonation on uranyl oxygens would be negated in this last scenario.

Equation 1.4 The disproportionation reaction of [[UO$_2$(py)$_3$][KI$_2$(py)$_2$]]$_n$ in the presence of benzoic acid.$^{137}$

Fig. 1.21 Polyhedral representation of [U$_6$O$_4$(OH)$_4$(PhCOO)$_{12}$(py)$_3$].$^{137}$ Reproduced from reference [18].

Magnetic susceptibility data has been used to ascertain the oxidation state of uranyl(V) in work by the Mazzanti$^{182,128}$ and Arnold groups$^{123}$ due to the presence of the solitary $f$ electron in uranyl(V). Further work has investigated the role of CCIs in magnetism, with the Arnold group reporting preferred superexchange interaction between uranyl(V) and Sm(III), as opposed to between uranyl(V) centres in their report (due to the closer proximity of the 5$f^1$-4$^6$ centres compared to the 5$f^1$-5$f^1$ separation).$^{134}$ The Mazzanti group
have reported that the type of CCI heavily influences the magnetic behaviour of uranyl(V): T-shaped and diamond shaped CCIs present lower effective magnetic moments at 300 K (1.64 and 1.69 \( \mu_B \) respectively) when compared to interaction with potassium (2.57 \( \mu_B \), close to the value calculated for the free ion).\(^{[82]}\) Further work on the magnetic susceptibility of uranyl(V) complexes in which all uranyl moieties are connected (i.e., in a tetramer,\(^{[100]}\) T-shaped trimer\(^{[80]}\) and in a wheel\(^{[129]}\)) indicate that the communication between the uranyl(V) ions in the tetramer is weaker than for the trimer, owing to the closer proximity of the uranium centres in the latter (3.57 vs. 4.32 Å).\(^{[80,100]}\) Insertion of a d-metal (manganese) to create a uranyl(V)-based wheel results in a complex (Fig. 1.22) which presents promising single-molecular magnetic (SMM) properties with some attributes exceeding that of any known molecular wheel.\(^{[129]}\)

Fig. 1.22 The SMM \([(\text{UO}_2\text{salen})_2\text{Mn(py)}_3)_6]\) The equatorial NONO coordination ring represents the salen ligand (Fig. 1.19). Acquired from reference [127].

As stated in section 1.4.6, CCIs between uranyl(V) and uranyl(VI) are rare. The only two solid-state literature examples are the tetrameric \([\{\text{U}^\text{VI}\text{O}_2\text{salen}\}_2\mu-
K(18C6)}{UO_2(salen)}_3(\mu_8-K)_2, elucidated by the Mazzanti group,\textsuperscript{[101]} and the more recent trimeric complex \([\text{UO}(\mu-O)(\text{HC(PPh}_2\text{NSiMe}_3)_2)(\mu_3-\text{Cl})\{\text{UO}(\mu-O)(\text{HC(PPh}_2\text{NSiMe}_3)_2}\}_2\] prepared by Liddle \textit{et al.}\textsuperscript{[139]} In both examples, the uranyl(VI) oxygens partake in CCIs alongside those of uranyl(V), despite the increased propensity of uranyl(V) to form CCIs compared to uranyl(VI). It is possible that uranyl(V) qualifies as a strong electron-donor in the equatorial plane that can promote the formation of CCIs in uranyl(VI)\textsuperscript{[69]} (Section 1.4.2). The uranyl(VI) cation can be crystallographically identified amongst the uranyl(V) ions by the shorter bond lengths; e.g. In \([UVI\text{O}_2(salen)\mu-K(18C6)}{UO_2(salen)}_3(\mu_8-K)_2] the uranyl(VI) bond lengths are 1.804(12) and 1.862(14) Å, compared to 1.833(12) and 2.022(11) Å, 1.797 (14) and 1.941(12) Å and 1.863(13) and 1.964(12) Å for uranyl(V).	extsuperscript{[101]} Characteristic asymmetric uranyl stretches for both the (V) and (VI) oxidation state identify the mixed oxidation states; in \([\text{UO}(\mu-O)(\text{HC(PPh}_2\text{NSiMe}_3)_2)(\mu_3-\text{Cl})\{\text{UO}(\mu-O)(\text{HC(PPh}_2\text{NSiMe}_3)_2}\}_2\] the vibrational modes were identified at 905, 835 and 803 cm\textsuperscript{-1}.\textsuperscript{[139]} These results suggest that the \(f\) electrons are localised on each uranyl(V) ion and the uranyl(VI) centre is distinct in each example.\textsuperscript{[101,139]}

The Arnold group have taken the step of placing a second uranyl(VI) centre in the lower jaw of the ‘pacman’ complex\textsuperscript{[140]} seen in Fig. 1.09,\textsuperscript{[72]} preparing a bimetallic uranyl complex. The use of the reagent UO\textsubscript{2}{N(SiR\textsubscript{3})\textsubscript{2}(py)\textsubscript{2}} (R\textsubscript{3} = Me\textsubscript{3} or PhMe\textsubscript{2}) to introduce the second uranyl cation into the macrocycle results in the silylative reduction of both uranyl units. In addition, the \textit{endo} oxygens are distorted to leave a diamond geometry (a ‘butterfly’ motif) between the uranium ions and the oxygen atoms (Scheme 1.5).\textsuperscript{[140]} The reaction presents a disruption of the normally thermodynamically strong uranyl moiety, and also presents an unusual arrangement of a relatively redox stable U(V) complex. Exposure of this complex to the atmosphere in ‘wet’ benzene shows no signs of decomposition after 48 h. and only 20 % decomposition after five days).\textsuperscript{[140]} An analogous reaction with an extended ‘pacman’ ligand (the upper and lower ‘jaws’ of the ligand are bridged by anthracene, as opposed to benzene) shows no deviation of the uranyl geometry from linearity,\textsuperscript{[141]} therefore the steric conditions imposed in the original ‘pacman’ complex (U-U distance 3.3557(5) Å, not entirely dissimilar to the U=O-U distance in the trimeric \([UO_2(2-(4-tolyl)-1,3-bis(quinolyl)malondiiminate])_3\] of 3.57 Å,\textsuperscript{[80]} are responsible for the geometric disposition of the two uranyl centres.\textsuperscript{[140]} The use of lithium or potassium salts can lead to successful reduction of the uranyl(VI) centres and formation of the ‘butterfly’
motif, and the silyl groups present can be exchanged for trialkyldtin and even iso-propyl groups, all the while retaining the ‘butterfly’ geometry of the complex.[142]

Scheme 1.5 Formation of the butterfly-shaped U(V) complex [(R$_3$SiO)UO$_2$(L)] (L = ‘pacman’). Taken from reference [140].

1.7 Neptunyl Chemistry

1.7.1 Neptunyl(V)

Despite being considerably more radioactive than uranium, $^{237}$Np has a long enough half-life (214,400 years) to be studied in specially designed facilities.[3] Although it can exist in the oxidation states +III to +VII, the +V oxidation state is the most common (Table 1.1).[4] In this oxidation state, the chemistry is dominated by the neptunyl cation and CCIs, which are commonly observed in solution and the solid state.[3]

Whilst the uranyl(V) ion is often employed as a model for transuranic actinyl(V) chemistry, examples of neptunyl(V) chemistry related to uranyl(V) chemistry are rare. The work of the Mazzanti group in preparing $\left\{\text{NpO}_2\left(\text{py}\right)_5\right\}\text{K}_{2}\text{(py)}_2][\text{K}(18\text{C}6)(\text{py})]$ are notable exceptions and allow for comparison between analogous uranyl(V) and neptunyl(V) complexes. In this case, the similarity of the geometries (Fig. 1.11) suggests that uranyl(V) can provide structural information on neptunyl(V) and is a suitable surrogate. The structures also show that neptunyl(V) can coordinate in CCIs with other neptunyl(V) cations and/or alkali metals in a similar fashion to uranyl(V).[84,85] Comparison of bond lengths between neptunyl(V) and uranyl(V) complexes reveals a slight shortening of the bonds for the neptunyl(V) complexes; 1.82 Å for Np=O bonds vs. 1.84 for U=O,[84] explained by the slightly smaller neptunium atom due to the ‘actinide contraction’. In the report of the neptunyl(V) tetramer, $\left\{\text{NpO}_2\left(\text{salen}\right)\text{K}_{2}\right\}\text{K}(18\text{C}6)(\text{py})_2$, the decreased Np=O bond lengths results in a lengthened (Np=O)-Np interaction (2.49(3) Å vs. 2.39(3) Å for (U=O)-U), which suggests
a weaker CCI in the neptunyl(V) complex.\textsuperscript{[85]} This is in spite of the stability of neptunyl(V) CCIs against disproportionation.\textsuperscript{[105]} Nonetheless, as possibly the only example comparing uranyl(V) and neptunyl(V) CCIs in anhydrous organic media, this observation may not be anomalous. A preliminary investigation into the use of lithium in place of potassium shows the same tetrameric structure is formed.\textsuperscript{[85]}

Coordination of 2,2'-bipyridine to neptunyl(V) confirms the ability of neptunyl(V) to form pentagonal bipyramidal geometries,\textsuperscript{[92,143]} with the structure of [NpO\textsubscript{2}(2,2'-bipyridine)(OOCC\textsubscript{6}H\textsubscript{5})\textsubscript{2}], completed by a diamond-shaped CCI between adjacent neptunyl(V) cations (Fig. 1.23).\textsuperscript{[92]} The structure of [NpO\textsubscript{2}(2,2'-bipyridine)(H\textsubscript{2}O)\textsubscript{3}][NO\textsubscript{3}]\textsuperscript{[143]} is more reminiscent of uranyl(VI) in the lack of CCIs in its simple coordination geometry (with the exception that uranyl(VI) oligopyridines complexes are usually 6-coordinate in the equatorial plane).\textsuperscript{[144,145]} The 5-coordinate equatorial plane is preferred for neptunyl(V), as demonstrated by [NpO\textsubscript{2}(NO\textsubscript{3})(2,2':6',2''-terpyridine)(H\textsubscript{2}O)] in which the nitrate anion coordinates in a monodentate fashion.\textsuperscript{[146]}

Fig. 1.23 X-ray crystal structure of NpO\textsubscript{2}(2,2'-bipyridine)(OOCC\textsubscript{6}H\textsubscript{5})\textsubscript{2}. Adapted from reference [92]. Thermal ellipsoids shown at the 50 % probability level. Hydrogen atoms omitted for clarity.

Further neptunyl(V) chemistry documents the extended frameworks that can be constructed through CCIs (Section 1.4.4, Fig. 1.12),\textsuperscript{[89]} often in aqueous or semi-aqueous conditions.\textsuperscript{[86-88]} It is reported that CCIs can stabilise structures on their own and bridging ligands aren’t always necessary to stabilise the structure.\textsuperscript{[87,147]} This trend is followed in uranyl(V) chemistry,\textsuperscript{[80,127]} which enforces the use of uranyl(V) as a model for neptunyl(V).
1.7.2 Neptunyl(VI)

Reports of neptunyl(VI) complexes are less common than that of neptunyl(V), likely due to the instability of neptunyl(VI) towards reduction; neptunyl(VI) is often prepared by heating in concentrated perchloric acid,[148] however this is only stable for up to three days and must be used immediately.[149] The instability is illustrated by the neptunyl(VI) salt [NpO₂Cl₂(thf)]ₙ, which partially reduces in THF solution to give the mixed oxidation state compound [{Np⁶⁺O₂Cl₂}{Np⁵⁺O₂Cl(THF)₃}₂] (Fig. 1.14).[98] In this compound, the two neptunyl(V) centres coordinate to neptunyl(VI) via CCIs. The neptunyl(VI) bond lengths (1.771(12), and 1.793(10) Å) are shorter than the neptunyl(V) bond lengths, which show great variation due to the role of CCIs (1.912(11), 1.885(11), 1.805(12) and 1.751(13) Å).[98]

Krot et al. have studied the structures of uranyl(VI), neptunyl(VI) and plutonyl(VI) perchlorates[150] to determine a common pentagonal bipyramidal motif around the actinyl cation for all three, where the actinyl ion is coordinated by five water molecules in the equatorial plane, which in turn coordinate to perchlorate anions (Fig. 1.24). A decrease in bond length is found for the actinyl moiety across the three actinides; 1.752(4) and 1.755(4) Å for uranyl(VI); 1.7479(9) and 1.7403(10) Å for neptunyl(VI) and 1.7274(17) and 1.7356(17) Å for plutonyl(VI). The three related structures all present near linear O=An=O bond angles (177.98(5) to 179.74(9) °) and the decrease in bond length follows the actinide contraction.[150] A similar study on 2,2’-bipyridyl complexes of the three actinyls, of general formula [AnO₂(2,2’-bipyridine)(C₆H₅COO)ₓ] (x = 1,2), presents a similar case of bond length shortening (1.780 – 1.762 – 1.7512 Å) as the triad is traversed.[151] The coordination geometry around the actinyl cation is conserved between uranyl(VI) and neptunyl(VI) with an equatorial coordination number of six, whereas the analogous plutonyl(VI) complex is five coordinate in the equatorial plane.[151] However, the coordination topology of the uranyl(VI) cation is completed by a peroxy bridge (despite no suitable reagent being added), which is not present in the neptunyl(VI) structure, instead preferring to bind to a second benzoate cation.[151] Nonetheless, the two papers indicate a strong similarity between the coordination chemistry of uranyl(VI) and neptunyl(VI).
As stated in Section 1.4.4, neptunyl(VI) does not readily form CCIs. The solitary report of neptunyl(VI) CCIs does indicate that such an interaction is possible, at least in extended solid state structures.\[^90^\] With uranyl(VI) CCIs comparatively rare compared to the number of uranyl(VI) compounds,\[^69^\] it is perhaps only a matter of time before more neptunyl(VI) CCIs are documented and criteria governing their formation are determined (such as the strong equatorial electron donation required for uranyl(VI)).\[^69^\]

1.8 Spectroscopic Characterisation of Actinides and Oxidation State Assignment

1.8.1 IR and Raman spectroscopy

Vibrational spectroscopy is frequently used in the study of actinides, in particular actinyl ions. Observation of the asymmetric uranyl(VI) stretch (\(\nu_{as}(\text{U}=\text{O})\)) near 900 cm\(^{-1}\) in the IR spectrum is accompanied by the symmetric stretch approximately 100 cm\(^{-1}\) lower in energy in both the IR and Raman spectra in non-centrosymmetric molecules\[^{152,153}\] (in actinyl ions with a centre of symmetry the symmetric vibration (\(g\)) is observable in the Raman spectrum and asymmetric vibrations (\(u\)) are IR active, following the mutual exclusion rule).\[^{154}\] Such vibrations are commonly seen in all actinyl species\[^{84,153,155}\] and can often be used to help distinguish between oxidation states of an actinide.\[^{120,125}\] This is due to the weaker actinyl bond of an actinyl(V) vs. actinyl(VI) ion and consequently the lower vibrational frequency of the bond (Section 1.3.3).

IR and Raman spectroscopy can be used to provide an indirect insight into equatorial coordination nature of an actinyl ion.\[^{152,156,157}\] A weaker actinyl bond results in a lower energy stretch in the IR and Raman spectra, with strong equatorial donation into uranyl(VI) resulting in weakening of the bond, as described in Section 1.4.2.\[^{70}\] Therefore the effect of
strength of coordination of ligand is observable by its stretching modes; the stronger the electron donation from the ligand the weaker the actinyl An=O bond as observed by IR and Raman spectroscopy. For example, the uranyl(VI) complex [UO$_2$(Ar$_2$acnac)(MeC(O)CHC(O)Me)] (Section 1.6.2) displays an asymmetric stretch at 933 cm$^{-1}$, which is reduced in energy to 838 cm$^{-1}$ upon reduction to its analogous uranyl(V) complex.$^{[121]}$

### 1.8.2 Absorption spectrophotometry

Besides vibrational spectroscopy, UV/vis-nIR absorption spectrophotometry is commonly used for identification of the oxidation state of actinide ions,$^{[3]}$ particularly in aqueous solution where oxidation state can sometimes be ambiguous. For example, neptunium, and in particular neptunyl, species give a ‘fingerprint’ spectrum in aqueous solution (Fig. 1.25) in the nIR arising from $f$-$f$ transitions. This enables quick and easy classification of the sample. The location of the maxima can vary (by >100 nm) depending on media and coordination chemistry,$^{[84,148,149,155,158]}$ although not significantly enough to prevent identification of oxidation state. Typically, neptunyl(V) is identified by a transition at 980 nm in aqueous solution, with neptunyl(VI) observed at approximately 1220 nm.$^{[3]}

![Fig. 1.25 UV/vis-NIR absorption spectra of neptunium ions in 2 M HClO$_4$ solution: a) Np(III); b) Np(IV); c) Np(V); d) Np(VI). Taken from reference [3].](image)
Similar to IR and Raman spectroscopy, the position of the absorption maxima can vary depending on the coordination environment of the actinide, and for actinyl absorptions (both An=O charge transfer bands and those arising from f-f transitions) can be used to interpret the relative strength of the An=O bonds,\textsuperscript{[159]} with weaker An=O bonds producing maxima at lower energy. Sarsfield \textit{et al.} assigned a neptunyl(V)-Np(IV) CCI at 1004 nm in their work on the disproportionation of neptunyl(V) in organic solvents.\textsuperscript{[104]} The lower energy of the absorption maximum reflects the elongation of the neptunyl(V) Np=O bond to participate in a CCI.

### 1.9 Luminescence Spectroscopy

Emission spectroscopy can often be used to characterise a compound in solution, particularly for lanthanides, but also, to a lesser extent, the transition metals. The emission from \textit{d}-block compounds largely originates from crystal-field effects, the relative ease of oxidation and reduction of a given oxidation state and the presence of covalent metal-ligand bonds (\textit{d}-\textit{d} transitions and charge transfer transitions respectively). However the \textit{f}-elements experience strong spin-orbit coupling effects (Fig. 1.26) which are essential in understanding their emissive properties.\textsuperscript{[29,160]}

![Christmas tree diagram showing the contribution of crystal field effects (W) and spin-orbit coupling (SO) to valence electron energy bands. Taken from reference [161].](image)

#### 1.9.1 Spin-orbit coupling

The effects of relativity on heavier elements have been described in Section 1.2.2. For the \textit{f}-elements, this results in a strong coupling between an electron’s spin, \textit{S} and its orbital angular momentum, \textit{L}.\textsuperscript{[45,160]} The effect of \textit{L} is to create a dipole moment, \textit{\Lambda}. With significant spin-orbit coupling, \textit{S} contributes to the moment, \textit{\Sigma}, and so spin-orbit coupling results in a total electronic angular momentum of \textit{\Omega} (\textit{\Sigma} + \textit{\Lambda}) (Fig. 1.27), as opposed to
This then combines with the molecular rotation angular momentum, \( R \), to create a total angular momentum, \( J \).

Fig. 1.27 The interaction of the spin of an electron with its orbital angular momentum on a dipole moment. Redrawn from reference [162].

1.9.2 Lanthanide luminescence
The lanthanides suffer from weak, formally Laporte-forbidden \( f-f \) transitions\(^{[4,160]}\) resulting in low molar absorption coefficients. This results in long-lived excited states and \( f-f \) based lanthanide emission (up to the millisecond range for molecular complexes of europium and terbium in solution).\(^{[163]}\) However, to enhance these forbidden transitions an ‘antenna’ is often used;\(^{[163,164]}\) a chromophore (often organic) in close proximity to the metal ion that is similar in energy to the lanthanide emissive state (it must have a higher energy triplet excited state compared to the metal excited state).\(^{[164]}\) Due to the limited radial extension of the \( 4f \) orbitals, crystal field effects are usually negligible\(^{[4]}\) and the resulting emission is dominated by spin-orbit coupling, described by Russell-Saunders L-S coupling.\(^{[4]}\) The energy gap law dictates that the emissive state is usually (but not always) the lowest energy of the described energy levels since this normally possesses the largest energy gap to the next lower lying electronic state.\(^{[165]}\)

1.9.3 Emission quenching
Several aspects of the emission are governed by the lanthanides coordination environment; principally effectiveness of non-radiative decay through efficient overlap of the excited states with other electronic or vibrational states of a similar energy (Fig. 1.28). This is particularly noticeable with the presence of X-H oscillators for visible and nIR emitting lanthanides \((X = C,N,O)\), from coordinated solvent/ water molecules to X-H bonds in the...
ligand architecture. In these cases, the energy level of a X-H oscillator is similar in energy to that of the emissive excited state and is therefore accessible as an alternate route to emission.[166]

Fig. 1.28 Simplified energy level diagram depicting the process of sensitised emission for a lanthanide complex. The transfer of energy to an X-H oscillator is included. Redrawn from reference [167]. IC = Internal Conversion. ISC = InterSystem Crossing.

Use of X-D bonds where X-H bonds were previously is a common theme in preventing emission quenching[168] and is especially effective with closer proximity to the metal.[169] Choice of ligand is highly dependent on the lanthanide; certain oscillators will overlap in energy level more efficiently with lanthanides that have a \( ^{2S+1}L_J \) excited state of similar energy. Clearly this is dependant on the lanthanide and thus C-D bonds are not a universal remedy for the problem,[169,170] neither is fluorination of a bond.[171] Such problems can be anticipated for the actinides.[167]
Fig. 1.29 Examples of left a per-deutero ligand\cite{169} and right a per-fluoro ligand\cite{171} coordinated to lanthanide ions. Adapted from references [169,171].

1.9.4 Uranyl(VI) photophysics

The history of uranium (in the form of uranyl(VI)) and luminescence has crossed on notable occasions. In 1852, George Stokes coined the term ‘fluorescence’ to describe uranium-containing glasses,\cite{172} deriving the term from optically anomalous fluorite minerals.\cite{160} The fluorescent properties of uranium were also fundamental to the discovery of radioactivity by Becquerel.\cite{160} The photophysical properties of uranyl(VI) have intriguingly arisen interest in their potential use for chemical storage of energy derived from solar radiation.\cite{173,174}

Uranyl(VI) is devoid of $f$ electrons (Section 1.3.2) and emission arises from U=O LMCT (Ligand-to-Metal Charge Transfer); excitation into one of the uranyl bonding orbitals ($\sigma_u$, $\sigma_g$, $\pi_u$, $\pi_g$) promotes an electron into the 5$f$ non-bonding orbitals ($\delta$ and $\varphi$),\cite{45,47} coupling with the symmetric vibrational O=U=O mode\cite{175} (observable in the Raman spectrum) to produce up to 12 excitation bands, usually centred around 420 nm (superimposed upon the uranyl LMCT absorption spectrum) (Fig. 1.30). Deactivation of the excited state results in characteristic green emission around 500 nm (Fig. 1.30), with up to 6 bands observable through coupling with the same symmetric vibrational O=U=O mode in the ground state.\cite{175}
Fig. 1.30 Excitation of an electron from a valence band into one of the non-bonding 5f orbitals of the uranium, resulting in absorption spectra around 420 nm. Quenching of the excited state by radiative decay produces the green emission spectrum (~500 nm) shown.

The excited state is a mixture of triplet and singlet in character,\textsuperscript{[160]} although relaxation proceeds \textit{via} a formal uranyl(V) triplet state.\textsuperscript{[176,177]} The transition is formally Laporte forbidden,\textsuperscript{[45,175]} but increased crystal-field effects (\textit{cf.} lanthanides, Fig. 1.26) along with increased vibrational coupling allow relaxation of parity, consequently emission lifetimes can range from nanoseconds to hundreds of microseconds (shorter than in most trivalent lanthanide species).\textsuperscript{[175]} The Russell-Saunders coupling scheme is not applicable to uranyl(VI) (or indeed the actinides in general),\textsuperscript{[45,160]} because of mixing of multiple \( \Omega \) values in the uranyl(VI) ion.\textsuperscript{[160]}

The coordination of ligands to make a uranyl(VI) complex does not affect the nature of uranyl(VI) emission,\textsuperscript{[178]} but can change the profile of the emission. Complexation of weakly coordinating ligands in the equatorial plane produces a higher energy LMCT emission than if strong coordinating ligands are used,\textsuperscript{[179,180]} analogous to the absorption spectra (Section 1.8.2). In aqueous media, the effect of pH and concentration can be differentiated by emission spectroscopy\textsuperscript{[181]} and distinction between hydroxide species can also be attempted (increasing conjugation between uranyl aqua ions \textit{via} hydroxide ions results in increasing emission lifetimes).\textsuperscript{[182]} Evaluation of emission lifetimes can provide information on ligand exchange and the electronic nature of the ligands in the equatorial plane.\textsuperscript{[183]} The weakening of the uranyl bond to produce lower energy emission\textsuperscript{[179,180]} has
been explored in more detail; sufficient weakening of the uranyl bond can, in certain circumstances, promote the formation of CCIIs in uranyl(VI) complexes (Section 1.4.2). The resulting red-shifted emission is a result of the elongation of the U=O bonds and subsequent lowering of the HOMO-LUMO energy levels, but this interaction with the neighbouring uranyl ion acts to quench the emission, reducing the emission lifetime. 

1.9.5 Emission from lower oxidation states of uranium

The luminescence spectroscopy of uranyl(VI) is well-studied, especially in aqueous solution, however studies of uranyl(V) are comparatively rare. Uranyl(V) in perchlorate solution, generated by irradiation of a uranyl(VI) solution with a mercury lamp, has been observed by emission spectroscopy. The result is blue shifted emission and excitation maxima compared to uranyl(VI); optimum excitation at 255 nm leads to an emission band with a maximum at 440 nm, which overlaps with a uranyl(VI) maximum at 510 nm (Fig. 1.31), probably due to uranyl(V) that had either disproportionated or re-oxidised to uranyl(VI), or that had not been successfully reduced from uranyl(VI) initially. The emission lifetime is reported to be approximately 1.1 µs, slightly longer than uranyl(VI) under the same conditions (0.9 µs). Uranyl(V) in carbonate media has been studied and the spectra reveal slightly lower energy uranyl(V) emission maxima centred at 404.7 nm, with a band at 443.3 nm representing the lowest energy of the emission maxima. Although these studies have paved the way for research into studies of uranyl(V/VI) in biofilms, the uranyl(V) species in these studies were either chemically or electrochemically reduced under non-air sensitive conditions and suffer from the presence of uranyl(VI) as a contaminant (Fig. 1.31). As yet no emission studies of chemically pure uranyl(V) species have been reported. In addition, it is not specified if these transitions originate from a U=O LMCT, although it is presumed (f-f transitions are expected to occur at much lower energy).
Uranium(IV) is not an actinyl ion. The emissive properties of uranium(IV) complexes have been observed in the UV/vis region for solid state, aqueous and, more recently, organic samples. For the aqua ion, the transitions are assigned as a rearrangement of the valence electrons in the 5f sub-shell, arising from transitions from the Russell-Saunders LS coupled $^1S_0$ excited state. However, in doped solids, in organic samples of uranium chloride salts and organic solutions of $[\text{U(DO3A(dmso)}_2]\text{][Br]}$, the dominant transitions are charge transfer in nature ($\text{DO3A} = [4,7,10\text{-tris-carboxymethyl-1,4,7,10-tetraaza-cyclododec-1-yl]}$-acetic acid). They arise from the deactivation of the $^3F_2 \ 5f^16d^1$ configuration to the $5f^2 \ ^3P_1$, $^1D_2$ and $^3F_4$ levels. $f-f$ Transitions have yet to be observed for uranium(IV). It is thought these transitions will be found at lower energy, akin to those seen for Np(IV) and Pu(IV). Uranium(III) emission has been observed in the solid state.

The redox-sensitive and radioactive nature of the actinides are limitations that hinder study of their emissive properties. Also of prohibiting influence is the increased spin-orbit coupling and crystal field splitting experienced by the actinides (vs. the lanthanides, Fig. 1.25), resulting in a large mixing of $J$ states. As a result, neither Russell-Saunders coupling nor $J-J$ coupling accurately describe the emissive properties of the actinides,
although both can give reasonable approximations for the light and heavy actinides respectively, as demonstrated by U(IV) compounds.\textsuperscript{[175,197]}

1.9.6 Emissive properties of the transuranic ions
In spite of these limitations, the emissive properties of An(III) ions have been studied to varying extent.\textsuperscript{[175,198]} The emission of Cm(III) is of particular note, with a large energy gap between the excited and ground states (Fig. 1.32), long lifetimes can be observed for the samples (the aqua ion is measured at 65 \(\mu\)s in H\(_2\)O, 1270 \(\mu\)s in D\(_2\)O at 595 nm).\textsuperscript{[199]} Combined with the role of Cm(III) in separation processes,\textsuperscript{[3]} the emissive properties of the ion are comparatively well studied. Emission is generally seen to occur around the 600 nm region following direct excitation into the \(f-f\) manifold (the \(6I_{11/2}\) energy level, which collapses to the \(6D_{7/2}\) level before emitting)\textsuperscript{[200]} at 375 nm.

![Fig. 1.32 An energy level diagram for the An(III) cations. Taken from reference [167].](image)

Reports on the emission of transuranic actinyl ions are rare, although this is anticipated due to the potential cross-over of excited and ground state energy levels in transuranic actinyls.\textsuperscript{[160]} Regarding plutonyl(VI), there is but a solitary report regarding its emissive properties, with excitation at 628 nm leading to emission in the nIR and assigned to \(f-f\) transitions.\textsuperscript{[201]} Similarly, neptunyl(VI) exhibits \(f-f\) transitions between 1300 and 1800 nm in both the solid state,\textsuperscript{[202]} by excitation at 628 nm, and in aqueous solution (Fig. 1.33).\textsuperscript{[149]}
In the latter case, quenching from the solvent is prominent due to the efficient energy overlap of the O-H oscillator. Use of a polyoxometallate complex, \([\text{Na}_2(\text{NpO}_2)_2(\text{GeW}_{9}\text{O}_{34})_2]^{14-}\) allowed for increased emissive properties (an emission lifetime of 62 ns, compared to the immeasurable lifetime of the aqua ion), and also the use of sensitised emission, excitation at 337 nm.\[^{[149]}\] The report of the emission of neptunyl(V) Np=O LMCT at around 550 nm (excitation at 393 nm) is the only report of a transuranic An=O LMCT emission.\[^{[203]}\] Similar to neptunyl(VI) emissions, the emission lifetime is short, even in deuterated solvents with the presence of the strongly coordinating ligand acetylacetonate (acac). Emissions arising from \(f-f\) transitions are anticipated to occur at much lower energy,\[^{[192]}\] similar to those seen for all U-Pu compounds so far.\[^{[175]}\]

Fig. 1.33 Time-resolved emission spectrum of the neptunyl(VI) aqua ion in \(\text{H}_2\text{O}\) following excitation at 337 nm. Taken from reference \([149]\).

1.10 Nuclear Magnetic Resonance Spectroscopy

1.10.1 Paramagnetic effects

The ability of an unpaired electron to contribute to the relaxation of nuclear spins is noticeable;\[^{[204,205]}\] being of significantly larger magnetic moment than the nucleus, it dominates the relaxation mechanism.\[^{[204,205]}\] The spin-lattice relaxation time is inversely proportional to the gyromagnetic ratio, resulting in very quick relaxation for protons under paramagnetic conditions.\[^{[205]}\] According to the Heisenberg uncertainty principle (Equation 1.5), a decrease in relaxation time must result in an increase in energy and subsequently an
increase in uncertainty of the NMR frequency – leading to broad resonances in the NMR spectrum.\textsuperscript{[205]}

\[ \Delta E \Delta \tau = \frac{\hbar}{2} \]

\textit{Equation 1.5} The Heisenberg uncertainty principle, \( \Delta \tau \) represents the lifetime of the nuclear spin state.\textsuperscript{[206]}

Unpaired electrons also contribute to the chemical shift of a proton significantly; a proton interacts with a magnetic dipole that is introduced by electrons on a neighbouring atom.\textsuperscript{[204]} The effect to which it shields or deshields a nucleus depends on the orientation of the nucleus towards the induced dipole as it tumbles through solution, and therefore on the geometry of the complex.\textsuperscript{[204]} The effect of this magnetic dipole is proportional to the gyromagnetic ratio of both the proton (or other nucleus) experiencing it and to that causing the dipole;\textsuperscript{[204]} the large gyromagnetic ratio of the unpaired electron therefore generates a large magnetic dipole, and subsequent shielding/deshielding effects are considerably large.\textsuperscript{[204]} The effects of paramagnetism are inversely proportional to distance,\textsuperscript{[204,205]} hence, as a general rule protons further away from the paramagnetic centre in the molecule experience less paramagnetic effects. The magnitude and sign of the chemical shift are also dependent upon the angle of the proton from the principal magnetic axis (\( \theta \)) and is proportional to \( \cos^2 \theta \),\textsuperscript{[206]} as described by Equation 1.6.

\[ \frac{\Delta v}{v_0} = \frac{\beta^2}{60(kT)^2} \times \frac{(3\cos^2 \theta - 1)}{r^3} \times 2A^0_2 < r^2 > \times g^2 J(J+1)(2J-1)(2J+3) < J \parallel \alpha \parallel J > \]

\textit{Equation 1.6} The Bleaney Equation.\textsuperscript{[206]} \( \nu \) is the nuclear resonance frequency, \( \beta \) is the Bohr magneton, \( k \) is the Boltzmann constant, \( T \) is the temperature, \( r \) is the distance of the proton from the principal magnetic axis, \( A \) is an energy coefficient, \( g \) is the g-value of the electron and \( J \) is the electron energy level.

Such effects are well known and documented for lanthanide complexes.\textsuperscript{[206,207]} For example, Ln(DOTA) complexes can experience proton chemical shifts from past +100 and -100 ppm (depending on the metal ion, DOTA = 1,4,7,10-tetraazacyclododecane-N,N’,N”,N’’-tetraacetic acid).\textsuperscript{[207]} In these complexes, the magnetic axis coincides with the principal axis of symmetry. It is assumed that the spin polarisation transfer occurs through space and not through bonds.\textsuperscript{[190]} Their effects in actinide complexes are less well documented. This is because of the lack of data on actinides due to their radioactivity, with uranyl(VI) the only example studied to a great extent. With no \( f \) electrons, no
paramagnetic effects are experienced in resulting NMR spectra. For what few NMR spectroscopic studies exist outside of this, the effects of paramagnetism can clearly be seen. $5f^3$ and $5f^2$ complexes exhibit a range of broadened resonances at extreme chemical shifts,\cite{1,2,3,4,5} with the uranium(IV) complex [U(DO3A)] exhibiting proton resonances between -70 and +80 ppm.\cite{6} For actinides, the contact contribution of spin polarisation transfer may no longer be negligible.

Actinides with a $5f^4$ electronic configuration experience less deleterious effects,\cite{7,8,9,10,11} with NMR spectroscopic shifts for uranyl(V) complexes typically only a few ppm different to analogous uranyl(VI) complexes. As the actinide series is progressed, fewer NMR spectroscopic studies have been undertaken, although americium(III) complexes have received interest due to the seemingly weak effects of paramagnetism on NMR spectra (cf. Eu(III)).\cite{12,13}

1.10.2 Giant spin-orbit coupling effects

Recent work has studied the large spin-orbit effects experienced by the actinides and the strong deshielding to nuclei with which they interact.\cite{14} NMR spectroscopic studies on diamagnetic uranyl(VI) systems show NMR resonances at 100s of ppm,\cite{15,16} which confirms the role of giant spin-orbit coupling due to a lack of unpaired electrons in the sample. The effects are greatly dependant on distance, with nuclei more than one bond from the actinide experiencing only negligible contributions from spin-orbit coupling in the NMR spectrum.\cite{14}

In a more convoluted example, the $^{15}$N NMR spectrum of [Am($^n$PrBTP)$_3$(NO$_3$)$_3$ ($^n$PrBTP = $^n$propyl bis-triazinyl pyridine) exhibits unusual chemical shifts of -26 and -18 ppm for nitrogen atoms coordinated to the americium, with uncoordinated nitrogen nuclei usually observed around 300 ppm and those coordinated to lanthanides between 250 and 300 ppm (Fig. 1.3).

However, the relative contributions of paramagnetism (in particular the contact contribution to the chemical shift) and spin-orbit coupling to the chemical shift is uncertain as the latter can only be calculated and not measured.\cite{17} Certainly, it is likely to contribute.
1.10.3 Diffusion-ordered NMR spectroscopy (DOSY)

The ability to determine a diffusion coefficient from an NMR spectrum derives from the dependency of a species spin-lattice relaxation time on its molecular mass.\(^{204,214}\) In particular, the use of pulsed magnetic field gradient NMR spectroscopic experiments\(^{215}\) allow for the displacement of magnetic vectors due to a molecule's diffusion coefficient to be measured (Appendix 0).

Diffusion-ordered NMR spectroscopy suffers from many limitations, notably the assumption that the species under investigation are of infinite dilution, are spherical in nature and that the molecules undergo unrestricted diffusion in which the molecules motion is described by a 3D random walk.\(^{216}\) The samples are also subject to the formation of local magnetic fields caused by eddy currents in the probe and magnet that arise from the gradient pulses\(^{214}\) and local convection flows from within the samples can arise if a large enough thermal gradient is applied to the sample (due to the design of NMR probes).\(^{217,218}\) Both of these lead to distortion of the spectra under measurement. A final limitation of DOSY-NMR spectroscopy is the necessity for resonances to be separated from one another with good spectral resolution,\(^{219}\) with overlapping signals resulting in averaging of diffusion coefficients; problematic if the diffusion coefficients of each resonance are unique.

In spite of the limitations, since DOSY-NMR spectroscopy was first utilised in 1992\(^{220}\) it has found great use in analysing mixtures in solution for organic and biological purposes.
investigations of drug-binding studies and investigations of polymers. Developments in the field have led to the discovery of advanced techniques such as heteronuclear 2D and 3D DOSY techniques and also improved practical techniques e.g. new types of sample tubes to reduce convection currents. Improved pulse sequences in attempts to overcome the limitations of DOSY have also been made.

More recently inorganic chemists have found use for DOSY techniques for investigating metal complexes in solution, including a variety of work with actinides (primarily uranium), such as investigations of nanoclusters incorporating uranium and uranyl based polymerisation mechanisms.

Of great use to inorganic chemists are Equations 1.7 and 1.8, which allow for an approximation of the size of a species in solution and comparison with a different sample under analogous conditions.

$$D = \frac{k_BT}{6\pi \eta r_H}$$

Equation 1.7 The Stokes-Einstein equation. \(D\) represents the diffusion coefficient in \(m^2s^{-1}\), \(k_B\) is the Boltzmann constant, \(T\) is the temperature in K, \(\eta\) is the viscosity of the solvent in \(mNsm^{-3}\) and \(r_H\) is the spherical hydrated radius in \(10^{-10}\) m.

$$\frac{D_1}{D_2} = 3 \sqrt{\frac{M_2}{M_1}}$$

Equation 1.8 Comparison of molecular weights between two species in a solution. \(D\) represents the diffusion coefficient of a species in \(m^2s^{-1}\) and \(M\) the molecular weight.

Within actinide chemistry, Equations 1.7 and 1.8 have been utilised by the Mazzanti group who looked at a series of uranyl(V) structures in solution by \(^1H\) NMR spectroscopy, several of which bear CCIs in the solid state. By comparison against a monomeric analogue, the group was able to state which structures existed in an aggregated form in solution based on a comparison of their molecular weights from the use of Equation 1.8 (Fig. 1.35). DOSY-NMR spectroscopy is therefore a useful tool for the study of solution behaviour for actinide chemists, in spite of its apparent limitations.
Fig. 1.35 Representation of the Mazzanti group complexes compared by DOSY-NMR spectroscopy. Ligands removed for clarity. The use of equation 1.7 allowed the extended structures to be compared to a monomeric analogue. Adapted from references [82,127].

1.11 Aims of the PhD Project

Despite being a fundamental aspect of actinyl(V) chemistry, CCIs in actinyl(VI) chemistry are rare, particularly solution-based studies. Luminescence and NMR spectroscopy have shown use in investigations of such species in solution, and it is in the agenda of this work to investigate such interactions, principally in uranyl(VI) complexes.

In addition, work on emissive properties of actinides is generally performed in aqueous solution (due to industrial relevance), and knowledge of basic properties and trends is infantile in comparison to other metals, such as complexes of the lanthanide series. Although studies on luminescent friendly ligands are not unheard of, work in this thesis will help contribute with respect to studies of fluorinated ligands.

By taking advantage of the unique facilities at the Centre for Radiochemistry Research, and EURACT-NMR funded trips to the Karlsruher Institut für Technologie, Institut für Nukleare Entsorgung (KIT-INE), Karlsruhe, the study of transuranic complexes can take place; providing a rare opportunity to investigate analogous complexes to uranyl and lanthanide systems with a view to increasing knowledge of spectroscopic characteristics of these actinides.

Uranyl(V) is an unstable and uncommon oxidation state of uranium. It is a key goal of this thesis to devise and synthesise a series of ligands which will be useful in studying this oxidation state of uranyl. By synthesising a variety of ligands that possess different steric
parameters, a thorough investigation into fundamental aspects of the instability of uranyl(V) can begin.

In exploring the instability of uranyl(V), ideally some insight into the mechanics of disproportionation reaction can be imparted and expanded upon to neptunyl(V).

1.12 References


Chapter 2

Studying the Coordination Chemistry of Uranyl(VI) TPIP Complexes
2.1 Introduction

TPIP (tetraphenylimidodiphosphinate) was first synthesised in 1963.\(^1\) Described as an analogue of acac-based ligands,\(^2\) it has found use as a ligand in the coordination chemistry of metals with work on \(d\)-metal complexes well studied by the late 1990s.\(^3\) Despite this, it wasn’t until the work of the Pikramenou group near the turn of the millennium that TPIP was coordinated to lanthanides.\(^4\) Over the course of three papers, the coordination chemistry of lanthanide TPIP complexes is discussed (where \(\text{Ln} = \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Er}^{3+}\)),\(^4\)\(^-\)\(^6\) and in the process the potential of the ligand for enhancing the luminescent properties of these metals realised. In all cases, the complex is defined as \(\text{Ln(TPIP)}_3\) (Fig. 2.01) and all are reported to exhibit long-lived emission lifetimes. This is attributed to the lack of O-H and N-H oscillators and proximal C-H oscillators (the C-H oscillators present are several bonds away from the metal centre) in addition to the hydrophobic nature of the phenyl groups on the ligand. The geometry of the complexes is said to form a hydrophobic shell around the metal centre, discouraging solvent quenching of emission, although the addition of water did result in reduction of emission lifetimes: from 1.8 to 0.8 ms for \(\text{Eu(TPIP)}_3\) and 2.8 to 1.4 ms for \(\text{Tb(TPIP)}_3\) in dry MeCN.\(^5\)

![Fig. 2.01 Sketch of [Ln(TPIP)\(_3\)]. Adapted from reference [6].](image)

More recently, the ternary complex, \(\text{Eu(1,10-phenanthroline)(TPIP)}_3\) was synthesised by the addition of one equivalent of 1,10-phenanthroline to \(\text{Eu(TPIP)}_3\).\(^7\) The resulting complex displayed an emission lifetime of 1.84 ms in cyclohexane.
By comparison, work on actinide complexes of TPIP is less extensive. Cea-Olivares et al. reported the synthesis of Th(TPIP)$_4$ and U(TPIP)$_4$,[8] where the actinides are in the +IV oxidation state and are able to incorporate an extra TPIP ligand than Ln(III) complexes. The synthesis of UCl(TPIP)$_3$ in the same report highlights the steric demand the fourth TPIP ligand may impart upon the complex. Further work led to the isolation of the first TPIP complex of uranyl(VI)[9] (Fig. 2.02). In this unusual trimeric complex the middle uranyl unit is said to participate in cation-cation interactions (CCIs) with both terminal uranyl groups. These bonding interactions were corroborated by the extended bond lengths of the bridging uranyl ion seen in the X-ray crystal structure (1.793(4) Å for the bridging uranyl U=O bonds vs. an average of 1.739 Å for the terminal uranyl bonds) and in measurement of the uranyl symmetric stretch in the Raman spectrum. The structure is supported by bridging TPIP ligands, which brings the uranyl centres in close proximity to one another. The formation of T-shaped cation-cation interactions from both oxo-groups of the bridging uranyl unit is the first example of such in uranyl(VI) chemistry.[9] Further work performed by M. Redmond at the University of Manchester led to the preparation of mononuclear uranyl(VI) TPIP complexes when crystallised from polar, coordinating solvents (THF and MeOH) and also when a monodentate ligand (Cy$_3$PO) is used in tandem with TPIP. In these complexes, either a solvent or Cy$_3$PO molecule completes the fifth equatorial coordination site of the uranyl moiety: no cation-cation interactions are observed.[10,11]

![Fig. 2.02 The X-ray crystal structure of the uranyl(VI) TPIP trimer [UO$_2$(TPIP)$_2$]$_3$.[9] The fifth equatorial coordination site on the terminal uranium atoms is occupied by a CCI from an oxygen atom of the central uranyl ion.](image)
Lanthanide TPIP studies were continued using derivatives of TPIP (Fig. 2.03). MeTPIP (a TPIP derivative with one ortho position of every phenyl ring occupied by a methyl group, Fig. 2.03) showed an increase in the steric bulk of lanthanide structures of Eu(III) and Tb(III), which increased shielding from solvent molecules.\(^5\) The addition of water to Eu(TPIP)\(_3\) and Tb(TPIP)\(_3\) saw the luminescence lifetime decrease by approximately 50 %; by contrast the decrease in lifetimes of Eu(MeTPIP)\(_3\) (from 1.3 ms to 1.1 ms) and Tb(MeTPIP)\(_3\) (from 1.9 ms to 1.7 ms) are less severe (< 20 % in both cases) than the parent Ln(TPIP)\(_3\) complexes. The fully fluorinated derivative of TPIP, F\(_2\)TPIP (Fig. 2.03), was studied by Long et al.\(^{12}\) to the conclusion that full removal of the C-H bond in the ligand leads to increased luminescence lifetimes of the corresponding lanthanide complexes. In the article, the lifetimes of Er(TPIP)\(_3\) and Er(F\(_2\)TPIP)\(_3\) are compared; the TPIP complex decays bi-exponentially with values of 5.0 μs (87 %) and 2.4 μs (13 %) in CDCl\(_3\), which is remarkably shorter than the lifetime of 145 μs (27 %) and 28 μs (73 %) seen by the F\(_2\)TPIP complex in the same solvent. Pikramenou effectively summarised F\(_2\)TPIP lanthanide luminescence in her 2007 report\(^{13}\) and found that the ligand did increase the luminescence lifetime of all lanthanides that emit in the NIR region in comparison to their TPIP counterparts. Although Dy(III) also showed a significant increase in luminescence lifetime, other visible emitting lanthanides studied in the report (Eu(III) and Tb(III), with Sm(III) emitting too weakly to measure effectively) experience a decrease in emission lifetime when compared to TPIP complexes due to a low-lying σπ* energy state of the ligand at 26667 cm\(^{-1}\), affecting the ligands ability to sensitise the emission of the visibly emitting lanthanides.
Given the success of TPIP derivatives in enhancing the luminescence of many of the trivalent lanthanides, it is reasonable to assume they may have potential in enhancing the emissive properties of uranyl(VI) and the actinides. In addition, the structure of 
\[\text{[UO}_2\text{(TPIP)}_2]\text{]}_3\] presents an opportunity to study the effect of CCIs on the luminescent properties of uranyl(VI). At the time of writing, there are no reports on the chemistry of \(^{19}\text{F}\text{TPIP}\) with any actinide.

2.2 Synthesis of Uranyl(VI) TPIP Complexes

In the synthesis of uranyl(VI) TPIP complexes, NaTPIP is reacted with uranyl nitrate in water and/or alcohol and the intermediate product ("\text{UO}_2\text{(TPIP)}_2\) that precipitates from this reaction mixture is isolated and recrystallised.\[^{19,10}\] The choice of recrystallisation solvent is important in determining the nuclearity of the product.\[^{11}\] Following this mantra, the monomeric uranyl TPIP complexes \[\text{[UO}_2\text{(TPIP)}_2\text{Py}]\] (1) and \[\text{[UO}_2\text{(TPIP)}_2\text{H}_2\text{O}]\] (2) were isolated, with 1 recrystallised from pyridine and 2 crystallised from HPLC grade acetonitrile. The high moisture content of the acetonitrile is responsible for the formation of \[\text{[UO}_2\text{(TPIP)}_2\text{H}_2\text{O}]\]; "\text{UO}_2\text{(TPIP)}_2\) was not recrystallisable from anhydrous acetonitrile due to a lack of solubility. The same was observed for \[\text{[UO}_2\text{(TPIP)}_2]\text{]}_3\]. Dissolution of the intermediate product in anhydrous DCM followed by layering with anhydrous acetonitrile
resulted in the crystallisation of the acetonitrile adduct $[\text{UO}_2(\text{TPIP})_2\text{MeCN}]$ (3). In addition, the 5th equatorial coordination site of uranyl(VI) can be capped by the addition of $\text{Ph}_3\text{PO}$ to the intermediate product and recrystallisation from DCM to synthesise $[\text{UO}_2(\text{TPIP})_2\text{Ph}_3\text{PO}]$ (4), resulting in a uranyl(VI) TPIP monomer with a full phenylphosphineoxide coordination in the equatorial plane.

Attempts to replicate the formation of $[\text{UO}_2(\text{TPIP})_2]_3$ as reported by Cea-Olivares et al. by recrystallisation from DCM resulted in the formation of the dimeric complex $[\text{UO}_2(\text{TPIP})_2]_2$ (5), where each uranyl moiety is coordinated by a bidentate terminal TPIP ligand and two bridging TPIP ligands, producing in a coordinatively unsaturated uranyl(VI) centre. Further study led to the observation that the trimeric $[\text{UO}_2(\text{TPIP})_2]_3\cdot 1/2\text{C}_6\text{H}_{14}$ (6) complex can be synthesised by immediate layering of the DCM solution of “$\text{UO}_2(\text{TPIP})_2$” with $n$-hexane. Allowing the solution to stand overnight and then layering with $n$-hexane produced the dimeric oligomer 5. A similar chemistry was seen with a benzene solution of “$\text{UO}_2(\text{TPIP})_2$”; immediate layering with $n$-hexane results in the formation of 6; allowing the solution to stand and then layering with $n$-hexane yields $[\text{UO}_2(\text{TPIP})_2]_3\cdot 2\text{C}_6\text{H}_6$ (7). These two complexes differ only in the solvent of crystallisation in the crystal lattice, however slight differences in their interatomic coordinates in the solid state can be observed by single crystal X-ray diffraction (See Section 2.3) In addition, a sample of 7 that had been stored under argon was recrystallised from DCM/ hexane to produce $[\text{UO}_2(\text{TPIP})_2]_3\cdot \text{CH}_2\text{Cl}_2$ (8), although this synthesis was non-reproducible. Dissolution of 7 in DCM and layering with $n$-hexane leads to the isolation of 5; dissolution of 5 in benzene and layering with $n$-hexane yields 7. Dissolution of 6 in either DCM or benzene and immediate layering with $n$-hexane produces 5 or 7 respectively. Complex 8 dissolved in benzene and layered with $n$-hexane yields 7. The complexation of TPIP to uranyl(VI) appears to change considerably with only a minor change in reaction conditions, this is summarised in Scheme 2.1.

The oligomeric uranyl(VI) TPIP complexes 5 and 6 are found to favourably form monomeric complexes upon addition of either a coordinating solvent, such as THF, or the monodentate ligand triphenylphosphineoxide, therefore the cation-cation interactions of the trimer (and the incomplete equatorial coordination of the dimer) are of lower stability than coordination to Lewis bases (producing monomers). This reactivity is unsurprising given the high affinity of uranyl with O and N donor atoms of coordinating solvents.
Scheme 2.1 Summary of solvent dependency on the coordination of TPIP to uranyl(VI). The use of THF, from previous work\textsuperscript{[10,11]} is included to show loss of aggregation of the uranyl(VI) TPIP oligomers in a coordinating solvent. I = 6 and II = 7.

The synthesis of 1 can be achieved by reaction of UO\(_2\)I\(_2\)THF\(_3\) and NaTPIP in anhydrous pyridine. Compounds 1 and 6 are also successfully synthesised from the reaction of uranyl nitrate with one equivalent of NaTPIP. A stoichiometric uranyl(VI) 1:1 TPIP complex has yet to be isolated and the 2:1 ligand:metal complex is therefore the thermodynamically favoured product.

2.3 X-Ray Crystallographic Studies of Uranyl(VI) TPIP complexes
All recrystallisations from solvents produced crystals suitable for single crystal X-ray diffraction when layered with an appropriate anti-solvent, enabling a comprehensive structural study.

2.3.1 Monomeric uranyl(VI) TPIP complexes
The monomeric uranyl(VI) complexes crystallise in approximate pentagonal bipyramidal geometries (Figs. 2.04 and 2.05).
Fig. 2.04 X-ray crystal structure of left [UO$_2$(TPIP)$_2$py].1/2py (1) and right [UO$_2$(TPIP)$_2$H$_2$O].2MeCN (2). Hydrogen atoms and solvent molecules omitted for clarity. Thermal ellipsoids set at the 50 % probability level.

Fig. 2.05 X-ray crystal structure of left [UO$_2$(TPIP)$_2$MeCN] (3) and right [UO$_2$(TPIP)$_2$Ph$_3$PO].CH$_2$Cl$_2$ (4). Hydrogen atoms and solvent molecules omitted for clarity. Thermal ellipsoids set at the 50 % probability level.

Notable bond lengths and angles are presented in Table 2.1. When summarising the measured bond lengths for the uranyl(VI) TPIP monomers, it is prudent to include those reported for [UO$_2$(TPIP)$_2$THF], [UO$_2$(TPIP)$_2$MeOH] and [UO$_2$(TPIP)$_2$Cy$_3$PO]$^{10,11}$ to provide a more comprehensive summary. In general, the uranyl bond lengths are unremarkable and all fall within the region 1.76 to 1.78 Å, except for those reported for [UO$_2$(TPIP)$_2$MeOH] due to hydrogen bonding between the uranyl oxygen and methanol
solvent. The two U=O bond lengths in 1 are statistically different; 1.773(2) and 1.782(2) Å. The slightly longer uranyl bond is in close proximity to the pyridine solvent molecule in the crystal lattice and the CH-O bond lengths of 2.486 and 2.551 Å are within reported limits for hydrogen bonds formed between oxygen and hydrogen atoms on carbon. However, the elongation of the U=O bond is far less severe than in the report of [UO₂(TPIP)₂MeOH]. It is therefore uncertain if the uranyl oxygen is interacting with the pyridyl hydrogens in 1.

Table 2.1 Summary of X-ray crystallographic data for uranyl(VI) TPIP monomers. a The quoted value is an average of the four U-Oₜₚₚ bond lengths. b X = O or N and represents the bond length of uranium to the molecule in the 5th equatorial coordination site. c Recrystallised from pyridine. d Recrystallised from DCM. e The 2nd uranyl U=O bond is considerably more elongated than the first due to the formation of a hydrogen bond with a solvent methanol molecule.

<table>
<thead>
<tr>
<th>Complex</th>
<th>O=U=O / °</th>
<th>U=O / Å</th>
<th>U-Oₜₚₚ / Å a</th>
<th>U-X₅th / Å b</th>
</tr>
</thead>
<tbody>
<tr>
<td>[UO₂(TPIP)₂THF]¹¹</td>
<td>175.97 (11)</td>
<td>1.777(3)</td>
<td>1.783(3)</td>
<td>2.353(2)</td>
</tr>
<tr>
<td>[UO₂(TPIP)₂py]³ (1)</td>
<td>176.21 (11)</td>
<td>1.773(2)</td>
<td>1.782(2)</td>
<td>2.365(2)</td>
</tr>
<tr>
<td>[UO₂(TPIP)₂py]¹¹</td>
<td>176.62 (11)</td>
<td>1.768(2)</td>
<td>1.775(2)</td>
<td>2.366(2)</td>
</tr>
<tr>
<td>[UO₂(TPIP)₂MeOH]¹¹</td>
<td>176.90 (40)</td>
<td>1.791(8)</td>
<td>1.817(7)</td>
<td>2.352(9)</td>
</tr>
<tr>
<td>[UO₂(TPIP)₂MeCN] (2)</td>
<td>177.37 (11)</td>
<td>1.775(2)</td>
<td>1.776(2)</td>
<td>2.348(2)</td>
</tr>
<tr>
<td>[UO₂(TPIP)₂H₂O] (3)</td>
<td>178.10 (18)</td>
<td>1.761(4)</td>
<td>1.763(4)</td>
<td>2.349(4)</td>
</tr>
<tr>
<td>[UO₂(TPIP)₂Cy₃PO]¹¹</td>
<td>179.90 (17)</td>
<td>1.769(3)</td>
<td>1.773(3)</td>
<td>2.393(3)</td>
</tr>
<tr>
<td>[UO₂(TPIP)₂Ph₃PO] (4)</td>
<td>179.12 (14)</td>
<td>1.766(3)</td>
<td>1.768(3)</td>
<td>2.395(3)</td>
</tr>
</tbody>
</table>

A trend can be seen for the equatorial coordination geometry; more weakly coordinating solvents for each donor group (O, N) present longer interatomic distances between uranium and the solvent molecule. This lengthening of the bond results in a shorter average U-Oₜₚₚ
bond, indicating a stronger coordination between the uranium and TPIP. This trend continues for the U-O_5th bond lengths through to the monodentate phosphineoxide ligands, with weaker U-O_TPIP bonds reflecting the stronger U-O_Ph_3PO bond vs. U-X for solvents. Although the dataset is much shorter for U-N_5th bond lengths, they appear to follow the same trend (with the noticeable addition of the need for air sensitive conditions to synthesise 3; conditions which are not necessary for the synthesis of 1). In non-dry and degassed MeCN, the water adduct of uranyl TPIP is formed). It is noted that the two complexes with the complete phenylphosphine oxide equatorial coordination appear to have uranyl O=U=O bond angles closer to 180°, but no discernable trend can be found between the uranyl bond angle and equatorial coordination geometry.

2.3.2 Oligomeric uranyl(VI) TPIP complexes

The uranyl(VI) TPIP trimer, [UO_2(TPIP)_2]_3, was synthesised by the Cea-Olivares group in 2005.[9] However, attempts to replicate the synthesis resulted in a slightly different solid state structure to that reported; 6 crystallises with half a molecule of n-hexane per trimeric unit; [UO_2(TPIP)_2]_3.1/2C_6H_14. Both crystallise in the space group P2_1/c but with marginally different lattice parameters.[10] In addition, the repeated structure has half a hexane solvent molecule in the crystal lattice. The bond angles discussed are for 6 (Fig. 2.06). 7 and 8 present similar crystal structures (Fig. 2.06)

![Fig. 2.06 X-ray crystal structure of [UO_2(TPIP)_2]_3; 6, 7 and 8. Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids set at the 50 % probability level.](image)

The uranyl geometric parameters are presented in Table 2.2. Of note are the longer uranyl U=O bonds of 1.798(4) and 1.817(4) Å present in the bridging uranyl cation of 6 vs. the terminal uranyl bonds (1.758(4) to 1.785(4) Å), a result of the elongation of the bridging
uranyl U=O bonds to participate in CCIs. The length of the terminal uranyl U=O bonds are similar to those observed for the monomeric uranyl(VI) TPIP complexes (Table 2.1). The distance measured for the (U=O)-U CCI bonds are on a par with the U-O\textsubscript{H2O} bond in 2, although longer than any of the U-O\textsubscript{TPIP} bonds seen in each of the trimers (2.311(5) - 2.407(4) Å for 6).

The difference between the trimers lies in the bridging uranyl; 8 presents statistically shorter U=O bonds (1.765(10) and 1.784(9) Å) for the bridging uranyl than the other two trimers, suggesting that this structure may not exhibit CCIs. Compound 7 bears a more linear O=U=O bond (179.40(20)) for the bridging uranyl than either 6 or 8. These parameters result in non-identical solid-state structures for the three trimers.

Table 2.2 Summary of X-ray crystallographic data for uranyl(VI) TPIP trimers. * The CCI bond length and angle represents the geometric data measured for the coordination of the bridging uranyl oxygen to the terminal uranyl uranium ion.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Terminal O=U=O / Å</th>
<th>Terminal U=O / Å</th>
<th>Bridging O=U=O / Å</th>
<th>Bridging U=O / Å</th>
<th>CCI\textsuperscript{a} U-O / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>[UO\textsubscript{2}(TPIP)\textsubscript{2}]\textsubscript{3} \textsubscript{.1/2C\textsubscript{6}H\textsubscript{14}} (6)</td>
<td>179.30 (20)</td>
<td>1.768(5)</td>
<td>177.90 (20)</td>
<td>1.798(4)</td>
<td>176.60 (30)</td>
</tr>
<tr>
<td></td>
<td>179.10 (20)</td>
<td>1.758(4), 1.773(4), 1.785(4)</td>
<td></td>
<td>1.817(4)</td>
<td>176.50 (20)</td>
</tr>
<tr>
<td>[UO\textsubscript{2}(TPIP)\textsubscript{2}]\textsubscript{3} \textsubscript{.2C\textsubscript{6}H\textsubscript{6}} (7)</td>
<td>178.90 (20)</td>
<td>1.760(4)</td>
<td>179.40 (20)</td>
<td>1.802(4)</td>
<td>177.00 (20)</td>
</tr>
<tr>
<td></td>
<td>179.00 (20)</td>
<td>1.752(4), 1.773(4), 1.776(4)</td>
<td></td>
<td>1.798(4)</td>
<td>172.40 (20)</td>
</tr>
<tr>
<td>[UO\textsubscript{2}(TPIP)\textsubscript{2}]\textsubscript{3} \textsubscript{.3CH\textsubscript{2}Cl\textsubscript{2}} (8)</td>
<td>178.90 (50)</td>
<td>1.757(9)</td>
<td>177.40 (20)</td>
<td>1.765(10)</td>
<td>173.50 (50)</td>
</tr>
<tr>
<td></td>
<td>178.60 (50)</td>
<td>1.736(9), 1.774(9), 1.768(9)</td>
<td></td>
<td>1.784(9)</td>
<td>177.40 (50)</td>
</tr>
</tbody>
</table>

Also of note are the shorter U-O\textsubscript{TPIP} bonds for the bridging uranyl vs. terminal uranyl ions in each of the three structures (Table 2.3) by ~ 0.1 Å. The bridging uranyl cation in each structure is four-coordinate, compared to the five-coordinate terminal uranyl moieties, and it is likely that the bridging uranyl uranium is receiving more of the negative charge from
the bridging TPIP (compared to the terminal uranyl ions) to compensate for the equatorial coordinative unsaturation. In each case, the terminal uranyl ions exhibit similar U-O\textsubscript{TPIP} bond lengths between the terminal and bridging ligands.

Table. 2.3 Summary of X-ray crystallographic data for U-O\textsubscript{TPIP} bond lengths in the trimeric complexes.

*The quoted value is an average of the U-O\textsubscript{TPIP} bond lengths

<table>
<thead>
<tr>
<th>Complex</th>
<th>Bridging UU\textsubscript{O\textsubscript{TPIP}} / Å\textsuperscript{a}</th>
<th>Terminal UU\textsubscript{O\textsubscript{TPIP}} / Å\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>[UO\textsubscript{2}(TPIP)\textsubscript{2}]\textsubscript{3}.1/2C\textsubscript{6}H\textsubscript{14}</td>
<td>2.230(4)</td>
<td>2.321(4)</td>
</tr>
<tr>
<td>[UO\textsubscript{2}(TPIP)\textsubscript{2}]\textsubscript{3}.2C\textsubscript{6}H\textsubscript{6}</td>
<td>2.239(4)</td>
<td>2.355(4)</td>
</tr>
<tr>
<td>[UO\textsubscript{2}(TPIP)\textsubscript{2}]\textsubscript{3}.CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>2.228(9)</td>
<td>2.348(9)</td>
</tr>
</tbody>
</table>

The dimeric uranyl(VI) TPIP complex 5 is C\textsubscript{2}-symmetric and has two coordinatively unsaturated uranyl moieties, each with a terminal TPIP ligand and joined to the adjacent uranyl ion by two bridging TPIP ligands (Fig. 2.7). The uranyl U=O bond lengths are 1.799(11) and 1.800(11) Å and the uranyl O=U=O bond angles are statistically indistinguishable at 178.9(7)° and 179.3(7)°. In this complex, the terminal TPIP ligands have longer U-O\textsubscript{TPIP} bonds of 2.294(11) and 2.256(11) Å, compared to the bridging TPIP U-O bonds of 2.267(11) and 2.237(11) Å. All are in the range of the bond lengths seen for U-O\textsubscript{TPIP} in the bridging uranyl cations of the trimers except for the value of 2.294(11) Å, which is likely anomalous due to the lower quality of the crystal data compared to the 6 and 7.
Fig. 2.07 X-ray crystal structure of \([\text{UO}_2(\text{TPIP})_2]_2 \cdot 3\text{CH}_2\text{Cl}_2\) (5). Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids set at the 50 % probability level.

The dimer is perhaps an anticipated structure, more so than the trimers. The use of 15-crown-5 ethers with NaTPIP in DCM allowed the crystal structure of the ligand to be resolved in a study by Cea-Olivares.\(^{[15]}\) The sodium salt NaTPIP forms a dimeric structure in solution where four TPIP ligands, two bridging and two terminal, cap two sodium atoms. A third sodium atom sits interstitially coordinated to the crown ether in the complex. The formation of \([\text{UO}_2(\text{TPIP})_2]_2\) represents the most structurally similar uranyl complex to that seen for the ligand salt.

2.4 Raman and IR Spectroscopy of Uranyl(VI) TPIP Complexes

The Raman spectra of the uranyl(VI) TPIP complexes display numerous peaks, as displayed in Fig. 2.08. Previous work on transition metal complexes identified many of these as vibrations from the TPIP ligand,\(^{[16]}\) including the most intense resonance at approximately 1000 cm\(^{-1}\), arising from C-H vibrations in the phenyl rings.
Fig. 2.08 The solid state Raman spectrum of [UO$_2$(TPIP)$_2$]$_3$.2C$_6$H$_6$ (7) in absorbance between 3200 and 100 cm$^{-1}$.

Amongst the ligand resonances, the symmetric uranyl U=O stretch ($v_1$(U=O)) can be observed in the early 800 cm$^{-1}$ region. Previous work by M. Redmond compared the trimer, [UO$_2$(TPIP)$_2$]$_3$,[9] to the monomers [UO$_2$(TPIP)$_2$THF], [UO$_2$(TPIP)$_2$MeOH] and [UO$_2$(TPIP)$_2$Cy$_3$PO].[11] In the Raman spectra, the two $v_1$(U=O) stretches observed for [UO$_2$(TPIP)$_2$]$_3$ were compared to the solitary $v_1$(U=O) stretches of [UO$_2$(TPIP)$_2$THF] and [UO$_2$(TPIP)$_2$Cy$_3$PO] to state that both uranyl units of the trimeric complex were observable by Raman spectroscopy, with the elongated uranyl cation vibrating at lower energy. Although [UO$_2$(TPIP)$_2$MeOH] also displayed two $v_1$(U=O) resonances, this was assigned to impurities in the solid, evidenced by microanalysis of the sample.[11]

The solid state Raman spectra of the uranyl(VI) TPIP oligomers (5-8) all exhibit two $v_1$(U=O) stretches, summarised in Table 2.4. For the trimeric complexes, these are assigned to the bridging and terminal uranyl symmetric stretches, similar to the study by M. Redmond.[11] In the solid state structure of 5, the two uranyl units have statistically indistinguishable uranyl bond lengths, therefore the origin of the two Raman stretches is unclear. Compounds 1 and 2 also display two $v_1$(U=O) stretches in the Raman spectrum (both are analytically pure by microanalysis).

The origin of the 2nd resonance around 800 cm$^{-1}$ is uncertain. These may arise due to different U=O bond lengths within an individual uranyl moiety, as observed in the solid state structures of [UO$_2$(TPIP)$_2$MeOH] and 1, although previous uranyl complexes with different U=O bond lengths within the same uranyl moiety have displayed a single $v_1$(U=O) stretch in the Raman spectrum[17] and 2 has statistically identical U=O bond
lengths whilst presenting two $\nu_1(U=O)$ stretches. It is also possible that the resonance may arise from a P-N-P vibration.\cite{16} In the IR spectra, only one peak is observed for the symmetric uranyl stretch in all uranyl(VI) TPIP complexes. The $\nu_1(U=O)$ stretch in 7 occurs at a lower frequency than any of the monomeric complexes recorded (see Table 2.4), however 5 and 8 exhibit bands at higher energy than the monomeric complexes. It is hypothesised that the presence of the CCI leads to a lowering of energy of the $\nu_1(U=O)$ stretch due to an elongation of the U=O bond, but in 4-coordinate uranyl centres (that do not bear CCIs) $\nu_1(U=O)$ is moved to higher energy. As suggested by analysis of the bond lengths in Section 2.3.2, these vibrational data suggest that 8 may not be a complex that bears CCIs.

Table 2.4 Summary of the IR and Raman $\nu_1(U=O)$ resonances for uranyl(VI) TPIP complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Raman $\nu_1(U=O)$ / cm$^{-1}$</th>
<th>IR $\nu_1(U=O)$ / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[UO$_2$(TPIP)$_2$py] (1)</td>
<td>842, 822</td>
<td>821</td>
</tr>
<tr>
<td>[UO$_2$(TPIP)$_2$H$_2$O] (2)</td>
<td>834, 823</td>
<td>820</td>
</tr>
<tr>
<td>[UO$_2$(TPIP)$_2$Ph$_3$PO] (4)</td>
<td>825</td>
<td>825</td>
</tr>
<tr>
<td>[UO$_2$(TPIP)$_2$]$_2$ (5)</td>
<td>839, 817</td>
<td>830</td>
</tr>
<tr>
<td>[UO$_2$(TPIP)$_2$]$_3$.2C$_6$H$_6$ (7)</td>
<td>836, 816</td>
<td>814</td>
</tr>
<tr>
<td>[UO$_2$(TPIP)$_2$]$_3$.CH$_2$Cl$_2$ (8)</td>
<td>838, 825</td>
<td>831</td>
</tr>
</tbody>
</table>

2.5 Diffusion-Ordered NMR Spectroscopy of Uranyl(VI) TPIP Complexes

Room temperature multinuclear NMR analysis of uranyl(VI) TPIP complexes was found not to be effective in differentiating between oligomers and monomers in solution, although confirmed that the reactions had gone to completion.\cite{9-11} All proton resonances in TPIP are aromatic and tend to be broad, often with ortho and para proton environments in the phenyl rings overlapping. The phosphorus environments of TPIP all resonate around 25 ppm; any differences between complexes are negligible and insufficient for use in
comparing complexes in solution. Therefore, the use of $^1$H DOSY-NMR spectroscopy is seen as a potential tool for assessing the extent of aggregation of the oligomers in solution.

Of all the monomers, 2 represents the complex with the smallest group in the 5th equatorial coordination site of the uranium, and therefore the complex with the molecular mass closest to UO$_2$(TPIP)$_2$, the empirical formula of the oligomers. Measurement of the diffusion coefficient in Fig. 2.09 reveals one species present in solution with a diffusion coefficient between 7.55 and 7.65 x $10^{-10}$ m$^2$s$^{-1}$ in CD$_2$Cl$_2$, giving an average diffusion coefficient of 7.60 (+/- 0.10) x $10^{-10}$ m$^2$s$^{-1}$. Use of Equation 1.7$^{[18]}$ allows the spherical hydrodynamic radius, r$_H$, to be estimated. The spherical hydrodynamic radius for 2 is equal to 6.34 (+/- 0.33) Å, using the values of 1.3806503 x $10^{-23}$ m$^2$kgs$^{-2}$K$^{-1}$ and 0.4482 x $10^{-3}$ mNsm$^{-3}$ for k$_B$ and η respectively.$^{[19,20]}$ Comparison with X-ray crystal structures is impractical due to their highly non-spherical nature.

Fig. 2.09 The $^1$H DOSY-NMR spectrum of the aromatic resonances of [UO$_2$(TPIP)$_2$H$_2$O]$_2$. Recorded in d$_2$-DCM at 295 K.

Measurement of the diffusion coefficients of 5-8 in CD$_2$Cl$_2$ reveals the retention of the dimeric 5 in solution by use of Equation 1.8.$^{[21]}$ along with the trimeric nature of 8, presenting relative solution molecular weights of 1:2:3 for 2:5:8 (Table 2.5). Complex 7 appears to diffuse faster in solution than 8, with the marginally different structural properties of this trimer affecting the stability of the structure in solution. The diffusion coefficients of 6 are recorded as 3.40 (+/− 0.20), 5.40 (+/− 0.20) and between 6.95 to 7.35 (average 7.10 (+/− 0.25)) x $10^{-10}$ m$^2$s$^{-1}$. The middle diffusion coefficient of 6 bears resemblance to that recorded for 8 (it is within error), although the fastest and slowest diffusion coefficients resemble no other recorded uranyl(VI) TPIP complex. Complex 6 is too unstable to accurately measure the solution diffusion coefficient by DOSY-NMR.
spectroscopy, and is not summarised in Table 2.5. The DOSY-NMR spectra of 5-8 are presented in Appendix 1.

The diffusion coefficients of NaTPIP and HTPIP in d$_2$-DCM are also presented in Table 2.5 for comparison, revealing the polymeric nature of NaTPIP (approximately four times the size of HTPIP).

Table 2.5 Summary of the comparison of uranyl(VI) TPIP oligomers by $^1$H DOSY-NMR spectroscopy. Recorded at 295 K in d$_2$-DCM. $^a$ calculated from the crystal structure without solvent molecules in the crystal lattice. $^b$ obtained by comparison of M$_w$ values in $^a$. $^c$ obtained by use of Equation X.2 with the D values calculated for each sample. Errors are given in brackets (+/-) after values.

<table>
<thead>
<tr>
<th>Complex</th>
<th>M$_w$/$\text{g mol}^{-1}$</th>
<th>Relative M$_w$</th>
<th>D / $\text{m}^2\text{s}^{-1}$</th>
<th>Relative M$_w$</th>
<th>r$_H$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>[UO$_2$(TPIP)$_2$H$_2$O] (2)</td>
<td>1120</td>
<td>1</td>
<td>7.60 (0.10)</td>
<td>1</td>
<td>6.34 (0.33)</td>
</tr>
<tr>
<td>[UO$_2$(TPIP)$_2$]$_2$ (5)</td>
<td>2204</td>
<td>1.97</td>
<td>6.00 (0.25)</td>
<td>2.03</td>
<td>8.03 (0.52)</td>
</tr>
<tr>
<td>[UO$_2$(TPIP)$_2$]$_3$.2C$_6$H$_6$ (7)</td>
<td>3306</td>
<td>2.95</td>
<td>5.85 (0.10)</td>
<td>2.20</td>
<td>8.24 (0.44)</td>
</tr>
<tr>
<td>[UO$_2$(TPIP)$_2$]$_3$.CH$_2$Cl$_2$ (8)</td>
<td>3306</td>
<td>2.95</td>
<td>5.30 (0.15)</td>
<td>2.95</td>
<td>9.10 (0.52)</td>
</tr>
<tr>
<td>HTPIP</td>
<td>417</td>
<td>0.37</td>
<td>10.65 (0.20)</td>
<td>0.36</td>
<td>4.53 (0.24)</td>
</tr>
<tr>
<td>NaTPIP</td>
<td>-</td>
<td>-</td>
<td>6.70 (0.20)</td>
<td>1.46</td>
<td>7.20 (0.42)</td>
</tr>
</tbody>
</table>

The oligomers display a second set of diffusion coefficients in their DOSY solution spectra (Fig. 2.10, Table 2.6). For 8, this corresponds to the degradation product of the trimer (which is observed as the only diffusion coefficient in solution when recorded after several days standing), therefore each of the oligomeric species diffuses alongside a degradation product, highlighting their limited stability in solution.
Fig. 2.10 The $^1$H DOSY-NMR spectrum of the aromatic resonances of [UO$_2$(TPIP)$_2$]$_3$CH$_2$Cl$_2$ (8). Recorded in dry and degassed d$_2$-DCM at 295 K.

Table 2.6 Summary of the diffusion coefficients found for the uranyl(VI) TPIP oligomeric complexes by $^1$H DOSY-NMR spectroscopy in d$_2$-DCM. Recorded at 295 K. Errors given in brackets (+/-) after values.

<table>
<thead>
<tr>
<th>Complex</th>
<th>D / $10^{-10}$ m$^2$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[UO$_2$(TPIP)$_2$]$_3$.CH$_2$Cl$_2$ (8)</td>
<td>5.30 (0.15), 8.20 (0.20)</td>
</tr>
<tr>
<td>Degraded [UO$_2$(TPIP)$_2$]$_3$.CH$_2$Cl$_2$</td>
<td>7.80 (0.20)</td>
</tr>
<tr>
<td>[UO$_2$(TPIP)$_2$.2C$_6$H$_6$ (7)</td>
<td>5.85 (0.15), 8.20 (0.15)</td>
</tr>
<tr>
<td>[UO$_2$(TPIP)$_2$]$_2$.3CH$_2$Cl$_2$ (5)</td>
<td>6.00 (0.25), 11.40 (0.20)</td>
</tr>
</tbody>
</table>

The hydrodynamic spherical radius of degraded 8 is measured as 6.18 (+/- 0.35) Å, within error of that of 2 (Table 2.5) and also within error of the second species in the 8 (5.80 (+/- 0.33) Å). This implies that the degraded product of 8 is a monomeric complex, however the variety of diffusion coefficients (between 6.34 Å for 2 and 5.80 Å for 8) represent a limitation on the use of DOSY-NMR spectroscopy; namely the large error associated with the measurement.

The comparison of molecular weights in solution by DOSY-NMR spectroscopy confirms the comparative size and retention of the complexes in solution. However, it offers no insight into the cation-cation interactions in the trimeric species. Equation 1.8 also allows confirmation of the complexation of TPIP to uranyl(VI) in solution by comparison with the uncomplexed HTPIP ligand (Table 2.5).

Use of Equation 1.8 to compare NaTPIP and HTPIP in DCM shows NaTPIP to exist with a molecular weight 4.02 times the size of HTPIP, giving it a molecular weight in solution of
around 1675 g mol\(^{-1}\). The empirical formula of NaTPIP is 439 g mol\(^{-1}\), and thus this confirms an extent of aggregation of NaTPIP in DCM (3.8 times the molecular weight). The Na\(_3\)TPIP\(_4\) structure elucidated by Cea-Oliviares et al.\(^{[15]}\) has a molecular weight of 1733 g mol\(^{-1}\) and is therefore a good representation of how NaTPIP may exist in DCM solution even without crown-ethers.

### 2.6 Optical Spectroscopy of Uranyl(VI) TPIP Complexes

The sensitive techniques of UV/vis and luminescence spectroscopies were employed to understand further the solution behaviour of the uranyl(VI) TPIP complexes.

#### 2.6.1 UV/vis spectroscopy

The absorption spectrum of NaTPIP in DCM shows a strong featureless absorption in the UV region centred at 240 nm attributed to phenyl \(\pi-\pi^*\) transitions. The high energy absorption profile of the ligands enables study of the uranyl absorption in uranyl(VI) TPIP complexes (> 400 nm) and also renders this technique ideal for study by emission spectroscopy because of the lack of overlap between the TPIP and uranyl(VI) absorption bands.

The UV/vis spectra of the uranyl(VI) TPIP complexes are similar to each other and display characteristic uranyl(VI) absorption > 400 nm with associated vibrational fine structure (Fig. 2.11) and absorption maxima due to the TPIP ligand below 300 nm.

![Fig. 2.11 The UV/vis spectrum of \([\text{UO}_2\text{(TPIP)}_2]_x\text{CH}_2\text{Cl}_2\) (8) at 2.34 mM concentration between 380 and 500 nm in DCM, displaying the U=O LMCT absorption band.](image)
The absorption maxima of the U=O LMCT transitions in all the uranyl(VI) TPIP complexes are presented in Table 2.7. The absorption maxima of the uranyl(VI) TPIP monomeric complexes are similar, although the first band around 405 nm can not be seen for 2. The dimeric analogue, 5, and the trimeric complexes 6-8 all appear to have slightly lower energy absorption maxima than the monomers likely due to the elongated uranyl U=O bonds.

Table 2.7 Summary of the absorption wavelengths seen for uranyl(VI) TPIP complexes in the U=O LMCT region. All recorded in DCM at mM concentrations.

<table>
<thead>
<tr>
<th>Complex</th>
<th>U=O LMCT Absorption Wavelength / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[UO₂(TPIP)₂py] (1)</td>
<td>405 417 428 442 453</td>
</tr>
<tr>
<td>[UO₂(TPIP)₂H₂O] (2)</td>
<td>418 429 442 455</td>
</tr>
<tr>
<td>[UO₂(TPIP)₂Ph₃PO] (4)</td>
<td>404 417 429 442 454</td>
</tr>
<tr>
<td>[UO₂(TPIP)₂]₂ (5)</td>
<td>408 419 431 444 456</td>
</tr>
<tr>
<td>[UO₂(TPIP)₂][Cl][2CH₃Cl]₂ (8)</td>
<td>411 422 431 444 455</td>
</tr>
</tbody>
</table>

2.6.2 Luminescence spectroscopy of uranyl(VI) TPIP monomeric complexes

Previous work by L. Natrajan\cite{10} on [UO₂(TPIP)₂THF], [UO₂(TPIP)₂MeOH] and [UO₂(TPIP)₂Cy₃PO] revealed the three complexes to be emissive in DCM solution with similar emission profiles centred around 522 nm. In addition, these emission profiles were seen upon excitation into the U=O LMCT band (405-460 nm) or at wavelengths corresponding to the absorption spectrum of the TPIP ligand (between 200 and 350 nm), attributed to excitation into the phenyl π- π* absorption bands and the TPIP Ph₃P=O-U
LMCT transition. Work by the Wilkerson group on a series of structurally similar complexes revealed differentiation by emission spectroscopy between a monomeric complex and a similar tetrameric complex where each uranyl was coordinated to another in a CCI.\(^{(22)}\) This difference was attributed to the elongation of the uranyl bond to participate in a CCI. Therefore, the uranyl(VI) TPIP complexes should be readily identifiable in solution by luminescence spectroscopy.

The excitation and emission spectra of NaTPIP are displayed for comparison with the uranyl(VI) TPIP complexes (Fig. 2.12). NaTPIP is excited broadly around 310 nm, and emits broadly around 325 nm. Neither excitation nor emission overlaps with typical uranyl(VI) luminescence and measurement of uranyl(VI) TPIP complexes reveals no emission maxima attributable to emission from NaTPIP.

![Excitation and emission spectra of NaTPIP](image)

**Fig. 2.12** The excitation (emission $\lambda = 328$ nm) and emission (excitation $\lambda = 290$ nm) spectra of NaTPIP at 0.05 mM concentration in DCM. Excitation and emission slit widths set at 1 nm.

The solution state emission spectrum of 2 shows 5 emission maxima centred at 520 nm, with the estimated $E_{0-0}$ transition at 20747 cm\(^{-1}\) (Fig. 2.13). Excitation into the uranyl(VI) LMCT is weak with respect to the TPIP ligand excitation maxima. Notably, the excitation spectra show no absorptions corresponding to TPIP, further corroborating the suitability of this ligand for studying the uranyl(VI) emission alone and hence the electronic structure of the uranyl units in a given complex. Comparison with solid state measurements show a sharper resolution of the emission maxima but with little change in wavelength (within error of measurement) (Fig. 2.14), although excitation into the uranyl(VI) LMCT transitions is more prominent.
Fig. 2.13 The excitation (emission $\lambda = 520$ nm) and emission (emission $\lambda = 245$ nm) spectra of [UO$_2$(TPIP)$_2$H$_2$O] (2) in DCM solution. Excitation and emission slit widths set at 2 nm.

Fig. 2.14 The solid state excitation (emission $\lambda = 522$ nm) and emission (excitation $\lambda = 425$ nm) spectra of [UO$_2$(TPIP)$_2$H$_2$O] (2). * Raman band arising due to scattered light at half of the emission frequency. Excitation and emission slit widths set at 1 nm.

The luminescence spectra of the uranyl(VI) TPIP monomers (1, 2 and 4) are similar in both the solid state and in DCM solution (Table 2.8, Appendix 3); excitation broadly into the UV region (into the equatorial LMCT of the uranyl moiety, similar to that seen for previous uranyl(VI) TPIP monomers$^{[10]}$ or into the uranyl(VI) LMCT band at around 425 nm gives typical uranyl(VI) emission. Using UV excitation results in higher intensity emission compared to direct excitation into the uranyl(VI) LMCT bands. In all but one sample, five emission bands are apparent, centred around 521 nm (the solid state emission spectrum of 1 displays four bands). The average spacings between the vibrationally resolved emission maxima (Table 2.8) correspond to the symmetric stretching mode of the uranyl ions (Section 1.8).
Table 2.8 Summary of the emission profiles of the monomeric uranyl(VI) TPIP complexes. The average spacing in cm\(^{-1}\) between emission maxima are presented in brackets after the emission maxima.

<table>
<thead>
<tr>
<th>Solid state (E_{0-0}/ \text{cm}^{-1})</th>
<th>Solid state maxima / nm</th>
<th>Complex</th>
<th>DCM solution (E_{0-0}/ \text{cm}^{-1})</th>
<th>DCM solution maxima / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>20040</td>
<td>499, 522, 544, 572 (852)</td>
<td>[UO(_2)(TPIP)(_2)py] (1)</td>
<td>20747</td>
<td>482, 499, 522, 544, 571 (809)</td>
</tr>
<tr>
<td>20704</td>
<td>483, 501, 523, 546, 573 (813)</td>
<td>[UO(_2)(TPIP)(_2)H(_2)O] (2)</td>
<td>20747</td>
<td>482, 500, 520, 544, 570 (801)</td>
</tr>
<tr>
<td>20747</td>
<td>482, 500, 522, 543, 572 (816)</td>
<td>[UO(_2)(TPIP)(_2)Ph(_3)PO] (4)</td>
<td>20747</td>
<td>482, 499, 521, 544, 571 (809)</td>
</tr>
</tbody>
</table>

The emission lifetimes provide further information for investigating the solution electronic properties of the complexes; the radiative lifetimes of the uranyl(VI) TPIP monomeric complexes are summarised in Table 2.9. For comparison, lifetimes of complexes not recorded in this thesis have been reported. There is a clear trend between stability of the solvent/ligand emission lifetime in DCM solution – labile solvents used, such as THF and water, result in significantly shorter emission lifetimes. The complexes that possess a ligand in the 5th equatorial coordination site of uranium display the longest emission lifetimes. All the solution emission lifetimes are fitted to a mono-exponential decay. The solid state lifetimes produce a simplified result; 4 has the longest emission lifetime (at 373.38 µs), the complexes bearing a coordinated solvent in the complex possess shorter, biexponential lifetimes (possibly there are two degrees of solvation in the solid state). The reduction in lifetimes for solvent ligated complexes may be slightly due to the increase number of X-H oscillators in the 1st coordination sphere of the complex in unison with the solvents lability. The emission lifetimes allow good discrimination between uranyl(VI) TPIP monomeric complexes that excitation and emission spectra can not provide. The emission lifetimes for both the solid and DCM solution state emission profiles are obtainable at any observed emission maximum.
Table 2.9 Summary of the emission lifetimes of the monomeric uranyl(VI) TPIP complexes. The solid state lifetimes of $[\text{UO}_2(\text{TPIP})_2\text{THF}]$ and $[\text{UO}_2(\text{TPIP})_2\text{Cy}_3\text{PO}]$ were not recorded previously. * = not recorded. All kinetic traces were fitted using a mono-exponential or bi-exponential function. Estimation of error on lifetime data $= \pm 10\%$.

<table>
<thead>
<tr>
<th>Solid state Lifetime / μs</th>
<th>Fit ($\chi^2$)</th>
<th>Complex</th>
<th>Lifetime in DCM / μs</th>
<th>Fit ($\chi^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.47 (43 %)</td>
<td>1.169</td>
<td>$[\text{UO}_2(\text{TPIP})_2\text{py}]$ (1)</td>
<td>1.18</td>
<td>1.03</td>
</tr>
<tr>
<td>88.50 (57 %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>55.14 (51 %)</td>
<td>1.034</td>
<td>$[\text{UO}_2(\text{TPIP})_2\text{H}_2\text{O}]$ (2)</td>
<td>0.87</td>
<td>1.12</td>
</tr>
<tr>
<td>89.26 (49 %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>a</td>
<td>$[\text{UO}_2(\text{TPIP})_2\text{THF}]$\textsuperscript{[10]}</td>
<td>0.60</td>
<td>1.09</td>
</tr>
<tr>
<td>a</td>
<td>a</td>
<td>$[\text{UO}_2(\text{TPIP})_2\text{Cy}_3\text{PO}]$\textsuperscript{[10]}</td>
<td>2.00</td>
<td>1.01</td>
</tr>
<tr>
<td>373.38</td>
<td>1.028</td>
<td>$[\text{UO}_2(\text{TPIP})_2\text{Ph}_3\text{PO}]$ (4)</td>
<td>1.66</td>
<td>1.01</td>
</tr>
</tbody>
</table>

It is noted that 1 retains its emissive properties in pyridine. The excitation and emission spectra match that recorded in DCM except for the presence of a broad maxima underneath the uranyl(VI) emission. The solution radiative lifetime of 1 in pyridine is 1.06 μs, similar to that observed in DCM solution. This indicates that the coordinated pyridine solvent molecule is less labile in solution than THF even in the presence of excess pyridine.

### 2.6.3 Luminescence spectroscopy of oligomeric uranyl(VI) TPIP complexes

The solid state emission spectrum of 6 displays a clear difference to that seen for monomeric uranyl(VI) TPIP complexes (Fig 2.15). Three bands can be seen in the emission spectrum that resemble those seen for the monomeric complexes between the wavelengths centred at 521 nm ($E_{0-0} = 20000$ cm$^{-1}$). A second set of emission spectra can also be seen alongside the generic uranyl(VI) TPIP emission bands – between 509 and 557 nm, centred at 531 nm. The energy gap difference between the two sets of maxima differ (between 9 and 13 nm) suggesting that the emission arises from the two different uranyl environments present (bridging and terminal), as opposed to coupling of the uranyl(VI) excited state with the uranyl bending vibrational mode at approximately 200 cm$^{-1}$. The measured spacings are 382 cm$^{-1}$ and the spacings between each emission profile average at
837 and 867 cm\(^{-1}\) for the first and second profiles respectively. The range of vibrational spacings (between 769 and 909 cm\(^{-1}\)) precludes assignment of the individually emissive LMCT bands, as has been performed previously in the literature.\[^{22}\]

Fig. 2.15 The solid state excitation (emission \(\lambda = 521\) nm) and emission (excitation \(\lambda = 440\) nm) spectra of [UO\(_2\)(TPIP)\(_2\)]\(_3\).1/2C\(_6\)H\(_{14}\) (6). Excitation and emission slit widths set at 1 nm.

The excitation spectrum still maintains broad excitation between 200 and 350 nm. The excitation spectrum around 420 nm bears similarities to the emission spectrum, although the broadness of the maxima inhibits accurate comparison. The U=O LMCT excitation bands are red-shifted in comparison to the monomeric complexes, centred around 435 nm as opposed to 425 nm. Measurement of the luminescence of 6 in DCM solution was previously performed by L. Natrajan at low resolution (10 nm excitation and emission slits).\[^{10}\] However, repetition of measurement of the emission spectrum (Fig. 2.16) reveals the broad emission maxima previously seen to be composed of two sets of bands, similar to the solid state emission. Therefore, the oligomeric nature of 6 is retained in solution.

Fig. 2.16 The emission (excitation \(\lambda = 440\) nm) spectra of [UO\(_2\)(TPIP)\(_2\)]\(_3\).1/2C\(_6\)H\(_{14}\) (6) in DCM solution. Emission slit widths set at 1 nm.
The luminescence spectra of the uranyl(VI) TPIP complexes show that the different complexes can be distinguished in both solid state and DCM solution. It is prudent to compare 6 with 4 to investigate the presence of CCIs by emission spectroscopy; both have an equatorial coordination geometry otherwise saturated by phenyl-phosphineoxide bonds. The formation of a second set of emission maxima at lower energy to the first in 6 represent the visualisation of the two uranyl geometries present in the trimer, compared to the solitary uranyl environment in 4. The broadening of the emission maxima in 6 combined with the decrease in lifetime (from 373 μs for 4 to a biexponential decay of 27 (44 %) and 77 (56 %) μs) show the contribution to the emission of CCIs in the trimeric complex, with the resulting increased vibrational quenching via intermetallic communication perhaps responsible for the large decrease in emission lifetime. The trend is seen in the solution spectra of the complexes and the decrease in lifetime (from 1.66 μs to 0.98 μs) confirms the presence of the CCIs for the trimer in solution.

The emission spectrum of 7 conversely displays one set of emission bands centred at 522 nm in the solid state (Fig. 2.17). The bands are broad with respect to monomeric complexes such as 4 but notably lacking in the second set of emission and U=O LMCT excitation bands seen in 6. Comparison with measurement in DCM solution shows the retention of the solid state emission profile. The studies of the luminescence spectra of 7 reveal a difference between solvates of \([\text{UO}_2(\text{TPIP})_2]_3\) that appear to be retained in dissolution of the same solvent (DCM), and highlight the sensitivity of uranyl emission to minor geometrical changes in the uranyl moiety.

![Fig. 2.17 The solid state excitation (emission \(\lambda = 522\) nm) and emission (excitation \(\lambda = 425\) nm) spectra of \([\text{UO}_2(\text{TPIP})_2]_3\cdot2\text{C}_6\text{H}_6\) (7). Excitation and emission slit widths set at 1 nm.](image)

The solid state luminescence spectra of 8 resemble that seen for 7 (Table 2.10). When dissolved in DCM, the emission spectrum of 8 is a closer imitation to 6 (Fig. 2.16) than 7.
This represents a small but significant change in geometry of the trimeric structure in solution.

Table 2.10 Summary of the emission profiles of the oligomeric uranyl(VI) TPIP complexes.

<table>
<thead>
<tr>
<th>Solid state E₀₀₀ / cm⁻¹</th>
<th>Solid state maxima / nm</th>
<th>Complex</th>
<th>DCM solution E₀₀₀ / cm⁻¹</th>
<th>DCM solution maxima / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>20000</td>
<td>500, 509, 522, 531, 544, 557, 572, 585</td>
<td>[UO₂(TPIP)₂]₃₋₁/₂C₆H₁₄ (6)</td>
<td>19920</td>
<td>502, 509, 524, 531, 547, 556, 586</td>
</tr>
<tr>
<td>20661</td>
<td>484, 500, 522, 546, 573</td>
<td>[UO₂(TPIP)₂]₃₋₂C₆H₆ (7)</td>
<td>19920</td>
<td>502, 524, 546, 574</td>
</tr>
<tr>
<td>20661</td>
<td>485, 500, 522, 546, 571</td>
<td>[UO₂(TPIP)₂]₃₋CH₂Cl₂ (8)</td>
<td>19960</td>
<td>501, 509, 523, 533, 545, 557</td>
</tr>
<tr>
<td>20080</td>
<td>498, 506, 519, 530, 542, 554, 568</td>
<td>[UO₂(TPIP)₂]₂₋₃CH₂Cl₂ (5)</td>
<td>20000</td>
<td>500, 509, 522, 533, 545, 558</td>
</tr>
</tbody>
</table>

The solid state luminescence of 5 displays similarities to 6; a second set of emission maxima can be seen at lower energy to the first (Fig. 2.18). In 5, the second set of maxima are much weaker than observed for 6, where the two sets of emission bands are of similar intensity. The excitation spectrum shows broad excitation between 200 and 350 nm and U=O LMCT excitation centred at 425 nm but with minor maxima at higher wavelength, centred at 430 nm. The excitation spectrum therefore mirrors the absorption spectrum.

Fig. 2.18 The solid state excitation (emission λ = 522 nm) and emission (excitation λ = 405 nm) spectra of [UO₂(TPIP)₂]₁₂ (5). * Raman band arising due to scattered light at half of the emission frequency. Excitation and emission slit widths set at 1 nm.
The emission spectrum shows a change in relative intensities of the bands in DCM solution (Fig. 2.19), similar to that seen for 6.

![Emission Spectrum](image)

Fig. 2.19 The emission (excitation $\lambda = 300$ nm) spectra of $[\text{UO}_2(\text{TPIP})_2]_2$ (5) in DCM solution. Emission slit widths set at 1 nm.

It is noted that the emission spectra of all uranyl(VI) TPIP complexes, monomeric or oligomeric, emulate the respective excitation spectrum observed $> 400$ nm in terms of the presence of one or two sets of emission maxima and also band spacing. However, the second set of bands observed in certain cases for the oligomers is not observed in their absorption spectra (Section 2.6.1).

More information on the oligomeric complexes can be collected from study of the emission lifetimes presented in Table 2.11. The lifetimes justify the individuality of each solvate of the trimer in the solid state as seen in the luminescence spectra. The biexponential lifetime of 6 (27 (44 %) and 77 (56 %) $\mu$s) is maintained in the same percentage contribution at all measured wavelengths; the uranyl moieties therefore all contribute to the same emission. The monoexponential lifetime in DCM solution (0.98 $\mu$s) again represents the combined emission of all uranyl units in the complex – the intermetallic communication retained in solution via CCIs. The solution emission lifetime of 5 (0.99 $\mu$s) is within error of that reported for 6. The emission spectrum of 5 displayed in Fig. 2.18 is noted to show a likeness to that of 6, more so than to its own solid state emission spectrum. It is therefore possible to argue that 5 initially reverts to a trimeric array in DCM solution, although
DOSY-NMR studies exhibited in Section 2.5 confirm the solution existence of the dimeric complex over the longer lifetime of the NMR experiment.

The shorter solution lifetime of 8 (0.75 μs) compared to 6 (0.98 μs) supports the theory that the two complexes are geometrically non-identical in solution. The change in the emission spectrum of 8 from solid to DCM solution therefore represents a change in geometry (of the uranyl moieties and subsequent CCIs) but retention in identity of the complex.

Notably, the lifetime of 7 in benzene solution is recorded as 0.09 μs. The emission spectrum (presented later in Section 2.6.5) is also only visible at higher concentrations, in combination this indicates that benzene is a poor choice of solvent for study of uranyl(VI) TPIP luminescence.

Table 2.11 Summary of the emission lifetimes of the oligomeric uranyl(VI) TPIP complexes. All kinetic traces were fitted using a mono-exponential or bi-exponential function. Estimation of error on lifetime data = ±10%.

<table>
<thead>
<tr>
<th>Solid state Lifetime / μs</th>
<th>Fit (χ²)</th>
<th>Complex</th>
<th>Lifetime in DCM /μs</th>
<th>Fit (χ²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.79 (44 %)</td>
<td>1.17</td>
<td>[UO₂(TPIP)₂]₁.1/2C₆H₁₄ (6)</td>
<td>0.98</td>
<td>1.08</td>
</tr>
<tr>
<td>76.71 (56 %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>115.23</td>
<td>1.08</td>
<td>[UO₂(TPIP)₂]₂ (5)</td>
<td>0.99</td>
<td>1.01</td>
</tr>
<tr>
<td>20.99 (32 %)</td>
<td>1.03</td>
<td>[UO₂(TPIP)₂]₂.2C₆H₆ (7)</td>
<td>1.02</td>
<td>1.12</td>
</tr>
<tr>
<td>67.77 (68 %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>49.77 (11 %)</td>
<td>1.04</td>
<td>[UO₂(TPIP)₂]₃.CH₂Cl₂ (8)</td>
<td>0.75</td>
<td>1.20</td>
</tr>
<tr>
<td>250.17 (89 %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.6.4 Comparison of the uranyl(VI) TPIP trimers

The three uranyl(VI) TPIP trimers (6-8) measured by luminescence spectroscopy show little difference in their solid state structures by X-ray crystallography (Table 2.2). Therefore, the differences shown by the complexes in luminescence spectroscopy are of interest.
As noted in Section 2.6.4, the solid state emission spectrum and radiative lifetime of the complex 6 correlate well to the presence of CCIs in the solid state. By comparison, 8 shows an emission profile similar to that of the monomers (1, 2 and 4) in the solid state. This complex also emits for considerably longer than 6 (250.17 and 49.77 vs. 76.71 and 26.79 µs) and the monomeric complexes ligated by a solvent molecule. Combined with the short U=O uranyl bond lengths reported in Section 2.2, it can be summarised that the trimeric structure of 8 is supported only by the bridging ligands and not by CCIs between uranyl units, although this then brings further questions on the bond lengths of the four-coordinate uranyl cations present in the structure vs. 5. In DCM solution, 8 exhibits an emission profile most akin to 6, suggesting that it may structurally change to allow the bridging uranyl unit to participate in CCIs with the terminal uranyl cations. This would also explain the UV/vis data seen in Section 2.6.1, where the spectra of 8 and 6 in DCM solution are indistinguishable. The different emission lifetime of 8 in solution (0.75 vs. 0.98 µs) shows that it maintains some sense of individuality in solution and is not identical to 6.

To investigate the reason for the lack of the second set of emission bands in 7, a concentration dependant study of the emission profile was carried out. It could be reasoned that, in more concentrated samples, the potential to form CCIs is encouraged by increased proximity of uranyl(VI) units. The emission spectrum of 7 is compared to 8 at increasing concentrations (~ 0.49 to 3.75 mM). Fig. 2.20 reveals no effect of concentration on either sample and at the same concentrations neither sample exactly matches the other. The concentration of the sample at luminescence concentrations (mM) does therefore not affect the structure of the complexes in solution.
Fig. 2.20 *Above* The emission spectra of [UO$_2$(TPIP)$_2$]$_6$C$_6$H$_6$ (7) in DCM solution between the concentrations (in ascending order) of 488 and 2940 μM. *Below* The emission spectra of [UO$_2$(TPIP)$_2$]$_3$CH$_2$Cl$_2$ (8) in DCM solution between the concentrations (in ascending order) of 721 and 3750 μM. Excitation $\lambda = 405$ nm.

Emission profiles resembling 6 has been seen before.$^{[23,24]}$ The extra set of emission maxima are observed upon conversion of UO$_2$(OTf)$_2$ to UO$_2$Cl$_4^{2-}$ in ionic liquids. It has long been reported that such changes in the optical spectra of uranyl complexes can represent a change in geometry.$^{[25]}$ Therefore 7, which has very similar structural chemistry
to 6 by single crystal XRD, is geometrically different to 7. In the study of the emission profiles of uranyl(VI) TPIP complexes (in DCM solution and the solid state), the second set of emission bands only ever occur when multiple uranyl centres are present and therefore it is likely that the second set of emission maxima represents a second uranyl(VI) environment in the complex (as opposed to vibrational coupling of the LMCT excited state with the $\nu_2$ uranyl bending stretch). The complex 7 possesses two uranyl environments in the solid state crystal structure and, in addition, the solid state emission lifetime is similar to that recorded for 6, and not 4 or 8, suggesting the presence of CCIs in the solid state structure. Therefore, it is hypothesised that the minor geometrical differences between 6 and 7 are the reason for the absence of the second set of emission maxima in the spectra of the former, perhaps as a result of the near linear geometry of 7 (Table 2.2).

Further experimentation on the solution emission profiles of 7 reveals the formation of the second set of peaks. Measurement of 7 in benzene (Fig. 2.21) yields the appearance of a second set of emission bands at lower energy to the first, and of lower intensity, with emission maxima at similar wavelengths to 6 (in DCM, Table 2.10). When 7 is recorded in dry and degassed DCM (Table 2.12), it gives an emission spectrum with broad bands ranging from 510 to 557 nm, centred at 532 nm. Shoulders can be seen at lower wavelengths to the peaks at similar wavelengths to the emission maxima seen in the sample recorded in non-dry and -degassed DCM.

![Graph](image)

**Fig. 2.21** The emission spectrum of $[\text{UO}_2(\text{TPIP})_2]_{\text{H}_2}\text{C}_6\text{H}_6$(7) in benzene. Excitation $\lambda = 405$ nm.
Table 2.12 Summary of the emission maxima of [UO$_2$(TPIP)$_2$]$_2$.2C$_6$H$_6$ (7) in different solvents

<table>
<thead>
<tr>
<th>Solution</th>
<th>DCM solution E$_{0-0}$/ cm$^{-1}$</th>
<th>DCM solution maxima / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>19960</td>
<td>501, 510, 523, 531, 547, 558</td>
</tr>
<tr>
<td>Dry and degassed DCM</td>
<td>19608</td>
<td>510, 532, 558</td>
</tr>
</tbody>
</table>

It is not thought that the solvent present in the crystal lattice affects the emission profile given the retention of the emission profiles of 6 and 8 in DCM solution. As already stated, the extended U=O bonds in the bridging uranyl are vital in the appearance of the second set of emission maxima for 6, therefore the minor changes for this unit in 7 cause the change in emission profile in the solid state; U=O = 1.802(4) and 1.798(4) Å with O=U=O equal to 179.4(2)$^\circ$. For 6, U=O = 1.798(4) and 1.817(4) Å with O=U=O equal to 177.9(2)$^\circ$. The values for the bond angles and the longest bond length are statistically distinguishable.

In solution, the geometry of 7 is changed to a sufficient degree to observe varying levels of the full set of emission maxima, whilst never changing to sufficiently match that of 6 in DCM. Crystallisation from DCM or benzene always yields 5 or 7, respectively and so no further data can be discerned regarding the geometry of the complexes with respect to changes in solution. Nevertheless, a detailed investigation by emission spectroscopy is very useful in assessing the electronic and, by extension, chemical structure of the uranyl(VI) ion in a family of compounds.

2.7 Stability of [UO$_2$(TPIP)$_2$]$_3$.I/2C$_6$H$_{14}$

As described in Section 2.2, the structure of 6 can be broken up by addition of a coordinating solvent or phosphine-oxide ligand. However, the formation of the structure is dependent on crystallisation and, although observable in solution by luminescence spectroscopy, DOSY-NMR spectroscopy suggests the structure is not stable over time (several days).

The synthesis of uranyl(VI) TPIP complexes involves an intermediate product assigned the formula “UO$_2$(TPIP)$_2$”. Dissolution of this product in DCM shows an emission profile that
matches that seen for 6 (Fig. 2.22). In addition, the lifetime of the species matches that recorded for 6. Therefore, the structure of 6 is seen to form upon instant addition of DCM (minus the presence of hexane), confirming the trimeric form is the more thermodynamically favourable product in the absence of coordinating solvents or ligands. The emission profile is independent of sample concentration.

Fig. 2.22 The emission spectrum of “UO$_2$(TPIP)$_2$” in DCM. Excited at 405 nm.

Over the course of 90 minutes the sample of “UO$_2$(TPIP)$_2$” shows a degradation of the second set of emission maxima centred at 533 nm, indicating the trimeric structure is starting to decompose in solution, an observation which is consistent with the DOSY-NMR data presented in Section 2.5. Left standing over the weekend, the second set of emission maxima are almost gone and now represent little more than a shoulder on the first set of emission maxima (Fig. 2.23). The emission spectrum resembles that seen for 5 in the solid state. These data suggest that “UO$_2$(TPIP)$_2$” initially forms the trimeric complex upon dissolution in DCM but then forms the dimer over time, which explains the crystallisation of 5 if the sample is left to stand as described in Section 2.2. Inconsistencies with the DCM solution luminescence spectra of 5 may indicate that the dimer reforms the trimer for a brief period in time in DCM before reforming the dimer over the timescale of a DOSY-NMR measurement. Therefore, the structure of 6 is not an indefinitely stable structure outside of its crystallised form. However, it can be utilised to observe CCI transient
species, which may have considerable use in studying CCI mediated redox reactions in uranyl species.

Fig. 2.23 The emission spectra of “UO₂(TPIP)₂” in DCM left after 90 minutes standing and right after standing over the weekend. Excited at 405 nm.

2.8 Further Aggregates of Uranyl(VI) TPIP

The use of the non-coordinating solvents benzene and DCM have shown to be useful in synthesising aggregated uranyl(VI) TPIP complexes, and so other non-coordinating solvents may lead to geometrically different structures than those previously observed, perhaps displaying different CCIs. The intermediate product “UO₂(TPIP)₂” is insoluble in diethyl ether, ethyl acetate, hexane and pentane.

The intermediate product is sparingly soluble in toluene and immediate layering with hexane yielded a small quantity of tiny crystals of {Na[UO₂(TPIP)₂]₂(μ₂-TPIP)} (9) on the side of the vial and a large quantity of uncharacterised powder deposited at the base.

{Na[UO₂(TPIP)₂]₂(μ₂-TPIP)}C₆H₅CH₃ crystallises with one toluene solvent molecule in the crystal lattice, two inequivalent molecules of 9 complete the unit cell (Fig. 2.24). In contrast to any previous uranyl(VI) TPIP structures, the 5th equatorial coordination site of each uranium is occupied by a bridging TPIP ligand which connects the uranyl cation to one adjacent. The complexes each exist as a dimeric entity and the charge of the bridging TPIP is balanced by an interstitial sodium atom.
The crystallographic data is of insufficient quality to reliably discuss geometric parameters, preventing discussion of the coordination of the sodium cation to its neighbouring topography.

In an analogous reaction, KTPIP reacted with uranyl nitrate and the intermediate product is sparingly soluble in toluene. Immediate layering with hexane yielded tiny crystals of \{K[UO_2(TPIP)_2](\mu_2-TPIP)\} \(10\) on the side of the vial and a large quantity of uncharacterised powder at the base of the vial. Compound \(10\) crystallises with one solvent molecule in the crystal lattice, similar to \(9\) (Fig. 2.24). Two inequivalent complexes complete the unit cell. The crystal data is poor and standard deviations and reliable geometric information can not be ascertained.

The structure of both complexes are regarded as intermediates in the formation of “UO_2(TPIP)_2” from uranyl nitrate and a TPIP salt. They resemble well both the NaTPIP structure derived in the literature\(^{15}\) and \(5\). In addition, the alkali metal comes from the TPIP salt and should have been removed from the reaction as NaNO_3. The minute quantity of crystals found of each indicates that this is a step in the reaction to form “UO_2(TPIP)_2” that has remained as a minor impurity and crystallised from toluene – the bulk product that precipitates from the crystallisation is presumably still “UO_2(TPIP)_2”.

**2.9 Electrochemical Data on Uranyl(VI) TPIP Complexes**

Preliminary electrochemical data were recorded in DCM to allow differentiation between oligomers of uranyl(VI) TPIP and to determine if the complexes are able to form stable
uranyl(V) derivatives in solution. The influence of the CCIs may also affect the redox potentials and this can be investigated. This work was performed at Trinity College, Dublin as part the COST-1006 scheme alongside Dr Carola Schulzke. The subsequent time constraints placed on this analysis preclude further electrochemical studies on the uranyl(VI) TPIP complexes.

The redox potentials of NaTPIP were immeasurable in DCM, despite the use of varying scan rates. All measurements resulted in the same outcome; polymerisation of the ligand at the surface of the working electrode.

2.9.1 Cyclic voltammetry

Redox couples of interest in uranyl(VI) complexes are found at negative potential (with an $f^0$ electronic configuration uranyl(VI) can not be oxidised), which rules out interference from the electrolyte used in these studies; $[\text{Bu}_4\text{N}][\text{BPh}_4]$ displays redox chemistry at positive potentials near 0.9 V.\textsuperscript{[35]}

The complexes chosen: $[\text{UO}_2(\text{TPIP})_2\text{THF}]$: 4 ; 6 and 7, all display redox potentials at negative voltage in the cathodic sweep of the scan, yet are devoid of features at anodic currents (Fig. 2.25, Appendix 4). This suggests that any redox activity displayed by the complexes may be irreversible.

![Cyclic voltammogram of $[\text{UO}_2(\text{TPIP})_2\text{THF}]$ and $[\text{UO}_2(\text{TPIP})_2\text{C}_6\text{H}_6]$ between -2.0 and 2.0 V in DCM (vs. $\text{Fc}^+$/Fc\textsuperscript{[36]} 62.5 mM $[\text{Bu}_4\text{N}][\text{BPh}_4]$); 100 mVs\textsuperscript{-1}. Initial scan direction cathodic.](image-url)
A summary of observable peaks is presented in Table 2.13. The effect of coordination environment on the uranyl ion can clearly be seen, although there is no discernable trend between monomeric and oligomeric complexes. Complex 6 has one extra observable feature than the other uranyl(VI) TPIP complexes measured, however it is at a much greater negative potential (-1.82 V) than any other feature, near the limit of known uranyl(VI) redox potentials.\cite{37} Without knowledge of the reduction potentials for TPIP and \(\text{Ph}_3\text{PO}\) (although they may be similar to each other), assignment of the reduction features is not possible. However, it is known that the redox potential of uranyl(VI) to uranyl(V) in 1 M perchloric acid is 0.16 V vs. SHE.\cite{38}

Table 2.13 Summary of the reduction potentials recorded for the uranyl(VI) TPIP complexes in DCM (vs. \(\text{Fc}^+/\text{Fc}\))\cite{36} 62.5 mM \([\text{Bu}_4\text{N}]\[\text{BPh}_4]\); 100 mVs\(^{-1}\).

<table>
<thead>
<tr>
<th>Complex</th>
<th>([\text{UO}_2(\text{TPIP})_2]^{\text{THF}})</th>
<th>([\text{UO}_2(\text{TPIP})_2]^{\text{Ph}_3\text{PO}})</th>
<th>([\text{UO}_2(\text{TPIP})_2]^{1/2\text{C}<em>6\text{H}</em>{14}})</th>
<th>([\text{UO}_2(\text{TPIP})_2]^{2\text{C}_6\text{H}_6})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Value} / \text{V})</td>
<td>-0.10</td>
<td>-0.73</td>
<td>-0.55</td>
<td>-0.83</td>
</tr>
<tr>
<td>(\text{Value} / \text{V})</td>
<td>-0.90</td>
<td>-1.40</td>
<td>-1.30</td>
<td>-1.40</td>
</tr>
<tr>
<td>(\text{Value} / \text{V})</td>
<td>-</td>
<td>-</td>
<td>-1.82</td>
<td>-</td>
</tr>
</tbody>
</table>

2.9.2 Differential pulse voltammetry
An anodic peak is observed for 6 at -0.67 V and cathodic peaks at -0.61 and -0.87 V (Fig. 2.26). The peak at -0.61 V is similar in potential to the anodic peak and may represent the reduction potential of the same process seen in the anodic scan, whereas the value at -0.87 V has no corresponding anodic value and represents an irreversible process. None of the observed peaks correspond to peaks in the cyclic voltammetry (CV) scan.
Fig. 2.26 Differential pulse voltammogram of $[\text{UO}_2(\text{TPIP})_2]_3.1/2\text{C}_6\text{H}_{14}$ (6) between -2.0 and 0.5 V in DCM (vs. $\text{Fc}^+/\text{Fc}$) $62.5$ mM $[\text{Bu}_4\text{N}][\text{BPh}_4]$; 100 mVs$^{-1}$. Anodic scan above the $x$-axis; cathodic scan below.

Similar to the CV results, the uranyl(VI) TPIP complexes present varying redox potentials (Table 2.14). In each case there are reversible and irreversible processes occurring. The monomeric complexes appear to display a seemingly reversible redox potential at lower voltage than either of the trimeric complexes and may indicate a difference in the reduction chemistry of the uranyl moiety in the presence of CCIs. The irreversible processes display no obvious trend between different samples and even whether they appear in the anodic or cathodic scans. As with the CV data, determination of the redox processes is difficult when the electrochemistry of the ligands is unknown.

Table 2.14 Summary of the redox potentials for the uranyl(VI) TPIP complexes in DCM (vs. $\text{Fc}^+/\text{Fc}$) $62.5$ mM $[\text{Bu}_4\text{N}][\text{BPh}_4]$; 100 mVs$^{-1}$. An. = anodic, Cat. = cathodic.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$[\text{UO}_2(\text{TPIP})<em>2]</em>{\text{THF}}$</th>
<th>$[\text{UO}_2(\text{TPIP})<em>2]</em>{\text{Ph}_3\text{PO}}$</th>
<th>$[\text{UO}_2(\text{TPIP})_2]_3.\text{C}<em>6\text{H}</em>{14}$</th>
<th>$[\text{UO}_2(\text{TPIP})_2]_3.2\text{C}_6\text{H}_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan</td>
<td>An.</td>
<td>Cat.</td>
<td>An.</td>
<td>Cat.</td>
</tr>
<tr>
<td>Value / V</td>
<td>0.23</td>
<td>-0.27</td>
<td>0.25</td>
<td>-0.23</td>
</tr>
<tr>
<td>Value / V</td>
<td>-0.67</td>
<td>-0.61</td>
<td>-0.51</td>
<td>-</td>
</tr>
<tr>
<td>Value / V</td>
<td>-0.82</td>
<td>-0.87</td>
<td>-0.89</td>
<td>-0.90</td>
</tr>
<tr>
<td>Value / V</td>
<td>-1.35</td>
<td>-1.47</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
2.10 Attempted Reductions of Uranyl(VI) TPIP Complexes

2.10.1 Reaction of uranyl(VI) TPIP complexes with KCp

Literature studies demonstrate the effective use of KCp as a reducing agent for uranyl(VI) complexes,,[39,40] and so reductions of uranyl(VI) TPIP complexes were initially attempted with KCp. Reaction of either 1 or 4 with KCp in pyridine led to the formation of a brown solution. Layering this solution with \textit{n}-hexane yielded single crystals of 1 in each case, highlighting the competition for the uncharged monodentate Ph$_3$PO ligand from the uranophilic pyridine solvent. The attempted reduction of 4 displays absorption maxima due to uranyl(VI) in the UV/vis absorption spectrum, however additional maxima that are not assigned to uranyl(VI) are observed at 550 and 671 nm in Fig. 2.27. These could be due to the presence of uranium(IV). No absorption transitions are found at longer wavelengths \textit{i.e.} in the nIR region that would correspond to lower energy $f$-$f$ transitions.

![Absorbance vs. Wavelength](image.png)

Fig. 2.27 UV/vis absorption spectrum between 310 and 900 nm of the attempted reduction of [UO$_2$(TPIP)$_2$Ph$_3$PO] (4) by KCp. Recorded in pyridine.

Multinuclear NMR spectroscopy reveals the formation of at least one new species after reaction with KCp. The $^{31}$P NMR spectrum in Fig. 2.28 shows the appearance of extra resonances around that of the uranyl(VI) TPIP resonance, suggesting either that whatever reaction has taken place is incomplete, or perhaps that a resulting uranyl(V) complex has disproportionated.
The reaction of \([\text{UO}_2(\text{TPIP})_2\text{THF}]\) with \(\text{KCp}\) in THF led to the observation of both uranyl(VI) and unknown maxima in the UV/vis absorption spectrum. Maxima at 571 and 651 nm are a significant shift of electronic transitions observed for uranyl(VI) TPIP complexes. Attempts to grow single crystals from the orange solution were unsuccessful. \(^{31}\text{P}\) NMR spectroscopy reveals a single resonance, at 22.78 ppm, albeit broad. The \(^1\text{H}\) NMR spectrum is obscured by the residual benzene resonance, but a major and minor species is indicated, supporting the UV/vis spectrum indication that uranyl(VI) TPIP is present alongside other, possibly paramagnetic, species.

Luminescence spectroscopy does not reveal the presence of uranyl(VI) excitation and emission maxima. An excitation maximum at 352 nm leads to the emission profile seen in Fig. 2.29, with two maxima at 420 and 470 nm at comparatively higher energy than would be expected for uranyl(VI). No other electronic transitions are observed in either spectrum and the emissive species remains unknown due to the uncharacterised reaction products. The emissive lifetime of 5 ns (60 %) and 15 ns (40 %) is short, much shorter than uranyl(VI) TPIP complexes (Section 2.6) and also shorter than lifetimes reported for uranyl(V) species in the literature.\(^{41,42}\) Despite the resemblance in energy of the emission maxima to uranyl(V),\(^{41,42}\) it is unknown if the emission is uranium-based.
2.10.2 Other reducing reagents

The reduction of [UO$_2$(TPIP)$_2$THF] was also attempted with Cp*$_2$Co, due to the apparent success of the reducing agent for uranyl(VI) in the work of the Hayton and Mazzanti groups.\cite{43-49} Treatment of [UO$_2$(TPIP)$_2$THF] with Cp*$_2$Co in pyridine led to several resonances in the $^{31}$P NMR spectrum between 24 and 32 ppm. A similar result was observed when [UO$_2$(TPIP)THF] was stirred with potassium graphite for an hour in d$_6$-benzene but at different frequencies (25 – 50 ppm), likely due to solvent effects (Fig. 2.30) and contrasting reaction products. In both reactions, the $^{31}$P and $^1$H NMR spectra indicate that a clean reduction attempt has been unsuccessful, with uranyl(VI) TPIP likely still present in the reaction with Cp*$_2$Co.

![Fig. 2.29](image1)

**Fig. 2.29** The excitation (emission $\lambda = 475$ nm) and emission (excitation $\lambda = 352$ nm) spectra of the reaction of [UO$_2$(TPIP)$_2$THF] with KCp in THF.

![Fig. 2.30](image2)

**Fig. 2.30** $^{31}$P-$[^1$H] NMR spectrum of [UO$_2$(TPIP)$_2$THF] after reaction with Cp*$_2$Co (in d$_5$-pyridine) and potassium graphite (in d$_6$-benzene). Recorded at room temperature.
Attempts to crystallise the cobalt-blue solution of the attempted reduction of [UO$_2$(TPIP)$_2$THF] by potassium graphite resulted in crystals too small to analyse by single crystal X-ray diffraction. Allowing the reaction to stir for longer than an hour (i.e. overnight) resulted in a brown solution with grey precipitate. Agitation of the solution allowed temporary re-dissolution of the precipitate. Both products failed to yield resonances in $^1$H, $^{13}$C and $^{31}$P NMR spectroscopy and are suspected decomposition products. Attempts to reduce [UO$_2$(TPIP)$_2$THF] with potassium in d$_6$-benzene resulted in the production of the same brown solution and grey precipitate seen after prolonged reaction with potassium graphite. It is suspected that potassium has decomposed the uranyl(VI) TPIP complex. Similarly, attempts to reduce [UO$_2$(TPIP)$_2$]$_3$ with potassium graphite in d$_6$-benzene resulted in the formation of similar decomposition products.

2.10.3 Attempted comproportionation reaction of [UO$_2$(TPIP)$_2$]$_2$ and UI$_4$

Reaction of 5 with UI$_4$ in d$_6$-benzene resulted in a brown solution after stirring overnight (Equation 2.1). Attempts to grow single crystals were unsuccessful and the presence of a single resonance at 26.53 ppm in the $^{31}$P NMR (in C$_6$D$_6$) spectrum suggests only one major species as a reaction product at a similar frequency to uranyl(VI) TPIP complexes,\textsuperscript{10,11} albeit in a different solvent.

\[ [\text{UO}_2(\text{TPIP})_2]_2 + \text{UI}_4 - 2\text{Et}_2\text{O} \rightarrow "\text{U}^{\text{V}}\text{O}_2(\text{TPIP})_3" \]

\textit{Equation 2.1 The attempted comproportionation reaction between 5 and UI$_{4}$.}

The Raman spectrum of the resulting precipitate from crystallisation attempts reveals no symmetric stretching frequencies attributable to uranyl(V) or uranyl(VI), with all resonances present due to the TPIP ligand. Measurement of the Raman spectrum after one month and after exposure to oxygen gave no change, indicating an air stable reaction product.

2.11 Reaction of NaTPIP with Uranyl(V) Triflate

Reaction of the uranyl(V) salt $[\{\text{UO}_2(\text{py})_3\}_2\{\text{K}_3(\text{OTf})_5\}.\text{py}]$ with either one or two equivalents of NaTPIP in pyridine led to isolation of crystals of 1 after layering with hexane. $^1$H and $^{31}$P NMR spectroscopies confirm the presence of a minor and major species in solution (Fig. 2.31); 1 and a second species, potentially a uranyl(V) TPIP complex. UV/vis spectroscopy displays absorption maxima non-typical for uranyl(VI) wavelengths at 641 and 850 nm, with the latter a maximum present in the uranyl(V) triflate salt. Attempts
to excite into any of the observed electronic transitions, or at wavelengths typical for uranyl(VI) LMCT transitions (around 420 nm), yielded no emission spectra. This reaction suggests TPIP strongly prefers the +VI oxidation state of uranyl, partially oxidising a uranyl(V) salt. The second complex remains uncharacterised.

Fig. 2.31 Left $^1$H NMR and right $^{31}$P-$[^1$H]$^N$MR spectrum of the reaction of \([\{\text{UO}_2(\text{py})_5\}_2\{\text{K}_3(\text{OTf})_5\}_\text{py}\] with 2 equivalents of NaTPIP. Recorded in $d_6$-benzene at room temperature.

The uranyl(V) salt \([\text{UO}_2(\text{OTf})\text{THF}_{1.5}]\) reacted with 2.5 equivalents of NaTPIP in THF to yield a yellow/brown solution. Single crystals of \([\text{Na}_3(\text{TPIP})_2(\text{OTf})(\text{THF})_3]\).THF (11 ,Fig. 2.32) were isolable from a THF solution layered with hexane. The three sodium atoms are charge balanced by two TPIP ligands and one triflate anion. The two TPIP ligands are arranged in a similar fashion to the dimeric structure of 5 and the literature structure of \([\text{Na}(15\text{-crown-5})][\text{Na}_3(\text{TPIP})_4]\), further indicating the favourability of the dimeric array of metal TPIP complexes. The Na-O$_{\text{TPIP}}$ bonds range from 2.233(4) to 2.393(4) Å, within range of uranyl(VI) TPIP U-O$_{\text{TPIP}}$ bonds (Tables 2.1 and 2.3). The loss of the triflate anion from the uranyl(V) salt and the slight excess of TPIP used in the reaction suggests a uranyl(V) complex with 1 TPIP ligand may exist uncrystallised from the reaction mixture.
2.12 Synthesis of Na\textsuperscript{F}TPIP

Attempts to synthesise the fluorinated analogue of TPIP, F\textsubscript{TPIP}, initially followed that outlined in the literature.\textsuperscript{[12]} However, difficulties encountered during this and alternate synthetic schemes (Appendix 5) led to the purchase of (C\textsubscript{6}F\textsubscript{5})Br as a reagent. Attempts to follow the literature procedure from here led to the isolation of the hydrolysed product (C\textsubscript{6}F\textsubscript{5})\textsubscript{2}PH (12, Fig. 2.33). Uncertainties in the cause of the failure of the reaction led to the proposal of a different oxidation method; rather than hydrogen peroxide, \textit{meta}-chloroperoxybenzoic acid (\textit{m}-cpba) would be used to oxidise the product. The synthesis was first attempted on the reaction of Ph\textsubscript{2}PCl with hexamethyldisilazane; the post-reflux mixture was transferred to the glovebox and washed with hexane. Reaction of the subsequent white powder with \textit{m}-cpba after stirring for a week yielded analytically pure HTPIP. Repetition of the reaction with FPh\textsubscript{2}PBr, but leaving to reflux with hexamethyldisilazane to react over a weekend instead of 6 hours, yielded H\textsuperscript{F}TPIP. The extended reflux produced a brown solution (as opposed to the dark yellow solution yielded from a shorter reflux), and it is possible that success in the repeat reaction is down to this extended reaction time as opposed to the alternate oxygenation step. Indeed, difficulties in separating H\textsuperscript{F}TPIP from the salts formed from quenching remaining \textit{m}-cpba (used in slight excess to ensure complete oxidation) indicate that oxidation by hydrogen peroxide may be a more favourable oxidation route. Reaction with NaOH yielded the sodium salt of F\textsuperscript{F}TPIP as an analytically pure white powder after work up. It is noted that reaction of KOH with 12 produced an uncharacterised white solid (the $^{31}$P NMR spectrum displays a shift of...
nearly 4 ppm (Fig. 2.34), yet microanalysis indicates that there is one potassium atom per phosphorus atom.

Fig. 2.33 X-ray crystal structure of (C₆F₅)₂PH (12). Thermal ellipsoids set at the 50% probability level.

Fig. 2.34 ³¹P-{¹H} NMR spectrum of (C₆F₅)₂PH (12) and its unknown potassium salt. Recorded in d₆-DMSO at room temperature.

2.13 Reaction of Na⁺TPIP with Uranyl(VI) Nitrate
Reaction of Na⁺TPIP with uranyl(VI) nitrate is analogous to that of HTPIP: addition of Na⁺TPIP to uranyl(VI) nitrate in absolute ethanol/deionised water produces a cloudy green
solution which, when filtered and air dried, leaves a pale green powder. Dissolution in pyridine and layering with hexane did not yield crystals, unlike the analogous reaction with NaTPIP. Attempts to produce single crystals from DCM/ hexane (at room temperature and -18 °C) and benzene/ hexane were insufficient to yield single crystals, thus the proposed structure (13, Fig. 2.35) is based on the TPIP analogue. UV/ vis spectrophotometry exhibits a typical uranyl(VI) U=O LMCT absorption band centred at 419 nm, although lacking in any of the vibrational fine structure exhibited by the analogous uranyl(VI) TPIP complexes (Section 2.6).

Fig. 2.35 Proposed structure of [UO$_2$(F$_2$TPIP)py] (13).

Luminescence spectroscopy reveals a broad emission maximum centred around 475 nm (Fig. 2.36) following excitation around 420 nm, or at higher energy below 400 nm (analogous to uranyl(VI) TPIP complexes). Although severely blue-shifted compared to uranyl(VI) TPIP complexes (Section 2.6), the emission lifetimes of 14.53 ns (53 %) and 311.82 ns (47 %) firmly suggest a uranyl(VI) complex for 13. Vibrational fine structure is not observed in either the absorption or excitation spectrum, and is therefore not expected for the emission spectrum. Further study on the emission of 13 in the solid state or in a frozen glass would enable assessment of non-radiative quenching mechanisms present in this system compared to TPIP and evaluation of the relative energies of the excited states of the ligand π- π* and LMCT charge transfer states.$^{[13]}$
The synthesis of uranyl(VI) TPIP complexes has been studied in detail to conclude that all the complexes contain a ‘UO$_2$(TPIP)$_2$’ synthon, but the overall structure varies depending on the use of coordinating or non-coordinating solvents, or the introduction of a monodentate ligand. The use of non-coordinating solvents often results in a trimeric [UO$_2$(TPIP)$_2$]$_3$ structure, with an interstitial uranyl ion connected to terminal uranyl moieties by bridging TPIP ligands and potentially by CCIs.

Analysis of the complexes by $^1$H DOSY-NMR spectroscopy confirms that the structures retain their single crystal X-ray solid state aggregation in solution, but that the trimeric complexes are only stable for a limited time (between hours and days). Further study by luminescence spectroscopy allows for easy differentiation between the oligomers based on their emission profiles and radiative lifetimes. In addition, luminescence spectroscopy uncovers disparities between the trimeric structures, which arise from minor geometrical differences observable in the X-ray crystal structures of the products. Combined with vibrational spectroscopic observations, it is concluded that the trimeric structure is not always supported by CCIs.

The reduction and oxidation potentials of [UO$_2$(TPIP)$_2$THF], 4, 6 and 7 each possess a unique reduction potential, indicating a difference in energy in accessing the corresponding
+V oxidation state of uranyl. The presence of CCIs in 6 and 7 may enable the reduction process to occur at a higher reduction potential. Attempts to manufacture this oxidation state of the complexes by the use of one-electron reducing agents supports this hypothesis, with partial reactions varying in completeness from structure to structure, and with reducing agent used. The attempted reductions of the uranyl(VI) TPIP complexes, along with the observed oxidation of uranyl(V) in the presence of TPIP, suggests a strong affinity for the +VI oxidation state of this actinyl ion for TPIP.

Synthesis of the fluorinated analogue of TPIP proved non-trivial, with many footfalls discovered in the reaction schematic. A trial reaction of uranyl nitrate with NaF revealed an apparent inefficiency of the ligand for uranyl photophysics in comparison to the non-fluorinated ligand, which may be due to an efficient relaxation pathway for the uranyl(VI) LMCT excited state via ligand absorption transitions.

2.15 References


Chapter 3

Investigating Cation-Cation Interactions of Uranyl(VI) Fluorinated β-Diketonate Complexes
3.1 Introduction

β-Diketonates and their substituted derivatives have been widely used in transition metal and f-element chemistry. In the lanthanide series, the use of these ligands has become synonymous with the development of highly luminescent complexes.\(^1,2\) These bidentate ligands form both very kinetically and thermodynamically stable 3:1 metal:ligand chelates and the appended chromophores very efficiently sensitise both visible and nIR f-f based emission from lanthanide ions.\(^1,2\) Despite their success as luminophores for the trivalent lanthanide ions, uranyl(VI) β-diketonate complexes are not generally emissive in either the solid nor solution state at room temperature,\(^3,4\) due to efficient energy overlap of the absorption maxima of the ligand with the uranyl(VI) U=O LMCT excited state. This results in non-radiative decay of the excited state.\(^4\) However, substitution of protons in the ligand with fluorine can lead to observable emission (the absorption energy levels of the ligand are at higher energy than acetylacetonate, acac). Yayamura \textit{et al}.\(^3\) compared various acac based ligands with uranyl(VI) in frozen solution to show that, of the ligands studied, the hexa-fluorinated acac derivative (hfac) produced the longest emission lifetime of 484 ns at 77 K (in the complex \([\text{UO}_2(\text{hfac})_2\text{THF}]\)). The uranyl(VI) acac complexes displayed luminescence lifetimes that decreased in the order hfac> btfa> tta> tfac> acac, which emitted for 0.9 ns (btfa = benzoyltrifluoroacetylacetonate, tta = thenoyltrifluoroacetylacetonate and tfac = trifluoroacetylacetonate). All the samples were measured in dry and degassed CCl\(_4\) at 77 K.\(^1\)

The acac ligands qualify as strong σ-donating ligands that are capable of rendering the uranyl oxygen able to form Lewis-base adducts.\(^5,6\) Work carried out by Ekstrom \textit{et al}.\(^7\) followed the sublimation of an undefined uranyl(VI) hfac complex derived from uranyl(VI) nitrate and the ligand in non-coordinating solvents, which led to the discovery of a trimeric uranyl hfac complex, \([\text{UO}_2(\text{hfac})_2]_3\) in the solid state (Fig. 3.01).\(^8\) The uranyl oxygen atoms bind to an adjacent uranyl uranium ion in a cation-cation interaction (CCI) in such a fashion that an equilateral triangle is formed between the three uranium atoms. The near-linearity of the O=U=O bond angles is preserved, however the uranyl U=O bond lengths show an average of a 0.07 Å elongation for those coordinating to a neighbouring uranyl in a CCI.\(^8\)
The fluorination of the acac ligand in hfac affects the donation of electron density to the uranyl moiety – sublimation of UO$_2$(acac)$_2$H$_2$O leads to the formation of a dimeric complex, [UO$_2$(acac)$_2$]$_2$ (Fig. 3.02).$^9$ In this complex, the two uranium centres are connected by bridging oxygen atoms of the ligands and no CCIs are observed in the solid state.

Further work was carried out at The University of Manchester to study fluorinated-acac complexes of uranyl(VI). Isolation of the uranyl(VI) hfac complex used as the sublimation precursor in Ekstrom’s work$^{[7,8]}$ yielded [UO$_2$(hfac)$_2$H$_2$O].Et$_2$O. Attempts to replicate the formation of [UO$_2$(hfac)$_2$]$_3$ failed, however, instead leading to the isolation of a crystal structure of [UO$_2$(hfac)$_2$]$_4$ by single crystal X-ray diffraction (Fig. 3.03).$^{[10]}$ In the structure, each uranyl is coordinated to an adjacent uranyl by a T-shaped CCI through one uranyl oxygen. The product is assembled by bridging CCIs, with solid state IR spectroscopy showing two distinct uranyl symmetric and asymmetric stretches.$^{[10]}$ The interaction suggests a severe deviation of the uranyl bond angle at around 160 $^\circ$, although disorder of the structure means this requires further study.$^{[10]}$ The product is also recrystallised at 253
K upon dissolution in anhydrous DCM, indicating it is the thermodynamically favourable product.

![X-ray crystal structure of [UO$_2$(hfac)$_2$]$_4$. Hydrogen atoms omitted for clarity. Adapted from reference [10]. Thermal ellipsoids set at the 50% probability level.](image)

Work on the hfac analogue tta led to the isolation of the monomeric uranyl complex [UO$_2$(tta)$_2$MeOH], which was sublimed under vacuum to give [UO$_2$(tta)$_2$], a dimeric complex in which there is one T-shaped CCI between the uranyl units (Fig. 3.04) and also an interaction between one tta ligand with both uranium cations [11] (similar to that of [UO$_2$(acac)$_2$]).[9] This result, in addition to [UO$_2$(hfac)$_2$]$_4$[10] and [UO$_2$(acac)$_2$],[9] reveals the variation of uranyl oxygen Lewis basicity with varying degrees of fluorination and, therefore, structure in the absence of coordination in the 5th equatorial site of the uranium. Unfortunately, not all acac-based ligands crystallise easily after sublimation[7,11,12] (the isolation of [UO$_2$(tta)$_2$]$_2$ was difficult)[11,12] and so a complete study of sublimed uranyl(VI) acac complexes would be difficult to achieve.
3.2 Synthesis of Uranyl(VI) Hfac Complexes and Solid State Characterisation

3.2.1 Synthesis of uranyl(VI) hfac complexes

The sublimation of \([\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}]\cdot\text{Et}_2\text{O}\) to form the orange coloured \([\text{UO}_2(\text{hfac})_2]_4\) proceeded via a yellow intermediate. Repetition of the sublimation at low temperature (50 °C) yielded \([\text{UO}_2(\text{hfac})_2\text{Et}_2\text{O}]\) (14) as the yellow intermediate. 14 is unstable and desolvated over time to produce \([\text{UO}_2(\text{hfac})_2]_4\) (Scheme 3.1). Exposing the product to higher temperatures during sublimation also produced \([\text{UO}_2(\text{hfac})_2]_4\).

![Scheme 3.1](image)

Scheme 3.1 The sublimation of \([\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}]\cdot\text{Et}_2\text{O}\) (14). The ligands for \([\text{UO}_2(\text{hfac})_2]_4\) have been removed, instead the tetrameric nature of the uranyl moieties is presented.

Dissolution of \([\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}]\) in THF and diethyl ether followed by removal of solvents and then sublimation in an attempt to synthesise \([\text{UO}_2(\text{hfac})_2]_3\) led to the co-crystallisation of \([\text{UO}_2(\text{hfac})_2\text{Et}_2\text{O}]\) and \([\text{UO}_2(\text{hfac})_2]_4\) (15, Scheme 3.2). This sublimation indicates the tetrameric product is a recurring stable product in the sublimation of uranyl hfac complexes, with the trimeric \([\text{UO}_2(\text{hfac})_2]_3\) complex remaining elusive.
3.2.2 Single crystal structural analysis of $[\text{UO}_2(\text{hfac})_2\text{Et}_2\text{O}]$

The low temperature sublimation of $[\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}]$ results in the crystal structure of the diethyl ether adduct, which contains two structurally different $[\text{UO}_2(\text{hfac})_2\text{Et}_2\text{O}]$ complexes (14a and 14b, Fig. 3.05) in the crystal lattice. 14a has uranyl U=O bond lengths of 1.697(11) and 1.743(11) Å with a uranyl bond angle of 178.2(6)°. 14b has statistically indistinguishable bond lengths of 1.721(10) and 1.713(9) Å and a uranyl bond angle of 178.2(5)°. 14a has U-O$_{\text{hfac}}$ bond lengths of 2.326(12), 2.360(10), 2.386(13) and 2.372(12) Å and a longer U-O$_{\text{Et}_2\text{O}}$ bond length of 2.436(12) Å. 14b displays U-O$_{\text{hfac}}$ bond lengths within range of 14a at 2.365(11), 2.338(12), 2.381(12) and 2.406(12) Å and a similar U-O$_{\text{Et}_2\text{O}}$ bond length of 2.458(12) Å.

The reason for the elongation of one U=O bond in 14a is unclear but could be attributed to inaccurate crystal data. The inequivalent complexes follow the theme of the crystal structure of $[\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}].\text{Et}_2\text{O}$, which has four structurally different molecules in the crystal lattice. The uranyl bond lengths in $[\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}].\text{Et}_2\text{O}$ vary between 1.696(18) and 1.774(15) Å whilst the U-O$_{\text{hfac}}$ bond lengths are found between 2.228(9) and 2.458(17) Å, thus the bond lengths of U-O$_{\text{hfac}}$ and uranyl U=O in 14 are well within the range of those seen in $[\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}]$. The U-O$_{\text{H}_2\text{O}}$ bond lengths of between 2.376(16) and 2.440(20) Å are, on average (2.399 Å), slightly shorter than the U-O$_{\text{Et}_2\text{O}}$ bond lengths observed in 14, representing the stronger bond between uranium and water compared to uranium and diethyl ether.
Fig. 3.05 The X-ray crystal structure of $[\text{UO}_2(\text{hfac})_2\text{Et}_2\text{O}]$ (14). Hydrogen atoms omitted for clarity. Thermal ellipsoids set at the 50 % probability level.

Analysis of the $^1\text{H}$ NMR spectrum shows a resonance at 6.74 ppm belonging to the proton on the hfac ligand. Resonances at 4.89 and 1.62 integrate to four and six protons with respect to the two hfac protons, confirming the presence of one diethyl ether molecule per $\text{UO}_2(\text{hfac})_2$ in solution. The large chemical shift of the diethyl ether peaks with respect to free diethyl ether in deuterated DCM$^{[13]}$ confirms the coordination of the solvent molecule to uranyl in solution. No resonances occur at frequencies that would be anticipated for unbound diethyl ether.$^{[13]}$ $^{19}\text{F}$ NMR spectroscopy exhibits two resonances at around -78 ppm, unusual for uranyl(VI) hfac complexes.$^{[10]}$ The resonances are of equal intensity and represent the same complex. If the fluorine is coupling with the proton to produce a doublet, this would be repeated in the $^1\text{H}$ NMR spectrum, therefore the resonances are assigned as two singlets, and it is likely that the diethyl ether molecule has rendered the CF$_3$ groups closest to itself inequivalent compared to those furthest from it, leaving the protons equivalent.

3.2.3 Single crystal structural analysis of $[\text{UO}_2(\text{hfac})_2\text{Et}_2\text{O}]$$[\text{UO}_2(\text{hfac})_2]_4$

The two independent molecules in the crystal structure lie adjacent to one another with the $[\text{UO}_2(\text{hfac})_2\text{Et}_2\text{O}]$ uranyl moiety lying in the plane of the CCIs in the tetrametallic structure (Fig. 3.06). The uranyl U=O bond lengths in co-crystallised $[\text{UO}_2(\text{hfac})_2\text{Et}_2\text{O}]$ in 15 are 1.725(13) and 1.746(14) Å with a uranyl bond angle of 179.1(2) °, similar to the values observed in the crystal structure of 14. The U-O$_{\text{hfac}}$ bond lengths vary between 2.389(12) and 2.443(12) Å, longer than those observed in 14 and statistically indifferent to the U-O$_{\text{Et}_2\text{O}}$ bond length of 2.439(14) observed in the co-crystallised $[\text{UO}_2(\text{hfac})_2\text{Et}_2\text{O}]$ of 15. In the solid state structure of the tetrametallic complex, two of the uranyl moieties are related
by symmetry so the U=O bond lengths of 1.733(12) and 1.786(12) Å for one unit and 1.732(13) and 1.814(13) Å are replicated for the opposite uranyl units. The longer bond lengths in each pair belong to the uranyl U=O bond that is participating in a CCI. The uranyl bond angles of 178.1(6) and 178.6(6) ° are more linear than those seen for the tetrametallic structure shown in the introduction (considerably bent near 160 °). The bond angles around the CCIs are 170.0(7) and 167.2(7) °. The U=OCCI bond lengths of 2.479(12) and 2.443(13) Å are longer than the U=Ohfac bond lengths in the complex, which vary between 2.309(13) and 2.405(11) Å, but are similar to those seen for the equatorial U-O bond lengths in the co-crystallised [UO₂(hfac)₂Et₂O] structure. The reason for the weaker uranium-hfac bonds in the [UO₂(hfac)₂Et₂O] structure of 15 is unclear, but due to the difference from those reported for 14 it is indicated the co-crystallisation alongside the tetrametallic [UO₂(hfac)₂]₄ in 15 is responsible.

Fig. 3.06 The X-ray crystal structure of [UO₂(hfac)₂Et₂O][UO₂(hfac)]₂ (15). Fluorine and hydrogen atoms omitted for clarity. Thermal ellipsoids set at the 50 % probability level.

3.3 Spectroscopic Analysis of the Extent of Aggregation in Uranyl(VI) hfac Oligomers

3.3.1 Multinuclear diffusion-ordered NMR spectroscopy

Diffusion-ordered NMR spectroscopy enables comparison between [UO₂(hfac)₂H₂O] and [UO₂(hfac)₂]₄; if the latter exists as a monomer in solution, it will diffuse at approximately the same rate as [UO₂(hfac)₂H₂O].
The monomer [UO$_2$(hfac)$_2$H$_2$O] diffuses at a rate of 12.60 (+/− 0.10) x 10$^{-10}$ m$^2$s$^{-1}$ by measurement of the ligand proton. Use of Equation 1.7 gives a spherical hydrated radius of 3.83 (+/− 0.19) Å. The values of 1.3806503 x 10$^{-23}$ m$^2$kgs$^{-2}$K$^{-1}$ and 0.4482 x 10$^{-3}$ mNsm$^{-3}$ are used for $k_B$ and $\eta$ respectively.$^{[14,15,16]}$

The diffusion coefficient of [UO$_2$(hfac)$_2$]$_4$ is observed between 12.55 and 13.10 x10$^{-10}$ m$^2$s$^{-1}$, average value 12.85 (+/− 0.20) x 10$^{-10}$ m$^2$s$^{-1}$. Equation 1.7 gives $r_H = 3.75$ (+/− 0.20) Å. The calculated hydrated spherical radius is within error of that calculated for [UO$_2$(hfac)$_2$H$_2$O] and suggests that [UO$_2$(hfac)$_2$]$_4$ exists as a monomer in dry and degassed DCM solution.

The hfac ligand is abundant in fluorine atoms and so comparison between the two complexes in solution is also possible using $^{19}$F DOSY-NMR spectroscopy. The resonances are referenced to hexafluorobenzene as an internal standard, which is added to the solution.

The diffusion coefficient of [UO$_2$(hfac)$_2$H$_2$O] using $^{19}$F DOSY-NMR is 12.55 (+/− 0.10) x 10$^{-10}$ m$^2$s$^{-1}$ (Fig. 3.07) with a hydrated spherical radius of 3.84 (+/− 0.19) Å. [UO$_2$(hfac)$_2$]$_4$ diffuses at a rate of 12.25 (+/− 0.10) x 10$^{-10}$ m$^2$s$^{-1}$, leading to $r_H = 3.94$ (+/− 0.20). The hydrated spherical radii are within error of each other, as with the $^1$H DOSY-NMR measurements, and confirm the monomeric existence of [UO$_2$(hfac)$_2$]$_4$ as a monomer in anhydrous DCM solution. In addition, the values are also within error for comparison between $^1$H and $^{19}$F diffusion coefficients for each sample. A summary of the values is provided in Table 3.1.
Fig. 3.07 The $^{19}$F DOSY-NMR spectrum of above [UO$_2$(hfac)$_2$H$_2$O] and below [UO$_2$(hfac)$_2$]$_4$. Recorded in d$_2$-DCM at 295 K.

Table 3.1 Summary of the DOSY-NMR diffusion coefficients and hydrated spherical radii of [UO$_2$(hfac)$_2$H$_2$O] and [UO$_2$(hfac)$_2$]$_4$. $r_H$ calculated using Equation 1.7. Recorded in d$_2$-DCM at 295 K. Errors given in brackets (+/-) after values.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^1$H DOSY Data</th>
<th>$^{19}$F DOSY Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D / $10^{-10}$ m$^2$s$^{-1}$</td>
<td>$r_H$ / Å</td>
</tr>
<tr>
<td>[UO$_2$(hfac)$_2$H$_2$O]</td>
<td>12.60 (0.10)</td>
<td>3.83 (0.19)</td>
</tr>
<tr>
<td>[UO$_2$(hfac)$_2$]$_4$</td>
<td>12.85 (0.20)</td>
<td>3.75 (0.20)</td>
</tr>
</tbody>
</table>

The $^1$H diffusion coefficient of [UO$_2$(hfac)$_2$]$_4$ measured again in a saturated NMR sample shows the formation of extra resonances upfield with respect to the resonance present in the non-concentrated sample. The diffusion coefficients of the proton resonances are 10.80 (+/- 0.2) and 9.65 (+/- 0.15) x$10^{-10}$ m$^2$s$^{-1}$, leading to $r_H = 4.46$ (+/- 0.24) and 5.00 (+/- 0.26) Å respectively (Fig. 3.08). The $^{19}$F resonances give similar diffusion coefficients at 9.65
(+/- 0.15) and between 10.40 and 10.50 (average 10.45 (+/- 0.10)) x10^{-10} \text{m}^2\text{s}^{-1}. The hydrated spherical radii of the diffusion coefficients are 5.00 (+/-0.26) and 4.61 (+/- 0.23) Å. Both sets of diffusion coefficients are slower than those found for the non-saturated samples and $^1$H and $^{19}$F calculated diffusion coefficients and hydrated spherical radii compare well, within error. However, it is the non-saturated samples which best reflect the concentrations used in the luminescence measurements.

The hydration coefficients and hydrated spherical radii of [UO$_2$(hfac)$_2$)$_4$ in saturated and non-saturated samples are summarised in Table 3.2. The hydration coefficients can be compared using Equation 1.8.$^{[17]}$

<table>
<thead>
<tr>
<th>[UO$_2$(hfac)$_2$)$_4$ sample</th>
<th>$^1$H DOSY Data</th>
<th>$^{19}$F DOSY Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D / x10^{-10} \text{m}^2\text{s}^{-1}$</td>
<td>$r_H / \text{Å}$</td>
</tr>
<tr>
<td>Non-saturated</td>
<td>12.85 (0.20)</td>
<td>3.75 (0.20)</td>
</tr>
<tr>
<td>Saturated</td>
<td>10.80 (0.20)</td>
<td>4.46 (0.24)</td>
</tr>
<tr>
<td></td>
<td>9.65 (0.15)</td>
<td>5.00 (0.26)</td>
</tr>
</tbody>
</table>

Fig. 3.08 The DOSY-NMR spectrum of saturated [UO$_2$(hfac)$_2$)$_4$ derived from $^{19}$F resonances. Recorded in d$_2$-DCM at 295 K.
A comparison between the two species in the saturated sample and the non-saturated sample using Equation 1.8 is exhibited in Table 3.3. Comparison of the species present between the concentrated and non-concentrated samples is difficult – although $^{19}$F DOSY-NMR spectroscopy indicates that a dimeric complex of $[\text{UO}_2(hfac)_2]$ exists, the equivalent diffusion coefficients in the $^1$H NMR spectrum show a larger molecular mass difference. A change in speciation upon observation of a different nucleus is unlikely and so the appreciable difference is attributable to error in the diffusion measurement. The second species in the concentrated sample is not as large, between 1.6 and 1.7 times the size of the non-saturated sample. If the four-coordinate monomer $[\text{UO}_2(hfac)_2]$ is assumed to be the speciation of $[\text{UO}_2(hfac)_2]_4$ in dry and degassed DCM, as per Table 3.1, it would have a molecular mass of 684 gmol$^{-1}$. The smaller species in the concentrated sample would therefore have a molecular weight of 1101 or 1149 gmol$^{-1}$ (by use of $^{19}$F or $^1$H DOSY data respectively). Addition of one hfac ligand to make $\text{UO}_2(hfac)_3$ results in a molecular mass of 1098 gmol$^{-1}$, and could therefore be assigned as the smaller species in the concentrated $[\text{UO}_2(hfac)_2]_4$ sample.

Table 3.3 Summary of the DOSY-NMR diffusion coefficients and molecular weight of $[\text{UO}_2(hfac)_2]_4$ in saturated and non-saturated samples. Recorded in d$_2$-DCM at 295 K. Errors given in brackets (+/-) after values.

<table>
<thead>
<tr>
<th>[UO$_2$(hfac)$_2$]$_4$ sample</th>
<th>$^1$H DOSY Data</th>
<th>$^{19}$F DOSY Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D/x10^{-10} m^2 s^{-1}$</td>
<td>$M_w^*$</td>
</tr>
<tr>
<td>Non-saturated</td>
<td>12.85 (0.20)</td>
<td>1</td>
</tr>
<tr>
<td>Saturated</td>
<td>10.80 (0.20)</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>9.65 (0.15)</td>
<td>2.36</td>
</tr>
</tbody>
</table>

*Relative molecular weight with respect to the non-saturated sample.

3.3.2 Solid-state luminescence spectroscopic investigations

As demonstrated in Chapter 2, intermetallic communication between uranyl(VI) units can lead to broadening of emission profiles and considerably shorter emission lifetimes. The tetrametallic $[\text{UO}_2(hfac)_2]_4$ should therefore be distinguishable from $[\text{UO}_2(hfac)_2\text{H}_2\text{O}]$ by luminescence spectroscopy.

The excitation profile of $[\text{UO}_2(hfac)_2\text{H}_2\text{O}]$ in the solid state shows broad UV excitation centred at 260 nm with only weak excitation directly into the uranyl moiety at > 400 nm (Fig. 3.09). The resulting emission profile is typical of uranyl(VI); five bands observed between 478 and 570 nm, centred at 520 nm. The emission lifetime is biexponential with
the shorter component measured as 0.60 μs and the longer component 3.30 μs. (the shorter lifetime component is proposed to arise from the uranyl equatorial LMCT emission, which radiatively decays faster than the axial U=O LMCT emission).\textsuperscript{[18]}

By comparison, the solid state excitation spectrum of [UO\textsubscript{2}(hfac)\textsubscript{2}]\textsubscript{4} exhibits a more intense excitation band at 362 nm and slightly more pronounced uranyl excitation bands at 425 nm (Fig. 3.10). The four emission maxima are observed between 504 and 571 nm and are broad with respect to the emission maxima of [UO\textsubscript{2}(hfac)\textsubscript{2}H\textsubscript{2}O]. The centre is found at 523 nm, a marginal red-shift in energy compared to [UO\textsubscript{2}(hfac)\textsubscript{2}H\textsubscript{2}O] at 520 nm. The red-shift in emission maxima is likely to be due to the elongation of the uranyl U=O bonds. Crucially, the biexponential emission lifetime is more than ten times shorter at 0.05 μs and 0.21 μs (Table 3.4). The effect of 4 CCIs within the structure has reduced the emission lifetime significantly due to intermetallic quenching and elongation of the U=O bonds.

**Fig. 3.09** The solid state excitation (emission $\lambda = 524$ nm) and emission (excitation $\lambda = 375$ nm) spectra of [UO\textsubscript{2}(hfac)\textsubscript{2}H\textsubscript{2}O]. * Raman band arising due to scattered light at half of the emission frequency. Excitation and emission slit widths set at 1 nm.

**Fig. 3.10** The solid state excitation (emission $\lambda = 524$ nm) and emission (excitation $\lambda = 358$ nm) spectra of [UO\textsubscript{2}(hfac)\textsubscript{2}]\textsubscript{4}. Excitation and emission slit widths set at 1 nm.
Table 3.4 Summary of the emission lifetimes of the uranyl(VI) hfac complexes in the solid state

<table>
<thead>
<tr>
<th>Complex</th>
<th>Emission Maxima</th>
<th>Lifetime/ μs</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{UO}_2\text{(hfac)}_2\text{H}_2\text{O}]))</td>
<td>478, 497, 520, 543, 570</td>
<td>0.60 (12 %) 3.30 (88 %)</td>
<td>1.16</td>
</tr>
<tr>
<td>([\text{UO}_2\text{(hfac)}_2\text{]}_4)</td>
<td>497, 523, 546, 571</td>
<td>0.05 (27 %) 0.21 (73 %)</td>
<td>1.13</td>
</tr>
</tbody>
</table>

* The apparent electronic origin values (\(E_{0,0}\)) were determined from the observed energy of the first vibronic band in the emission spectra. The exact location of \(E_{0,0}\) however, is often difficult to ascertain in spectra of uranyl(VI) compounds especially at low resolution. The exact \(E_{0,0}\) may lie at higher energies depending on the local symmetry of the complex in question.

3.3.3 Solution state luminescence

The DOSY-NMR study in Section 3.3.1 concluded that the CCIs between \([\text{UO}_2\text{(hfac)}_2\text{]}_4\) did not exist in solution. This should also be observable by emission spectroscopy.

The excitation spectrum of \([\text{UO}_2\text{(hfac)}_2\text{H}_2\text{O}])\) in DCM is broad and featureless between UV excitation from 230 nm past uranyl excitation at 425 nm (Fig. 3.11). The emission spectrum reveals four emission peaks between 507 and 576 nm centred at 526 nm, red-shifted with respect to the solid state emission spectrum.

![Fig. 3.11 The excitation (emission \(\lambda = 524\) nm) and emission (excitation \(\lambda = 375\) nm) spectra of \([\text{UO}_2\text{(hfac)}_2\text{H}_2\text{O}])\) in DCM solution. * Raman band arising due to scattered light at half of the emission frequency. Excitation and emission slit widths set at 1 nm.](image)

\([\text{UO}_2\text{(hfac)}_2\text{]}_4\) gives similar excitation and emission profiles in DCM solution to \([\text{UO}_2\text{(hfac)}_2\text{H}_2\text{O}])\); the excitation spectrum is broad from 230 nm onwards and the emission profile gives four bands between 506 and 577 nm, centred at 527 nm (Fig. 3.12) (Table 3.5). The emission profile does not appear to differ from that seen for \([\text{UO}_2\text{(hfac)}_2\text{H}_2\text{O}])\) in DCM, suggesting a lack of the tetrametallic array in solution.
By freezing the DCM solution of [UO$_2$(hfac)$_2$]$_4$H$_2$O at 77 K and measuring the spectrum, an increase in resolution with the peaks can be seen in both the excitation spectrum at around 428 nm and in the emission spectrum (Fig. 3.13). The four peaks are found at lower energy compared to the solution emission spectrum between 527 and 611 nm, centred at 552 nm. The frozen DCM excitation and emission spectra of [UO$_2$(hfac)$_2$]$_4$ closely resemble that of [UO$_2$(hfac)$_2$H$_2$O] (Table 3.5). The frozen solution measurements indicate that the tetrametallic complex is not reformed upon freezing of the sample.

Fig. 3.12 The excitation (emission $\lambda = 526$ nm) and emission (excitation $\lambda = 375$ nm) spectra of [UO$_2$(hfac)$_2$]$_4$ in DCM solution. Excitation and emission slit widths set at 1 nm.

Fig. 3.13 The excitation (emission $\lambda = 527$ nm) and emission (excitation $\lambda = 428$ nm) spectra of [UO$_2$(hfac)$_2$H$_2$O] in frozen DCM solution. * Raman band arising due to scattered light at half of the emission frequency. Excitation and emission slit widths set at 1 nm.
Table 3.5 Summary of the emission maxima of the uranyl(VI) hfac complexes in DCM

<table>
<thead>
<tr>
<th>Complex</th>
<th>Maxima in DCM (298 K)</th>
<th>Maxima in frozen DCM (77 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{0} / \text{cm}^{-1}$</td>
<td>Wavelength/ nm</td>
</tr>
<tr>
<td>$[\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}]$</td>
<td>20040</td>
<td>499, 526, 551, 576</td>
</tr>
<tr>
<td>$[\text{UO}_2(\text{hfac})_2]_4$</td>
<td>19763</td>
<td>506, 527, 550, 577</td>
</tr>
</tbody>
</table>

The lifetimes of the samples are summarised in Table 3.6. The decrease in emission lifetime for $[\text{UO}_2(\text{hfac})_2]_4$ compared to $[\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}]$ in DCM is less than 50 %, much less severe than the decrease in lifetime for the solid state emission (~90 %). This supports the argument of the non-existence of the tetrametallic structure in DCM. Due to the use of dry and degassed solvents, the lifetimes of the two samples are expected to be different because it is not water which breaks up the structure of $[\text{UO}_2(\text{hfac})_2]_4$ (Fig. 3.14). Upon freezing the sample, the lifetime of the broken tetrametallic sample is increased, becoming longer than that seen for the $[\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}]$ complex. Possibly the effects of O-H quenching from the water are increased when the solvent is fixed in place upon freezing of the sample.

Table 3.6 Summary of the emission lifetimes for the uranyl(VI) hfac complexes in DCM.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Lifetime in frozen DCM</th>
<th>Lifetime in DCM solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_1 / \mu\text{s}$</td>
<td>$\tau_2 / \mu\text{s}$</td>
</tr>
<tr>
<td>$[\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}]$</td>
<td>50.97 (13 %)</td>
<td>193.93 (87 %)</td>
</tr>
<tr>
<td>$[\text{UO}_2(\text{hfac})_2]_4$</td>
<td>54.48 (8 %)</td>
<td>240.09 (92 %)</td>
</tr>
</tbody>
</table>

Fig. 3.14 Proposed structures of left $[\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}]$ and right $[\text{UO}_2(\text{hfac})_2]_4$ in DCM solution.
3.4 Synthesis of a Uranyl(VI) tta Oligomer and Investigation into Extent of Aggregation in Solution

3.4.1 Solid state characterisation of [UO$_2$(tta)$_2$]$_2$

Recrystallisation of previously sublimed [UO$_2$(tta)$_2$]$_2$ from DCM/ hexane at 233 K resulted in the retention of the oligomeric structure (Fig. 3.15), confirming its thermodynamic stability upon dissolution and recrystallisation. The U=O bond lengths of the uncoordinated uranyl moiety are 1.758(4) and 1.759(4) Å, similar in length to the one uncoordinated U=O bond of 1.754(5) Å. The remaining U=O bond is elongated to 1.805(4) Å due to its participation in a CCI. At 2.460 Å, the U-(O=U) CCI bond is longer than the range of monodentate U-O$_{tta}$ bonds (2.308(4) to 2.341(4) Å). The U-O$_{tta}$ bond for the bridging oxygen is elongated to 2.508(4) Å, weaker than the CCI interaction and slightly stronger than the ligand bridging interaction (2.591(4) Å).

Fig. 3.15 The X-ray crystal structure of [UO$_2$(tta)$_2$]$_2$. Hydrogen atoms omitted for clarity. Due to disorder the sulphur atoms on two of the tta ligands can not be positioned and are labelled here as C atoms. Thermal ellipsoids set at the 50 % probability level.

3.4.2 Multinuclear diffusion-ordered NMR spectroscopy

In a similar fashion to the comparison of uranyl(VI) hfac structures, $^1$H and $^{19}$F isotopes can be utilised for the DOSY-NMR study of uranyl(VI) tta structures.

The diffusion coefficient of [UO$_2$(tta)$_2$MeOH] is observed between 10.95 and 11.20 x $10^{-10}$ m$^2$s$^{-1}$ for proton resonances (Fig. 3.16), with an average value of 11.00 (+/- 0.20) x $10^{-10}$ m$^2$s$^{-1}$. Use of Equation 1.7 gives r$_H$ = 4.38 (+/- 0.23) Å. The $^1$H DOSY-NMR spectrum of
[UO₂(tta)₂]₂ reveals a diffusion coefficient between 8.85 and 8.95 x 10⁻¹⁰ m²s⁻¹ (average value 8.95 (+/- 0.15) x 10⁻¹⁰ m²s⁻¹) (Fig. 3.17), giving rᵢ₇ = 5.39 (+/- 0.28) Å. Equation 1.8 reveals the dimer to be 1.86 times the molecular weight of [UO₂(tta)₂MeOH] in DCM solution; comparison of the crystal structure molecular weights gives a ratio of 1.91 for the relative molecular masses, therefore the dimeric structure of [UO₂(tta)₂]₂ is retained in solution.

![Fig. 3.16 The ¹H DOSY-NMR spectrum of [UO₂(tta)₂MeOH]. Recorded in d₂-DCM at 295 K.](image1)

![Fig. 3.17 The ¹H DOSY-NMR spectrum of [UO₂(tta)₂]₂. Recorded in d₂-DCM at 295 K.](image2)

¹⁹F DOSY-NMR spectroscopy gives a diffusion coefficient of 11.15 (+/- 0.15) x 10⁻¹⁰ m²s⁻¹ for [UO₂(tta)₂MeOH] (rᵢ₇ = 4.32 (+/- 0.22) Å) and 8.70 (+/- 0.20) x10⁻¹⁰ m²s⁻¹ for [UO₂(tta)₂]₂ (rᵢ₇ = 5.54 (+/- 0.31) Å), summarised in Table 3.7. Equation 1.8 gives
[UO₂(tta)₂]₂ a relative molecular weight 2.10 times the size of [UO₂(tta)₂MeOH] in solution.

Table 3.7 Summary of the DOSY-NMR diffusion coefficients and hydrated spherical radii of [UO₂(tta)₂MeOH] and [UO₂(tta)₂]₂. r_H calculated using Equation 3.7. Recorded in d₂-DCM at 295 K. Errors given in brackets (+/-) after values.

<table>
<thead>
<tr>
<th>Complex</th>
<th>¹H DOSY Data</th>
<th>¹⁹F DOSY Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D / x10⁻⁹ m² s⁻¹</td>
<td>r_H / Å</td>
</tr>
<tr>
<td></td>
<td>D / x10⁻⁹ m² s⁻¹</td>
<td>r_H / Å</td>
</tr>
<tr>
<td>[UO₂(tta)₂MeOH]</td>
<td>11.00 (0.20)</td>
<td>4.38 (0.23)</td>
</tr>
<tr>
<td>[UO₂(tta)₂]₂</td>
<td>8.95 (0.15)</td>
<td>5.39 (0.28)</td>
</tr>
</tbody>
</table>

The dimeric nature of [UO₂(tta)₂]₂ is therefore observed in solution, in contrast to the aggregated structure of [UO₂(hfac)₂]₄. The bridging ligand interaction present in the structure of [UO₂(tta)₂]₂ provides a support for the uranyl CCI, allowing for the relative stability of the uranyl tta dimer in solution compared to [UO₂(hfac)₂]₄.

3.4.3 Emission spectroscopy

The reduced fluorination of tta in comparison to hfac leads to a decrease in luminescence intensity.₁ To such an extent, that solid and solution (in DCM) state luminescence spectroscopy yield no emission.¹¹ Upon freezing the DCM samples, emission can be observed for both [UO₂(tta)₂MeOH] and [UO₂(tta)₂]₂, shown in Figs. 3.18 and 3.19 respectively. The excitation spectrum of [UO₂(tta)₂MeOH] is broad in the UV region and uranyl excitation around 447 nm can be observed on the shoulder of the UV excitation bands. The emission maxima are of similar energy to the frozen DCM emission measurements of [UO₂(hfac)₂H₂O] and [UO₂(hfac)₂]₄; three bands between 531 nm and 582 nm, centred at 556 nm. The excitation and emission profiles of [UO₂(tta)₂]₂ are similar (Table 3.8); the emission profile red-shifts negligibly compared to [UO₂(tta)₂MeOH], unlike comparison between oligomers of uranyl(VI) hfac in the solid state.
Fig. 3.18 The excitation (emission $\lambda = 530$ nm) and emission (excitation $\lambda = 420$ nm) spectra of [UO$_2$(tta)$_2$MeOH] in frozen DCM solution. Excitation and emission slit widths set at 1 nm.

Fig. 3.19 The excitation (emission $\lambda = 530$ nm) and emission (excitation $\lambda = 420$ nm) spectra of [UO$_2$(tta)$_2$]$_2$ in frozen DCM solution. Excitation and emission slit widths set at 1 nm.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Emission maxima in frozen DCM (77 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{0-0}$/ cm$^{-1}$</td>
</tr>
<tr>
<td>[UO$_2$(tta)$_2$MeOH]</td>
<td>18832</td>
</tr>
<tr>
<td>[UO$_2$(tta)$_2$]$_2$</td>
<td>18762</td>
</tr>
</tbody>
</table>

Greater differentiation can be found between the emission lifetimes: [UO$_2$(tta)$_2$MeOH] exhibits biexponential decay kinetics, with radiative lifetimes of 61.18 $\mu$s (24 %) and 190.50 $\mu$s (76 %) ($\chi^2 = 1.24$); [UO$_2$(tta)$_2$]$_2$ exhibits emission lifetimes of 52.54 $\mu$s (20 %) and 158.28 $\mu$s (80 %) ($\chi^2 = 1.05$). The presence of one CCI in the dimetallic [UO$_2$(tta)$_2$]$_2$ sample results in a decrease in the emission lifetime, thus the CCI is observed in frozen DCM solution by luminescence spectroscopy.

### 3.4.4 Synthesis of [U(tta)$_4$]

Although dissolution of [UO$_2$(tta)$_2$]$_2$ in DCM/ hexane led to recrystallisation of the product at sub-zero temperatures, repetition of the process at room temperature in ambient light resulted in the isolation of a different product. The structure elucidated, [U(tta)$_4$] (16), reveals a uranium atom with no uranyl oxygens and four tta ligands complexed (Fig. 3.20). Due to the -1 charge associated with each ligand and the lack of counter ions in the crystal lattice, 16 is assigned as uranium(IV). Two inequivalent molecules reside in the asymmetric unit cell.
The $^1$H NMR spectrum shows a clear downfield shift of the non-aromatic proton (12.62 ppm) from normal $^1$H NMR frequencies due to the paramagnetic uranium(IV) centre. In contrast the proton resonances on the thenoyl group are less shifted, ranging between 6.7 and 8.4 ppm; only a marginal shift with respect to uranyl(VI) tta complexes.$^{[11,12]}$ This is attributed to the greater number of bonds between these protons and the uranium centre (5, 6 and 7 bonds vs. 4 bonds). $^{19}$F NMR spectroscopy shows the formation of two resonances of equal intensity upfield with respect to uranyl(VI) tta complexes. A plane of symmetry through the uranium atom in Fig. 3.20 indicates two environments for the tta ligands, and this is likely the reason for the two fluorine resonance environments. The lack of resonances due to uranyl(VI) complexes in the bulk sample indicates that the sample has completely converted to uranium(IV).

In addition, the UV/vis absorption spectrum in Fig. 3.21 reveals the absence of uranyl(VI) absorption features. The observable maxima mimic the wavelengths seen for uranium(IV) complexes in the literature.$^{[19,20]}$ Excitation into the absorption maxima does not lead to UV/vis emission as reported for U(IV) complexes in the literature,$^{[19,20]}$ nor nIR emission.
3.5 Attempted Reductions of Uranyl(VI) Fluorinated acac Complexes
3.5.1 Attempted reductions of \([\text{UO}_2(\text{hfac})_2]_4\)

The success of KCp in reducing uranyl(VI) complexes is documented in the literature. Reaction of \([\text{UO}_2(\text{hfac})_2]_4\) with either KCp or K metal in deuterated benzene resulted in an orange solution with a brown precipitate. $^1\text{H}$ and $^{19}\text{F}$ NMR spectroscopy reveal the formation of multiple new resonances in the NMR spectra (Fig. 3.22), with some exhibiting shifts in frequency that may indicate the presence of a paramagnetic centre. The use of the different reducing reagents gives rise to different new resonances in both the $^1\text{H}$ and $^{19}\text{F}$ NMR spectra, indicating each reagent undergoes a different reaction with \([\text{UO}_2(\text{hfac})_2]_4\). In both cases, the appearance of many different resonances combined with the retention of starting material peaks indicates the reaction has produced potentially many different products from incomplete reductions.

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**Fig. 3.21** The UV/vis absorption spectrum of U(tta)$_4$(16) between 235 and 600 nm. Recorded in DCM.
3.5.2 Attempted reductions of \([\text{UO}_2(\text{tta})_2]_2\)

Reaction of \([\text{UO}_2(\text{tta})_2]_2\) with potassium metal or with KCp led to the appearance of new resonances in both the \(^1\text{H}\) and \(^{19}\text{F}\) NMR spectra. Similar to the attempted reduction of \([\text{UO}_2(\text{hfac})_2]_4\), the NMR spectra suggest an incomplete reaction due to the presence of...
[UO$_2$(tta)$_2$]$_2$ resonances (Fig. 3.23). Although multiple products are inferred by the multitude of resonances present, the loss of the thenoyl protons indicates that the ligand itself may have reacted with the reducing agent, and incomplete reduction is certain. In addition, the appearance of the proton near 12.5 ppm is of similar frequency to that seen for 16, suggesting a uranium(IV) centre with some semblance of acac ligand coordinated to it.

Fig. 3.23 Left $^1$H and right $^{19}$F NMR spectra of [UO$_2$(tta)$_2$]$_2$, after reaction with K and after reaction with KCp. Recorded in C$_6$D$_6$ at room temperature.

Although the NMR spectra appear very similar between both attempted reductions, the appearance of the samples is in stark contrast: reaction with KCp led to an orange solution, whereas the reaction with potassium led to a blue solution. A blue colour is associated with uranyl(V) complexes that display CCIs,$^{23-35}$ and so a uranyl(V) complex could be one of the species present upon attempted reduction of [UO$_2$(tta)$_2$]$_2$ with potassium. Resulting single crystals from this reaction were too small for a structural analysis.

3.6 Conclusions
Sublimation of the monomeric compound [UO$_2$(hfac)$_2$H$_2$O].Et$_2$O yields [UO$_2$(hfac)$_2$]$_4$ via [UO$_2$(hfac)$_2$Et$_2$O]. The tetrameric structure, supported in the solid state only by bridging CCIs, is not retained in solution, as proven by DOSY-NMR, studied on both the $^1$H and $^{19}$F isotopes, and emission spectroscopy. The tetramer is proposed to exist as a coordinatively unsaturated monomer in solution. In contrast, sublimation of [UO$_2$(tta)$_2$MeOH] results in a dimeric structure, which is supported by a single CCI and a bridging ligand interaction, yet this structure retains its nuclearity in solution. It is suggested that extended aggregates of
uranyl(VI) exist in solution when the CCIs are supported by bridging ligand interactions, otherwise the complex dissociates.

CCIs between uranyl(VI) centres lead to a noticeable red shift in emission maxima and decrease in emission lifetime and can be used as a lead into deriving the structure of a complex. Furthermore, all attempts to reproduce \([\text{UO}_2(\text{hfac})_2]_3\)\(^6,7\) led to the isolation of \([\text{UO}_2(\text{hfac})_2]_4\) and attempted reductions to uranyl(V) have proved non-trivial. Finally, a novel uranium(IV) structure, \textbf{16}, has been synthesised serendipitously.

3.7 References


Chapter 4

Luminescence Investigations of Uranyl(VI/ V) Salts
4.1 Introduction
As described in Section 1.6, uranyl(V) salts are obtained either by reduction of uranyl(VI) or oxidation of uranium(III) salts,\(^1\)\(^-\)\(^3\) with a large percentage of uranyl(V) complexes obtained by reaction with uranyl(V) salts, particularly \([\{UO_2(py)_3\}\{KI_2(py)_2\}]\).\(^4\)\(^-\)\(^7\) However, whilst uranyl complexes are ideal candidates for study by spectroscopy, uranyl and uranium salts could also prove useful in spectroscopic investigations.\(^8\) It is also intriguing to note that no uranium(IV) to uranyl(V) oxidation reactions have been reported in the literature.

4.2 Synthesis and Reduction of Uranyl(VI) Salts

4.2.1 Synthesis and spectroscopy of uranyl(VI) salts
The compounds \([UO_2Cl_2(THF)_3]\), \([UO_2(OTf)_2(THF)_3]\) and \([UO_2I_2(THF)_3]\) were synthesised by existing literature methods.\(^9\)\(^-\)\(^11\) Dissolution of \([UO_2Cl_2(THF)_3]\) in pyridine led to the isolation of crystals of \([UO_2Cl_2(py)_3]\).\(^3\) Luminescence spectroscopy of \([UO_2Cl_2(py)_3]\) in pyridine reveals similar excitation and emission profiles as seen for \([UO_2Cl_2(THF)_3]\) in THF;\(^12\) broad uranyl excitation and emission maxima centred at 449 and 540 nm respectively (Fig. 4.01).

![Fig. 4.01 The excitation (emission $\lambda = 525$ nm) and emission (excitation $\lambda = 420$ nm) spectra of \([UO_2Cl_2(py)_3]\) in pyridine solution. Excitation and emission slit widths set at 3 nm.](image)

The complex \([UO_2(OTf)_2(THF)_3]\) was non-emissive in THF solution. Dissolution in pyridine led to the formation of \([UO_2(OTf)_2(py)_3]\).\(^13\) Similarly, measurement of the
luminescence spectrum of [UO$_2$(OTf)$_2$(py)$_3$] in pyridine revealed none of the complex’s photophysical properties. Freezing the pyridine sample at 77 K reveals an emission spectrum (Fig. 4.02); broad excitation maxima centred at 440 (directly into the uranyl U=O LMCT) and 320 nm leads to typical uranyl(VI) emission, five peaks centred at 542 nm between 495 and 591 nm with a biexponential emission lifetime of 84.20 (32 %) and 242.95 (68 %) μs ($\chi^2 = 1.15$). Similarly the emission profile of [UO$_2$(OTf)$_2$(py)$_3$] can be observed in the solid state (Fig. 4.03). The excitation spectrum shows excitation broadly in the UV region or directly into the uranyl U=O LMCT after 400 nm gives a typical uranyl(VI) emission spectrum; six bands between 472 and 587 nm, centred at 511 nm with a biexponential emission lifetime of 48.65 (22 %) and 124.47 (78 %) μs ($\chi^2 = 1.03$).

Fig. 4.02 The excitation (emission $\lambda = 520$ nm) and emission (excitation $\lambda = 350$ nm) spectra of [UO$_2$(OTf)$_2$(py)$_3$] in frozen pyridine at 77 K. Excitation and emission slit widths set at 1 nm.
Fig. 4.03 The solid state excitation (emission $\lambda = 510$ nm) and emission (excitation $\lambda = 420$ nm) spectra of [UO$_2$(OTf)$_2$(py)$_3$]. Excitation and emission slit widths set at 1 nm.

Attempts to measure the emission spectrum of [UO$_2$I$_2$(THF)$_3$] in THF solution and in the solid state were unsuccessful, as were attempts to measure the emission spectrum of [UO$_2$I$_2$(py)$_3$]$^{[11]}$ in pyridine solution. This is likely due to the existence of an intense iodide to uranium charge transfer band, which spans the visible region effectively relative to uranyl absorption around 420 nm (Fig. 4.04), quenching any uranyl(VI) emission.

Fig. 4.04 The UV/vis absorption spectrum of [UO$_2$I$_2$(THF)$_3$] in pyridine solution between 330 and 700 nm.
4.2.2 Attempted reductions of uranyl(VI) salts

Ephritikhine describes the attempted reduction of \([UO_2Cl_2(py)_3]\) in his 2009 paper.\(^3\) He surmises that \(\text{Tl}(\text{C}_5\text{H}_5)\) appears to produce a successful reduction whilst \(\text{Me}_3\text{SiC}_5\text{H}_5\) leads to incomplete reduction, complete with crystallisation of \([UO_2Cl_2(py)_3]\). It is also reported that separation of the uranyl(V) and (VI) adducts is non-trivial.\(^3\)

Attempts to replicate the reductions with potassium graphite and KCp have led to the isolation of \([UO_2Cl_2(py)_3]\) from yellow/brown solutions. UV/vis absorption spectrophotometry confirms the presence of uranyl(VI) with absorption centred near 420 nm (Fig. 4.05). Maxima located at lower energy (460, 480 and 665 nm) support the presence of uranyl(V) in solution alongside uranyl(VI), featuring at similar wavelengths to reported uranyl(V) UV/vis absorptions.\(^{14,15}\) The results confirm the difficulty in attempting to reduce uranyl(VI) chloride regardless of reducing agent.

The synthesis of \([UO_2(\text{OTf})(\text{THF})_{1.5}]\) was repeated from the literature.\(^3\) Attempts to characterise the product further met with difficulty. Single crystals were only obtained before attempts to purify the product and are the KOTf by-product (17) from the reduction (Fig. 4.05). Attempts to see emission from a pyridine solution were unsuccessful. \(^{19}\text{F}\) NMR spectroscopy reveals a minor shift in frequency (0.2 ppm) for the triflate resonance vs. \([UO_2(\text{OTf})_2(\text{THF})_3]\), which is due to the distance of the fluorine atoms from uranium and potential triflate solution lability. A noticeable chemical shift difference due to paramagnetism is not observed (Fig. 4.06).

Fig. 4.05 The X-ray crystal structure of \((\text{KOTf})_4(py)_2\) (17). Hydrogens omitted for clarity. Thermal ellipsoids set at the 50 % probability level.
Repetition of the synthesis of \([\text{UO}_2(\text{py})_5]\_2\{\text{K}_3(\text{OTf})_5\}\_\text{py}\) but on a larger scale (196 mg vs. 10 mg of \([\text{UO}_2(\text{OTf})_2(\text{THF})_3]\) led to a yield of 35\% (200 mg), confirming the salt can be produced on a scale similar to other uranyl(V) salts in the report.\[^3\] UV/vis spectrophotometry of the salt gives a significant maxima at 456 nm (Fig. 4.07), almost identical to that for \([\{\text{UO}_2(\text{py})_3\}\{\text{KI}_2(\text{py})_2\}]\).\[^{14}\] Other maxima exhibited at 611, 740 and, at high concentrations, 834 and 839 nm are consistent with uranyl(V).\[^{14,15}\] In addition, the absence of uranyl(VI) U=O LMCT bands indicate the successful removal of any remaining uranyl(VI) from the reaction by washing with toluene; the molar extinction coefficient of \([\{\text{UO}_2(\text{py})_3\}\{\text{K}_3(\text{OTf})_5\}\_\text{py}\) is 1632 cm\(^3\)mol\(^{-1}\)cm\(^{-1}\), \([\text{UO}_2(\text{OTf})_2(\text{py})_3]\) is 1848 cm\(^3\)mol\(^{-1}\)cm\(^{-1}\) and would therefore clearly be visible. Allowing oxygen to leach into the sample produced a typical uranyl(VI) UV/vis spectrum with a maxima at 419 nm with all uranyl(V) transitions gone (Fig. 4.08). Unfortunately, the use of pyridine does not allow for the detection of uranium(IV) peaks, and so it is unclear if the sample has oxidised or undergone disproportionation.
Fig. 4.07 The UV/vis spectrum of [(UO$_2$(py)$_5$)$_2$K$_3$(OTf)$_5$.py] in pyridine between 310 and 1000 nm.

Fig. 4.08 The UV/vis spectrum of [(UO$_2$(py)$_5$)$_2$K$_3$(OTf)$_5$.py] in pyridine after the addition of oxygen. Displayed between 350 and 1000 nm.

The IR spectrum of [(UO$_2$(py)$_5$)$_2$K$_3$(OTf)$_5$.py] displays a prominent peak at 807 cm$^{-1}$ (Fig. 4.09), within the region of reported mononuclear uranyl(V) salts and lacking in stretches associated with uranyl(VI) triflate.$^{3,13}$ The slight decrease in wavenumber of the uranyl(V) stretch compared to mononuclear uranyl(V) reports is likely to be due to the coordination of the uranyl oxygen to potassium in [(UO$_2$(py)$_5$)$_2$K$_3$(OTf)$_5$.py], elongating the uranyl U=O bond.
Fig. 4.09 The IR spectrum of \([\{\text{UO}_2\text{(py)}_5\}_2\{\text{K}_3\text{(OTf)}_5\}\text{py}]\) in a nujol mull in transmission mode between 700 and 1100 cm\(^{-1}\).

Attempts to measure the emission spectrum of \([\{\text{UO}_2\text{(py)}_5\}_2\{\text{K}_3\text{(OTf)}_5\}\text{py}]\) in pyridine and acetonitrile solution led to no emission in the UV, visible or IR regions. Freezing the samples offers no improvement on their emissive properties. Attempts to measure the solid state emission spectrum of \([\{\text{UO}_2\text{(py)}_5\}_2\{\text{K}_3\text{(OTf)}_5\}\text{py}]\) also failed at room temperature and at 77 K, indicating that \([\{\text{UO}_2\text{(py)}_5\}_2\{\text{K}_3\text{(OTf)}_5\}\text{py}]\) is not emissive under any conditions with current available instrumentation.

Reduction of \([\text{UO}_2\text{I}_2(\text{THF})_3]\) by KCp in pyridine led to \([\{\text{UO}_2\text{(py)}_5\}\{\text{KI}_2\text{(py)}_2]\}\).\(^{[2,3]}\) Attempts to observe the emission spectrum of \([\{\text{UO}_2\text{(py)}_5\}\{\text{KI}_2\text{(py)}_2]\}\) in pyridine solution and in the solid state failed, indicating that \([\{\text{UO}_2\text{(py)}_5\}\{\text{KI}_2\text{(py)}_2]\}\), like \([\{\text{UO}_2\text{(py)}_5\}_2\{\text{K}_3\text{(OTf)}_5\}\text{py}]\) and \([\text{UO}_2\text{I}_2(\text{THF})_3]\), is non-emissive.

### 4.2.3 Attempted comproportionation reaction of \([\text{UO}_2\text{I}_2(\text{THF})_3]\) and \([\text{UL}_4(\text{Et}_2\text{O})_2]\)

Reaction of \([\text{UO}_2\text{I}_2(\text{THF})_3]\) and \([\text{UL}_4(\text{Et}_2\text{O})_2]\) in pyridine with KI led to an orange solution. Attempts to grow crystals of \([\{\text{UO}_2\text{(py)}_5\}\{\text{KI}_2\text{(py)}_2]\}\) are unsuccessful; however, the use of IR spectroscopy confirms the formation of uranyl(V) by the presence of a broad stretch between 800 and 820 cm\(^{-1}\) (Fig. 4.10), consistent with uranyl(V) IR stretches.\(^{[1,3]}\) The broadness of the peak indicates that there may be a number of uranyl(V) species present, some that are coordinated to K and some that are not (present at a higher wavenumber and
therefore overlapping signals create a broad peak). The IR spectrum also displays a minor stretch near 920 cm\(^{-1}\) and it is likely that not all uranyl(VI) has reacted\(^{[3,13]}\). It is uncertain if all of the uranium(IV) has oxidised and the lack of characterisation of the uranyl(V) structure means it can not be determined if the comproportionation reaction has produced \([\{\text{UO}_2(\text{py})_5\}\{\text{KI(\text{py})}_2\}]\) or an alternative unknown uranyl(V) product.

Fig. 4.10 The IR spectrum of the comproportionation reaction of \([\text{UO}_2\text{I}_2(\text{THF})_3]\) and \([\text{UI}_4(\text{Et}_2\text{O})_2]\) in a nujol mull in transmission mode between 700 and 1000 cm\(^{-1}\).

4.3 Uranium(III/ IV) Oxidations

4.3.1 Uranium(IV)

The reaction of \(\text{UCl}_4\) with AgOTf in the dark in THF led to the formation of a silvery polymer and complete loss of solvent, indicating polymerisation of the THF. Further addition of THF resulted in additional polymerisation. Repetition of the reaction in acetonitrile resulted in the formation of a yellow solution. Precipitation with diethyl ether and redissolving in THF led to the isolation of single crystals of \([\text{UO}_2(\text{OTf})_2(\text{THF})_3]\) upon layering with hexane. Therefore, AgOTf is not thought to be a suitable reagent for reaction with \(\text{UCl}_4\), resulting in the two-electron oxidation of U(IV) to UO\(_2\)(VI). The two-electron oxidation of uranium(IV) by AgOTf has been reported in the literature previously\(^{[16]}\).
4.3.2 Uranium(III)

The oxidation of UI₃(thf)₄ to synthesise [{UO₂(py)₂}{KI₂(py)₂}] is more efficient than the alternative pathway involving reduction of [UO₂(OTf)₂(THF)₃]. However, the use of UI₃ instead of UI₃(thf)₄ proves to be a decisive factor in the synthesis of the uranyl(V) salt. The use of UI₃ resulted in a yellow/brown salt upon standing for several weeks, instead of an orange solution with crystals of [{UO₂(py)₅}{KI₂(py)₂}]. The decreased solubility of UI₃ means a quantity of the starting material remained standing in the solution and incomplete oxidation occurs. Additionally, the yellow solution is indicative of the presence of uranyl(VI).

In one attempt, the anhydrous nature of the pyridine in use was called into question, adopting the reaction procedure but without using the water-doped pyridine (and with the use of UI₃) leads to the formation of yellow crystals of [{UO₂(py)₂(μ₂-O)₂(μ₃-O)(μ₂-I)}I₂(py)₂] (18, Fig. 4.11). Attempts to repeat the synthesis using anhydrous pyridine do not lead to the same product. Similarly, repetition of the reaction purely in 0.1 M H₂O/pyridine also failed to reproduce [{UO₂(py)₂(μ₂-O)₂(μ₃-O)(μ₂-I)}I₂(py)₂].

![Fig. 4.11 The X-ray crystal structure of \{[UO₂(py)₂(μ₂-O)₂(μ₃-O)(μ₂-I)]I₂(py)₂\} (18). Hydrogens omitted for clarity. Thermal ellipsoids set at the 50% probability level.](image)

From the crystal structure it is not apparent whether the uranyl units in 18 are in the (V) or (VI) oxidation state, or a mixture of the two. Although the complex proves to be highly air sensitive, data for the bond lengths of the uranyl moieties in 18 suggest a mixed-valence system. The longest uranyl moiety bonds are 1.80 (2) and 1.83 (3), whilst the shortest
uranyl moiety has bond lengths of 1.73(2) and 1.78(2) Å. Whilst statistically different, the data is not accurate enough to confirm oxidation state. In addition, a lack of quality data allows for fractional potassium cations to remain undetected in the crystal lattice, exacerbating the problem by preventing an accurate charge-balancing count.

4.4 Conclusions
Reduction of uranyl(VI) salts to uranyl(V) is non-trivial and difficult to effect when using chloride salts. However, the reduction of [UO$_2$(OTf)$_2$(THF)$_3$] by KCp in pyridine to give [{UO$_2$(py)$_5$}]$_2$[K$_3$(OTf)$_5$.py] has been scaled up, proving it has the capacity to be used as a starting material for uranyl(V) complex syntheses. In addition, a comproportionation reaction between uranium(IV) and uranyl(VI) iodides is indicated to be a partial success, suggesting the possibility of a new area of research for uranium chemistry that could provide interesting possibilities in tandem with studies of the disproportionation reaction. Preliminary attempts to study the luminescence spectroscopy of uranyl(V) revealed the salts studied proved to be non-emissive. It is likely that coordination of potassium to the uranyl units has hindered this effort, as cation-cation interactions have proved to be detrimental to the emissive properties of uranyl(VI) (Section 3.3). The oxidation of U(III) to uranyl(V) is shown to be dependent on the U(III) salt, a slight change in material leads to a change in solubility and a different pathway of the reaction. Finally, a novel but not fully characterised trimeric uranyl structure has been serendipitously synthesised that could present a mixed-valence uranyl(VI/ V) system.

4.5 References


Chapter 5

Synthesis and Complexation of Silylated-Oligopyridines with Uranium
5.1 Introduction

Previous studies on the luminescent properties of uranyl(VI) have demonstrated the use of 2,2’-bipyridine-based ligands,[1,2] 2,2’:6’,2’’-terpyridine[3] and 1,10-phenanthroline[4] (Fig. 5.01) as suitable ligands to afford emissive uranyl(VI) complexes. This is in contrast to acac based uranyl(VI) complexes,[5,6] which are weakly emissive but generally well-studied complexes. Studies on the solid state structures of the 2,2’:6’,2’’-terpyridine and 2,2’-bipyridine uranyl(VI) complexes revealed the similar coordination environment of the polypyridyl ligands in both structures,[7] differing only in coordination number. Therefore, these ligands (and derivatives thereof) are proposed to be suitable frameworks for the study of the luminescent properties of uranyl(V) complexes.

![Fig. 5.01](image_url)

It is thought that the addition of a sterically bulky group adjacent to the nitrogen in the ligands would help to stabilise uranyl(V) complexes from disproportionation by discouraging the aggregation of uranyl moieties via steric hindrance. Trialkylsilyl groups have been used previously for the addition of steric bulk in reactive organometallic lanthanide and actinide complexes.[8-10] In particular, the use of trimethylsilyl groups in
Schaverian’s work\cite{9} with lanthanum successfully suppressed unwanted ligand redistribution reactions due to the steric bulk of the trimethylsilyl ligand, ligand redistribution reactions and enabling the isolation of a highly reactive La(III) alkyl complex (Fig. 5.02).

![Schaverian’s sterically hindered lanthanum complex](image)

These reports lead to the proposal of the use of trialkylchlorosilanes to synthesise the desired ligands. A detailed explanation of the attempted reactions and the literature review that led to these attempts can be found in Appendix 6. No route could be found to position the trialkylsilyl groups adjacent to the nitrogen atom of the pyridyl rings. Of note is the syntheses of the novel aromatics 4,5’-di-tert-butyldimethylsilyl-6,6’-dibromo-2,2’-bipyridine (19), 4-tert-butyldimethylsilyl-2,2’-bipyridine (20) and 4,4’-di-tert-butyldimethylsilyl-2,2’-bipyridine (21) (Appendix 6).

The work of Ullrich et al.\cite{11} is of potential use in the synthesis of sterically bulky pyridyl species. Addition of a methyl groups in the 6,6’- positions of 2,2’-bipyridine directed the subsequent metallation onto the aliphatic methyl carbon (Fig. 5.03). Work carried out on the 2,9-dimethyl-1,10-phenanthroline (neocuproine) equivalent also showed this to be the case.\cite{12,13}
Further work at The University of Manchester showed the lithiation of 6,6’-dimethyl-2,2’-bipyridine to be successful even when trapped by other silyl chlorides; the tert-butylidimethyl and tri-iso-propyl silylated 6,6’-dimethyl-2,2’-bipyridine compounds were synthesised.\[^{14}\] Combined with the trimethylsilyl- derivative from Schubert’s work\[^{11}\] a set of 2,2’-bipyridine based ligands have been synthesised. In an analogous reaction, the attempted lithiation of 6,6′′-dimethyl-2,2’:6’,2’’-terpyridine failed.\[^{14}\]

5.2 Lithiations of Neocuproine

5.2.1 Synthesis of 2,9-di-tert-butylidimethylsilylmethyl-1,10-phenanthroline and 2-tert-butylidimethylsilylmethyl-9-methyl-1,10-phenanthroline

Although attempts to lithiate adjacent to the nitrogen on the oligopyridine rings did not meet with success, work in the literature has shown the methyl arms of 6,6′-dimethyl-2,2’-bipyridine and neocuproine can be lithiated and then silylated,\[^{11-13}\] leading to the addition of steric bulk adjacent to the nitrogen atoms.

The reaction of neocuproine with LDA at 195 K followed by the addition of tert-butylidimethylsilylchloride affords the mono- and bis- tert-butylidimethylsilyl-neocuproine
products (Scheme 5.1, 22 and 23 respectively), where the trialkylsilyl group is bound to the methyl arm of the neocuproine (Fig. 5.04). The products were separated by silica gel column chromatography, giving the bis- species in 11 % yield and the mono- species in 55 % yield. Unreacted neocuproine also passed through the column as the last fraction when flushed with methanol.

Scheme 5.1 The reaction of neocuproine with LDA to yield 2,9-di-tert-butyldimethylsilylmethyl-1,10-phenanthroline (23) and 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22). Unreacted neocuproine is also found in the mixture of reaction products.

Fig. 5.04 The X-ray crystal structure of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22), grown from a sample in CDCl₃ over one week. Hydrogen atoms omitted for clarity. Thermal ellipsoids set at the 50 % probability level.
The crystal structure displays two unique molecules in the asymmetric unit cell. The Si-C bond lengths connecting the silicon to the methyl arm are 1.894(3) and 1.902(3) Å, longer than the bond lengths between silicon and the aromatic carbon in the structure of 4,4’-di-tert-butyldimethylsilyl-2,2’-bipyridine (Appendix 6) and suggesting a weaker bond between silicon and carbon in the silylated neocuproine.

The asymmetry of the mono-silylated product is observed in the $^1$H NMR spectrum (Fig. 5.05) with the appearance of non-identical resonances for protons in the 3/8 and 4/7 positions of the 1,10-phenanthroline backbone and two heavily roofed doublets in place of the previously magnetically equivalent 5 and 6 position singlet.

*Fig. 5.05 The $^1$H NMR spectrum of 2,9-di-tert-butyldimethylsilylmethyl-1,10-phenanthroline (23), 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) and neocuproine, focusing on the aromatic and methyl arm resonances. All recorded in CDCl$_3$ at 295 K.*

The appearance of 22 is unexpected, being unreported in the previous reaction of tert-butyldimethylsilylchloride and neocuproine.$^{[12]}$ In the report, six equivalents of LDA are used (approximately 2.5 equivalents are used in the reaction outlined above), and so the number of equivalents of lithiating reagent are thought to be important in the yields of the mono- and bis-silylated neocuproines. Increasing the amounts of LDA to approximately 4.5 equivalents improves the yields of products to 36 % and 60 % for 23 and 22 respectively. The reaction time also affects the product outcome; increasing the stirring time after addition of tert-butyldimethylsilylchloride from one hour to overnight led to product yields of 37 % and 33 % for 23 and 22 respectively. Thus it is hypothesised that increasing the equivalents of LDA, whilst encouraging the synthesis of the bis-substituted
neocuproine, increases the amount of lithiated neocuproine. Additionally, increasing the reaction time allowed for the second silylation of the neocuproine, probably the rate-limiting step in the synthesis of 23. In a final study, changing the lithiating reagent to ¹BuLi led to the isolation of neocuproine as the product, and so the choice of the aminated LDA as the lithiating reagent is crucial in the successful lithiation of neocuproine.

5.2.2 Synthesis of other silylated neocuproines

To increase the range of ligands for use, different trialkylsilylchlorides can be utilised (Fig. 5.06). Reaction of neocuproine with approximately three equivalents of LDA followed by addition of tri-iso-propylsilylchloride (with one hour stirring time) led to a mixture of 2-tri-iso-propylsilylmethyl-9-methyl-1,10-phenanthroline (24) and 2,9-di-tri-iso-propylsilylmethyl-1,10-phenanthroline (25). The products were separated by silica gel column chromatography, isolating 25 in a 49 % yield, 24 in an 18 % yield and neocuproine as the last fraction off the column when eluted with methanol. Following similar reaction conditions as those used for the reaction of neocuproine with tert-butyldimethylsilylchloride results in a favourable synthesis of 25, and so the choice of trialkylsilylchloride also affects product synthesis. This was observed for the reaction of neocuproine with three equivalents of LDA and tert-butyldiphenylsilylchloride; 55 % yield for 2-tert-butyldiphenylsilylmethyl-9-methyl-1,10-phenanthroline (26) and only 7 % yield is observed for 2,9-di-tert-butyldiphenylsilylmethyl-1,10-phenanthroline (27). Of the three trialkylsilanes, silylation of neocuproine appears to proceed favourably in the order tri-iso-propylsilylchloride > tert-butyldimethylsilylchloride > tert-butyldiphenylsilylchloride.
The reaction with trimethylsilylchloride was not as successful, as only neocuproine could be found at the end of the reaction. Despite repetition of the reaction with freshly distilled trimethylsilylchloride, no difference was observed upon completion. With reactions of other trialkylsilylchlorides, upon completion of stirring the reaction is quenched with ethanol, which leads to a prismatic series of colour changes as all remaining lithiated...
neocuproine and LDA are destroyed. The same series of colour changes is observed immediately upon addition of trimethylsilylchloride, and it is thought that this silyl chloride destroys the lithiated neocuproine rather than reacting with it.

5.2.3 Silylation of 6,6'-dimethyl-2,2'-bipyridine

Previous work at The University of Manchester[14] built upon the literature lithiation and trimethylsilylation of 6,6'-dimethyl-2,2'-bipyridine[11] to produce a range of silylated bipyridines. Although mono-substituted products were observed by $^1$H NMR spectroscopy, separation from 6,6'-dimethyl-2,2'-bipyridine and/or bis-silylated products proved unsuccessful. The synthesis of 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine (28) was achieved by reaction of approximately 12 equivalents of LDA in order to eliminate the mono-substituted product from the reaction (Scheme 5.2).

![Scheme 5.2](image)

Scheme 5.2 The reaction of 6,6'-dimethyl-2,2'-bipyridine with LDA to yield 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine (28).

Therefore a range of 2,2'-bipyridine based ligands have been synthesised for use as ligands.

Slow evaporation of 28 from n-hexane solution resulted in the formation of single crystals suitable for X-ray diffraction (Fig. 5.07). At 1.889(3) and 1.890(3) Å, the bonds between silicon and carbon on the methyl arm are, on average, shorter than those exhibited in 22 and statistically equivalent with the silicon-aromatic carbon bonds in 21.
5.2.4 Attempted silylation of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline – the ‘Stross’ reaction

The ability of neocuproine to produce mono- and bis- silylated products raises the prospect of synthesising a mixed bis-silylated product. The reaction of tri-iso-propylsilylchloride with 22 was chosen due to the seemingly favourable bis-silylation of tri-iso-propylsilylchloride with neocuproine. Dissolution of 22 in THF and reaction with four equivalents of LDA led to a black solution. Addition of tri-iso-propylsilylchloride resulted in the formation of an orange oil after work up of the reaction. $^1$H NMR spectroscopy shows the presence of the protons on $^1$Pr$_3$Si- alongside those of $^1$BuMe$_2$Si-; however, the resonances attributed to the methyl arm have moved downfield to approximately 4.23 ppm, significantly deshielded with respect to the methyl arm resonances of other silylated neocuproines (which are found around 2.8 ppm for $^1$Pr$_3$Si- and $^1$BuMe$_2$Si- neocuproines) (Fig. 5.08). In addition, the aromatic resonances overlap to appear as two multiplets and integration gives only three protons, half of the expected amount. Integration of the methyl arm gives three protons, one short of the amount expected for the successful reaction. Attempts to crystallise from hexane at 238 K yielded only an orange oil. Mass spectrometry displays peaks due to 22 and 24, with unknown peaks at masses at 507.6 and 565.7. Only a small peak (10% intensity) is present at the mass unit of the desired product (479.6). It is thought the reaction has failed due to unwanted lithiations, potentially in more than one position and including loss of the tert-butyldimethylsilyl group.
5.2.5 Stability of silylated neocuproines

Following observed trends on attempted lithiations of 2,2’-bipyridine and 1,10-phenanthroline, the silylation of neocuproine is not seen to be as favourable as that of 6,6’-dimethyl-2,2’-bipyridine. The formation of the bis-silylated 6,6’-dimethyl-2,2’-bipyridines occurred favourably with two equivalents of LDA and trialkylsilylchloride (with the exception of 28),[^14] whereas neocuproine needs greater equivalents of LDA and prolonged stirring times to favour bis-silylation. It is perhaps unsurprising then, that although silylated 6,6’-dimethyl-2,2’-bipyridines are stable under ambient conditions, their neocuproine counterparts are not. This is represented by the weaker Si-C bond to the methyl arm in 22 compared to 28. Over time, the bis-silylated neocuproines decompose to mono-silylated neocuproines, which in turn decompose to neocuproine. The silylated neocuproines are stable if stored under argon, and so it is thought the silyl groups undergo hydrolysis with moisture in the atmosphere to decompose to neocuproine (Scheme 5.3).

![Scheme 5.3 The proposed hydrolysis of bis- and mono-silylated neocuproines.](image)

[^14]: Reference number
The choice of silyl group affects the rate of decomposition, which can be followed by \(^1\)H NMR spectroscopy. Fig. 5.09 shows the decomposition of 23 over seven weeks. The decomposition is most easily observed by following the change in resonances due to the middle protons on the neocuproine backbone (positions 5- and 6-). The decomposition of 23 also highlights the decomposition of one silyl arm at a time – proceeding to neocuproine via 22.

![Fig. 5.09 The \(^1\)H NMR spectra of 2,9-di-tert-butyldimethylsilylmethyl-1,10-phenanthroline (23) left after one week middle after four weeks and right after seven weeks. Recorded in CDCl\(_3\) at room temperature. * Resonance due to 2,9-di-tert-butyldimethylsilylmethyl-1,10-phenanthroline (23). * Resonance due to 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22). * Resonance due to neocuproine.](image)

The choice of trialkylsilyl group affects the rate of decomposition. Although, conditions were not constant (concentration of sample, sample evaporation), the following timescales were observed for the decomposition of the silylated neocuproines in NMR tube reactions:

- 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) after 59 weeks
- 2-tri-iso-propylsilylmethyl-9-methyl-1,10-phenanthroline (24) after 40 weeks
- 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (26) after 21 weeks
- 2,9-di-tert-butyldimethylsilylmethyl-1,10-phenanthroline (23) after 12 weeks
- 2,9-di-tri-iso-propylsilylmethyl-1,10-phenanthroline (25) after 16 weeks
- 2,9-di-tert-butyldiphenylsilylmethyl-1,10-phenanthroline (27) after 5 weeks

The mono-silylated neocuproines are more stable than the bis-silylated neocuproines and the bulkiest silyl group, tert-butyldiphenylsilyl, leads to the least stable ligands.

5.3 Complexations to Uranyl(VI)

5.3.1 Complexations of silylated dimethyl-bipyridines

Work on the complexation of silylated dimethyl-bipyridines with uranyl nitrate resulted in the Lewis acid mediated hydrolysis of 6,6’-di-trimethylsilylmethyl-2,2’-bipyridine and the co-crystallisation of 6,6’-dimethyl-2,2’-bipyridine with uranyl(VI) nitrate.\(^{[14]}\) The use of
6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine and 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine resulted in crystallisation of the ligand, highlighting the importance of the choice of silyl group in stability of the ligand.

Although it is possible that the steric bulk of the ligands hinders their complexation with uranyl(VI),\textsuperscript{15} the co-crystallisation of 6,6’-dimethyl-2,2’-bipyridine with uranyl(VI) nitrate (29) from reaction of the latter with 6,6’-dimethyl-2,2’-bipyridine indicated this is not the case. The \textsuperscript{1}H NMR spectra (Fig. 5.10) of the two reactions suggests a different product in each circumstance, confirmed by analysis of the X-ray crystal structure (Fig. 5.11). In the reaction of 6,6’-dimethyl-2,2’-bipyridine with uranyl nitrate, the ligand crystallises facing and parallel with the uranyl moiety, and is strongly suggested to be protonated from the diffraction data.

![Fig. 5.10 The \textsuperscript{1}H NMR spectra of bottom 6,6’-dimethyl-2,2’-bipyridine, middle the co-crystallisation of 6,6’-dimethyl-2,2’-bipyridine with uranyl(VI) nitrate from 6,6’-di-trimethylsilylmethyl-2,2’-bipyridine and top the co-crystallisation of 6,6’-dimethyl-2,2’-bipyridine with uranyl(VI) nitrate from 6,6’-dimethyl-2,2’-bipyridine.](image-url)
Fig. 5.11 The X-ray crystal structure of the co-crystallisation of 6,6'-dimethyl-2,2'-bipyridine with uranyl nitrate (29) from the reaction of the two components. All hydrogen atoms bar the pyridyl proton removed for clarity. Ball and stick representation used due to accuracy of data.

Reaction of 28 with [UO_2(NO_3)_2].6H_2O resulted in crystallisation of the ligand. Luminescence spectroscopy of the reactions in methanol should provide an insight into the solution phase of the reaction. No emission was observable for any of the reactions, despite UV/vis spectrophotometry revealing a broad absorption maximum after 400 nm due to U=O LMCT (Fig. 5.12).

Fig. 5.12 The UV/vis absorption spectrum of the reaction of 5.18 mmol 6,6'-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine with uranyl nitrate hexahydrate between 370 and 600 nm.

Measurement of the ^1H NMR spectrum of each reveals a previously unseen instability of the ligands over time in the presence of uranyl(VI) as well as decomposition of the silylated dimethyl-bipyridine to give 6,6'-dimethyl-2,2'-bipyridine, presumably through
hydrolysis. The rate of decomposition is dependant on choice of silyl group, with the following timescales observed for decomposition of the ligands:

- 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine after 63 weeks
- 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine after 24 weeks
- 6,6’-di-tert-butylidiphenylsilylmethyl-2,2’-bipyridine after 24 weeks

The ligands are stable with respect to hydrolysis under ambient conditions, and so the presence of uranyl nitrate hexahydrate leads to their decomposition. Crystallisation of the product shows more similarity to the co-crystallisation observed for 29 than the hydrolysis of 6,6’-di-trimethylsilylmethyl-2,2’-bipyridine in that protonation of the ligand results in the ligand facing uranyl(VI) nitrate (30) (Fig. 5.13). In this structure, the ligand lies slightly off perpendicular with the uranyl moiety. The ligand proton to nitrate oxygen bond length of 2.118 Å also suggests a hydrogen-bond connecting ligand to uranyl complex.\(^{[16]}\) In a final difference, the 5th equatorial coordination site of the uranyl nitrate is occupied by water instead of methanol. This crystal structure is observed on the hydrolysis of 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine, 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine and 6,6’-di-tert-butylidiphenylsilylmethyl-2,2-bipyridine by uranyl nitrate hexahydrate.

Fig. 5.13 The X-ray crystal structure of the hydrolysed product from the reaction of 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine with uranyl nitrate (30). All hydrogen atoms except the pyridyl proton removed for clarity. Thermal ellipsoids set at the 50 % probability level.
5.3.2 The reaction of UO$_2$(NO$_3$)$_2$.6H$_2$O with silylated neocuproines

Reaction of uranyl(VI) nitrate with 22 and 25 can be monitored by $^1$H NMR spectroscopy (Fig. 5.14). Analysis of the aromatic region of the spectrum in the reaction of 25 with uranyl(VI) nitrate shows a downfield shift of the resonances. However, the protons on the trialkylsilyl groups all but vanish, therefore the ligand has completely hydrolysed to neocuproine before any complexation can be observed.

![Fig. 5.14 The $^1$H NMR spectra of 2,9-di-tri-iso-propylsilylmethyl-1,10-phenanthroline (25) and the reaction of the ligand with uranyl nitrate. Recorded in CDCl$_3$ at room temperature.](image)

The reaction of 22 with uranyl(VI) nitrate results in the formation of a greater number of resonances in the $^1$H NMR spectrum (Fig. 5.15). Most easily observable in the aromatic region, the resonances from 22 move to a higher frequency. The extra resonances are present in a 1:1 ratio by integration. Given the tendency of the silylated ligands to hydrolyse, it is likely that the extra resonances can be assigned as neocuproine. Attempts to crystallise this product were unsuccessful due to an apparent lipophilicity of the products and no structures were obtainable under the reaction conditions employed.
5.3.3 Anhydrous reactions of silylated dimethyl-bipyridines with uranyl triflate

Strictly anhydrous conditions may overcome the degradation difficulties encountered in the previous section. Attempts to crystallise silylated dimethyl-bipyridines after treatment with uranyl triflate resulted in the crystallisation only of uranyl triflate.\(^{[14]}\) The addition of two equivalents of each silylated ligand to uranyl triflate led to no observable change in the proton NMR spectrum after reaction in that no resonances appear to shift in frequency and no resonances form or disappear. This indicates the ligands may not bind to the uranyl(VI) ion.

UV/vis absorption spectrophotometry provides no insight into interactions between silylated dimethyl-bipyridines and uranyl(VI) triflate (Fig. 5.16). No uranyl(VI) U=O LMCT absorptions are visible. Instead all three samples give similar absorption profiles, with two maxima between 230 and 350 nm apparent. With no uranyl(VI) absorptions visible, no information regarding ligand-uranyl(VI) interactions can be garnered from the absorption spectra.
Fig. 5.16 The UV/vis absorption spectrum of the reaction of two equivalents of 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine with 2mM UO$_2$(OTf)$_2$(THF)$_3$. Recorded in MeCN.

Measurement of the same concentration of uranyl triflate without the presence of ligand results in a weak observation of uranyl U=O absorption maxima after 400 nm, confirming the role of the ligands in obscuring the uranyl absorption profile. Excitation into the uranyl absorption bands in uranyl triflate gives typical uranyl(VI) emission (Fig. 5.17), which are three bands centred at 509 nm with a biexponential emission lifetime of 14.33 (17 %) and 108.50 (83 %) ns.

Fig. 5.17 The MeCN solution excitation (emission $\lambda = 510$ nm) and emission (excitation $\lambda = 270$ nm) spectra of UO$_2$(OTf)$_2$(THF)$_3$.

Addition of 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine produces two broad maxima between 400 and 600 nm (Fig. 5.18). The excitation spectrum displays several features, with a broad absorption near 300 nm leading to the emission profile observed.
Additionally, excitation into the two bands observed at 382 nm and the broad band at 442 nm produces the same broad emission hump between 500 and 600 nm, suggesting the emission originates from both the ligand and the uranyl(VI) moiety. Attempts to measure the lifetime proved difficult as the decay is shorter than the instrument response function (<1 ns). Variation of the silyl group does not alter the ligands photophysical properties. No further indication of their ability to coordinate to the uranyl moiety is discernable from the spectra. The short ns based lifetimes alongside the excitation and emission profiles indicate that the bipyridyl ligands are quenching the uranyl(VI) based emission at room temperature, and non-radiative back energy transfer processes are dominating the photophysics at room temperature. This coordinative property contradicts the findings of the NMR spectra, perhaps indicating a difference in exchange on the timescales of the two analyses.

5.3.4 Anhydrous reactions of silylated neocuproines with uranyl triflate

UV/vis absorption spectra recorded for the reaction of silylated-neocuproines with uranyl(VI) triflate are similar to one another, in that two broad bands at ca. 235 and 275 nm with no visible uranyl absorption maxima after 400 nm are observed. The spectra are similar to those observed for the reaction of silylated dimethyl-bipyridines with uranyl(VI) triflate and are assigned as ligand absorption bands. No difference is observed upon the choice of silylated neocuproine, confirming the lack of effect on photophysical properties of the silyl groups. The excitation and emission spectra for the reaction of uranyl triflate with any silylated neocuproine produces no characteristic uranyl(VI) emission features (Fig. 5.19), and the emission decays too rapidly to reliably record emission lifetimes. Only two bands are found in the excitation spectrum, at 354 and 368 nm, with excitation into either band resulting in broad emission between 400 and 550 nm. Therefore, in light of the
spectral profiles with the silylated bipyridines, the luminescence profiles are assigned as ligand based.

Fig. 5.19 The MeCN solution excitation (emission $\lambda = 510$ nm) and emission (excitation $\lambda = 270$ nm) spectra of UO$_2$(OTf)$_2$(THF)$_3$ upon addition of 2-tri-iso-propylsilylmethyl-9-methyl-1,10-phenanthroline (24).

Attempts to crystallise any adducts present in solution were unsuccessful. Only uranyl(VI) triflate is present upon crystallisation, indicating that complexation of uranyl(VI) with these ligands is weak. Similar to the reaction of uranyl(VI) triflate with silylated dimethyl-bipyridines, uranyl triflate crystallises$^{[14]}$ in a different polymorph to any seen previously.$^{[14,17]}$ However, by allowing the reaction to stir for 24 hours a different structure was obtained by single crystal X-ray diffraction (Fig. 5.20). The reaction of 22 with uranyl(VI) triflate under such conditions led to the elucidation of the protonated ligand charge balanced by a triflate group, and no hydrogen bonds are presented between the charge balancing structures. The resulting nature of the uranyl(VI)-bearing complex remains unknown.

Fig. 5.20 The X-ray crystal structure of the crystallisation of protonated 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) and triflate. All hydrogens atoms removed for clarity except the phenanthroline proton. Thermal ellipsoids set at the 50 % probability level.
The $^1$H NMR spectrum of the reaction of 22 with uranyl(VI) triflate displays extra resonances (Fig. 5.21). Resonances similar to those for the uncomplexed ligand, though at slightly different frequencies, can be seen, alongside an extra set of resonances that are present at 50 % of the integration of the ligand-esque peaks. A resonance at 14.75 ppm can also be found due to protonated phenanthroline. Alongside the single crystals of the protonated ligand/triflate, an orange precipitate was found at the base of the reaction vial. The proton NMR spectrum suggests the resonances at more extreme shifts (those that are present at 50 % integration) belong to this powder, therefore it is assumed the ligand/triflate crystallisation presents the resonances more akin to 22. In order to determine whether the resonances belong to ligand that is uncomplexed or complexed (alongside the ligand/triflate structure elucidated by single crystal X-ray diffraction), DOSY-NMR spectroscopy was utilised.

![Fig. 5.21 The $^1$H NMR spectra of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) and the reaction of the ligand with 0.5 equivalents of uranyl triflate. Recorded in CDCl3 at room temperature.](image)

It is noted that the use of uranyl(VI) iodide instead of uranyl(VI) triflate leads to identical $^1$H NMR spectra. The same resonances are also present on the reaction of 22 with one equivalent of uranyl(VI) iodide or uranyl(VI) triflate.

### 5.3.5 Diffusion-ordered $^1$H NMR spectroscopy

The diffusion coefficients of the resonances in the reaction of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline with uranyl iodide indicate the presence of two different species in solution. The smaller species diffuses at 9.70 (+/- 0.10) x 10^{-10} m^2s^{-1} (Fig. 5.22), giving a spherical hydrated radius of 3.80 (+/- 0.19) Å (by using Equation 1.7)\(^{18}\). The larger species diffuses at 7.95 (+/- 0.10) x 10^{-10} m^2s^{-1}, giving r_H =
4.64 (+/- 0.24) Å. The values of $1.3806503 \times 10^{-23}$ m$^2$kgs$^{-2}$K$^{-1}$ and $0.5861 \times 10^{-3}$ mNsm$^{-3}$ are used for $k_B$ and $\eta$ respectively.$^{[19,20]}

By comparison with the $^1$H-DOSY NMR spectrum of 22 (Fig. 5.22), an idea of the species present in solution in the presence of uranyl iodide can be obtained. The uncomplexed ligand 22 diffuses at a rate of $10.55 (+/- 0.15) \times 10^{-10}$ m$^2$s$^{-1}$, $r_H = 3.50 (+/- 0.18)$ Å.

![Fig. 5.22 Comparison of the $^1$H DOSY-NMR spectrum of below 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline and above reaction with 0.5 equivalents of uranyl iodide (31). Recorded in CDCl$_3$ at 295 K. *No diffusion coefficient observed for TMS proton in either sample or CH$_2$ in reaction with 0.5 equivalents of uranyl iodide.](image)

Use of Equation 1.8$^{[21]}$ allows diffusion coefficients to be compared to gather an idea of the molecular mass of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline after reaction with uranyl(VI) iodide. With a molecular mass of 323 gmol$^{-1}$ for the uncomplexed ligand, the largest species in the reaction with uranyl iodide would have a molecular mass of 755 gmol$^{-1}$ and the smaller species 415 gmol$^{-1}$. The molecular mass of a proposed UO$_2$(I)(22) (31) complex is 720 gmol$^{-1}$, and it is therefore likely that the reaction of 22 with uranyl(VI) triflate leads to this product due to the similar molecular mass of iodide and triflate. The combination of 22 with iodide would lead to a molecular mass of 450 gmol$^{-1}$ and represents the closest molecular mass calculable for this diffusion coefficient.
The diffusion coefficients of the reaction of the silylated neocuproines with uranyl(VI) triflate are presented in Table 5.1. In many cases, overlap of proton resonances renders determination of D difficult, but protons located on the silyl arms are usually more isolated and therefore reliable in determining D. In each sample, the reaction between uranyl(VI) triflate with both one and two equivalents of ligand produces the same resonances in the resulting proton NMR spectrum.

Table 5.1 Summary of the DOSY-NMR diffusion coefficients and hydrated spherical radii of the reaction of two equivalents of the silylated ligands with [UO$_2$(OTf)$_2$(THF)$_3$]. Recorded in CDCl$_3$ at 295 K. Errors given in brackets (+/-) after values. *Three equivalents of ligand used.

<table>
<thead>
<tr>
<th>Ligand used</th>
<th>D ($\times 10^{-10}$ m$^2$s$^{-1}$)</th>
<th>r$_H$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>9.70 (0.10), 7.95 (0.10)</td>
<td>3.80 (0.19), 4.64 (0.24)</td>
</tr>
<tr>
<td>23$^*$</td>
<td>8.00 (0.05), 6.85 (0.05)</td>
<td>5.38 (0.27), 4.61 (0.23)</td>
</tr>
<tr>
<td>24</td>
<td>7.40 (0.10)</td>
<td>4.98 (0.26)</td>
</tr>
<tr>
<td>25</td>
<td>8.25 (0.15), 7.55 (0.10)</td>
<td>4.47 (0.24), 4.88 (0.25)</td>
</tr>
<tr>
<td>26</td>
<td>7.55 (0.10), 6.85 (0.10)</td>
<td>4.88 (0.32), 5.38 (0.27)</td>
</tr>
<tr>
<td>27</td>
<td>10.20 (0.15), 6.85 (0.10)</td>
<td>5.38 (0.29), 3.61 (0.18)</td>
</tr>
</tbody>
</table>

The $^1$H DOSY-NMR experiments of the reaction of silylated neocuproines with uranyl(VI) triflate indicate that the silyl groups of the ligands can dissociate themselves from neocuproine, and also that the triflate anion can tumble in solution with the ligands in accordance with the solid state structural data (Fig. 5.20). The existence of uranyl(VI) complexes with the ligands are suggested and are summarised in Table 5.2. The reaction of uranyl(VI) triflate with 24 appears to produce only one set of diffusion coefficients; however a hypothetical (OTf)$_2$24 compound would diffuse at approximately the same rate as the suggested uranyl(VI) complex. It is likely these two species are present in solution.
Table 5.2 Summary of the uranyl complexes expected in solution. Calculated from comparison with 2-tert-butyltrimethylsilylmethyl-9-methyl-1,10-phenanthroline.

<table>
<thead>
<tr>
<th>Ligand used</th>
<th>Proposed uranyl complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>UO$_2$(I)(22) (= 31)</td>
</tr>
<tr>
<td>23</td>
<td>UO$_2$(OTf)(22)(23) (= 32) and UO$_2$(OTf)(22)</td>
</tr>
<tr>
<td>24</td>
<td>UO$_2$(OTf)$_2$(24) (= 33)</td>
</tr>
<tr>
<td>25</td>
<td>33</td>
</tr>
<tr>
<td>26</td>
<td>UO$_2$(26)$_2$ (= 34) and UO$_2$(OTf)$_2$(26) (= 35)</td>
</tr>
<tr>
<td>27</td>
<td>34</td>
</tr>
</tbody>
</table>

5.4 Complexations to Uranyl(V)

5.4.1 $^1$H DOSY-NMR spectroscopy

Reaction of $[\{\text{UO}_2(\text{py})_5\}_2\{\text{K}_3(\text{OTf})_5\}].\text{py}]_n$ with 22 in acetonitrile resulted in the formation of new resonances in the $^1$H NMR spectrum alongside the original in the aromatic region, (Fig. 5.23). The NMR spectra indicate the same reaction occurs whether one or two equivalents of ligand are added. The interaction of acetonitrile with uranium can also be observed, with the formation of a singlet resonance overlapping with the residual protio-acetonitrile signal.

Fig. 5.23 The $^1$H NMR spectra of 2-tert-butyltrimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) and the reaction of the ligand with 0.5 equivalents of uranyl(V) triflate. Recorded in CD$_3$CN at room temperature.

$^1$H DOSY NMR spectroscopy produces a spread of diffusion coefficients between 13.40 (+/- 0.10) and 17.70 (+/- 0.30) x $10^{-10}$ m$^2$s$^{-1}$ (Fig. 5.24). 22 diffuses at 16.35 (+/- 0.10) x $10^{-10}$
$10 \text{ m}^2\text{s}^{-1}$, $r_H = 3.54 \pm 0.18 \text{ Å}$ (value of $0.373 \text{ mNsm}^{-3}$ used for $\eta$)\cite{22} with Equation 1.7 presenting a maximum molecular mass of 585 gmol$^{-1}$, too small to represent a uranyl complex. Crystallisation of the dried product from THF/ hexane led to single crystals of (22)(OTf), with the fast diffusion coefficients observed likely an averaging of 22 and its co-complex with triflate. No diffusion coefficients are observed for the new resonances that form in the aromatic region of the spectrum (Fig. 5.24). The protons may relax too fast to observe a signal in the DOSY-NMR experiment under these conditions.

![Diffusion coefficient vs. Chemical Shift](image)

**Fig. 5.24** The $^1\text{H}$ DOSY-NMR spectrum of the reaction of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) with 0.5 equivalents of uranyl(V) triflate. Recorded in CD$_3$CN at 295 K.

Reaction of two equivalents of 25 with [[UO$_2$(py)$_3$]$_2$K$_3$(OTf)$_5$.py]$_n$ in d$_3$-MeCN produced a brown solution with yellow precipitate. Filtration resulted in isolation of the yellow precipitate, identified as 25. Presumably two equivalents of the ligand can not react with the uranyl(V) salt. The resulting $^1\text{H}$ NMR spectrum (Fig. 5.25) is similar to that recorded for the reaction of uranyl(V) triflate with 22; the appearance of extra resonances in the aromatic region of the spectrum alongside resonances similar to that of the uncomplexed ligand, with no significant displacement of the silyl alkyl protons. The interaction of acetonitrile with uranyl is again implicated in the NMR spectra.
Fig. 5.25 The $^1$H NMR spectra of 2,9-tri-iso-propylsilylmethyl-1,10-phenanthroline (25) and the reaction of the ligand with 0.5 equivalents of uranyl(V) triflate. Recorded in CD$_3$CN at room temperature.

The $^1$H DOSY-NMR spectrum (Fig. 5.26) presents a similar story, with an array of diffusion coefficients between 9.55 (+/- 0.25) and 12.50 (+/- 0.10) x 10$^{-10}$ m$^2$s$^{-1}$ presented. No diffusion coefficients are obtained for the new aromatic resonances. The diffusion coefficient of 25 is 12.90 (+/- 0.20) x 10$^{-10}$ m$^2$s$^{-1}$, ($r_H = 4.49$ (+/- 0.24) Å) the resulting array of diffusion coefficients likely resulting from averaging between 25 and its co-complex with triflate. The slowest diffusion coefficient does present a hypothetical molecular mass of 1284 gmol$^{-1}$ by Equation 1.8 and comparison with the ligand and so may represent a uranyl(VI) complex.

Fig. 5.26 The $^1$H DOSY-NMR spectrum of the reaction of 2,9-tri-iso-propylsilylmethyl-1,10-phenanthroline (25) with 0.5 equivalents of uranyl(V) triflate. Recorded in CD$_3$CN at 295 K.

The poor solubility of 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine in acetonitrile means comparison between ligand and a potential uranyl complex took place in benzene (Fig. 5.27). The appearance of no extra resonances in the spectrum suggests poor
interaction between the ligand and metal, although there are minor resonances located near the silylalkyl proton signal in the reaction spectrum, with the residual benzene signal also contributing significantly to the aromatic region and possibly overlapping with resonances (Fig. 5.27).

Fig. 5.27 The $^1$H NMR spectra of 6,6'-di-tert-butylidimethyl-2,2'-bipyridine and the reaction of the ligand with 0.5 equivalents of uranyl(V) triflate. Recorded in C$_6$D$_6$ at room temperature.

Overlap of the aromatic resonances with benzene leads to an incomprehensible DOSY spectrum that is incomparable to the spectrum of 6,6'-di-tert-butylidimethyl-2,2'-bipyridine due to a significant resulting error. Therefore the size of the species in solution can not be estimated.

5.4.2 Optical spectroscopy of reactions of uranyl(V) with oligopyridines
Comparison of the UV/vis-nIR absorption spectrum of the reaction of the neocuproine-based ligands with [{UO$_2$(py)$_5$}]$_2$[K$_3$(OTf)$_5$.py]$_n$ provides little insight into the optical properties of the products. The UV/vis maxima observed for the ligand are easily obscured by the strong UV absorption of the uranyl ion at this concentration. Although slight maxima are hinted at in the spectra in the nIR region, comparison with the uranyl(V) salt reveals these to be present before addition of any ligand. Comparison of 6,6'-di-tert-butyldimethyl-2,2'-bipyridine with its reaction with [{UO$_2$(py)$_5$}]$_2$[K$_3$(OTf)$_5$.py]$_n$ is
uninformative, with the benzene solvent obscuring any maxima in the spectrum of the ligand and no peaks observable in the subsequent uranyl(V) spectrum.

The emissive properties of 22 in acetonitrile are limited to the UV, with excitation (Fig. 5.28) in to the bands at 250 or 330 nm leading to emission centred at 370 nm. By comparison, the luminescence properties of the reaction of the ligand with uranyl(V) triflate are lower in energy (Fig. 5.29), with excitation focused at 350 nm and emission at 470 nm, although weak emission can still be seen following excitation at 250 nm. Normalisation of the emission spectra and subsequent subtraction of the ligand based emission from that obtained in the uranyl(V) solution highlights the lower energy emission maxima of the uranyl solution (Fig. 5.30), with the maxima located at 470 nm close in wavelength to reports of uranyl(V) emission.[23] Although, excitation wavelengths overlap with the ligand and the lifetime is immeasurably short, on a par with the ligand fluorescence. It is not certain if the emission seen is from the ligand or uranyl(V).

Fig. 5.28 The excitation (emission $\lambda = 370$ nm) and emission (excitation $\lambda = 330$ nm) spectrum of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) in MeCN solution.

Fig. 5.29 The excitation (emission $\lambda = 415$ nm) and emission (excitation $\lambda = 350$ nm) spectrum of the reaction of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) with $[[\text{UO}_2(\text{py})_3]_2[\text{K}_3(\text{OTf})_5]\text{py}]_n$ in MeCN solution.
Fig. 5.30 Normalised Emission spectra of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22), its reaction with uranyl(V) triflate and the uranyl solution emission maxima after subtraction of ligand emission.

Use of 25 gives similar excitation and emission profiles (Fig. 5.31) in solution with [{UO$_2$(py)$_5$}]$_2$[K$_3$(OTf)$_5$.py]$_n$, with excitation around 350 nm leading to broad emission at 470 nm. The lifetime of the emission is immeasurably short. The similar nature of the emission to the spectrum produced by uranyl(V) and 22 suggests similar chemistry between the two ligands in solution with uranyl(V), although it does not clarify if the emission is ligand or uranyl(V) based in nature. It is not thought any uranyl(VI) is present in the spectrum by comparison with spectra observed in Section 5.3.4

Fig. 5.31 The excitation (emission $\lambda = 470$ nm) and emission (excitation $\lambda = 350$ nm) spectrum of the reaction of 2,9-tri-iso-propylsilylmethyl-1,10-phenanthroline (25) with [{UO$_2$(py)$_5$}]$_2$[K$_3$(OTf)$_5$.py]$_n$ in MeCN solution.
The photophysical properties of the reaction of 6,6′-di-tert-butyldimethyl-2,2′-bipyridine with uranyl(V) triflate are obscured by the benzene solution, with no maxima seen in either excitation or emission spectra.

5.5 Reaction of 2,9-tri-iso-propylsilylmethyl-1,10-phenanthroline with Non-Actinyl Metals

5.5.1 Complexation with uranium(IV)

The $^1$H NMR spectrum of the dark green mixture of 22 after reaction with one equivalent of [U(OTf)$_4$] shows much contrast to the spectrum of the uncomplexed ligand (Fig. 5.32). With resonances around the aromatic spectrum broadened and the appearance of resonances at unusual ppm downfield (up to 72 ppm, Fig. 5.33) there is indication of paramagnetic contribution to relaxation of the protons, confirming interaction between the ligand and the metal. Such an effect is expected for uranium(IV) complexes,[24] particularly for protons located close to the metal. The paramagnetic nature of the resonances combined with overlap from residual pyridine signals in the spectrum means absolute identification of the product is not feasible. In addition, the presence of protons in the standard aromatic region of the spectrum indicates that the ligand may be in exchange with a U(IV) complex.[24] The use of a variety of solvents resulted in unsuccessful crystallisation attempts and identification of any complex in this reaction mixture is ambiguous.

![Fig. 5.32 The $^1$H NMR spectra of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) and the reaction of the ligand with 0.5 equivalents of [U(OTf)$_4$]. Recorded in d$_5$-pyridine at room temperature.](image-url)
Fig. 5.33 The $^1$H NMR spectrum of the reaction of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) with 0.5 equivalents of [U(OTf)$_4$], focusing on the downfield part of the spectrum. Recorded in d$_5$-pyridine at room temperature.

5.5.2 Complexation to the Eu(III) ion

Non-anhydrous reactions of the silylated neocuproines result in their hydrolysis (Section 5.3.2). Emission spectroscopy indicates that 22 does not interact with [Eu(OTf)$_3$].2H$_2$O. Reaction of the ligand with [Eu(OTf)$_3$] (1:1 equivalents) under anhydrous conditions produced luminescence spectra which confirm the interaction of ligand with metal (Fig. 5.34). Excitation into the ligand absorption bands at 250 and 350 nm leads to sensitisation of europium(III) emission at 588 and 612 nm with broadened maxima. Measuring the sample after 1 and 1.5 weeks of standing (Fig. 5.34) showed the loss of intensity of the excitation and emission profiles, with slow leaching of oxygen/ water impeding the luminescence properties of the sample. Allowing the solvent to evaporate completely and dissolving the product in unpurified DCM resulted in the loss of the observed luminescence profile.
Fig. 5.34 Excitation (left, emission wavelength = 611 nm) and emission (right, excitation wavelength = 355 nm) spectra of the reaction of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) with Eu(OTf)$_3$ initially, after 1 week and after 1.5 weeks. Recorded in anhydrous and degassed DCM in a stoppered cuvette.

$^1$H NMR spectroscopy reveals little change between the spectrum of 22 as an uncomplexed ligand and after reaction with [Eu(OTf)]$_3$ under anhydrous conditions (Fig. 5.35). Interaction with the Eu(III) ion usually provides something of a paramagnetic shift for protons located close to the metal centre,$^{[25]}$ as the neocuproine protons are, although comparison with literature reports of europium(III)-neocuproine complexes are difficult due to a lack of NMR characterisation.$^{[26,27]}$ The slight change in frequency of the resonances suggests a change in structure in solution, whilst the conversion of the two roofed doublets to a singlet at 7.86 ppm indicates a change in symmetry of the system, with magnetic equivalence between the 5- and 6- protons restored (the other neocuproine protons appear to retain their inequivalence). The appearance of resonances at paramagnetically shifted frequencies (Fig. 5.36) is suggestive of interaction to the europium(III) ion (although the resonance at 13.79 ppm could belong to a protonated nitrogen on the phenanthroline ring). It is likely that there is exchange between a europium complex and a non-metal coordinated speciation of the ligand.
Fig. 5.35 The $^1$H NMR spectra of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) and the reaction of the ligand with 1 equivalent of [Eu(OTf)$_3$]. Recorded in anhydrous CD$_3$CN at room temperature.

Fig. 5.36 The $^1$H NMR spectrum of the reaction of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) with 1 equivalent of [Eu(OTf)$_3$]. Focusing on the downfield part of the spectrum. Recorded in CD$_3$CN at room temperature.

Comparison with the $^1$H NMR spectra of 22 after reaction with samarium and lutetium triflates (Fig. 5.37) confirms the presence of a non-metalled structure in solution, with almost identical frequencies of the resulting proton resonances (within 0.05 ppm of one another). Again, the presence of a minor species is hinted at for the reaction with lutetium triflate. By comparison with reaction with uranyl(VI) (Section 5.3), it is likely the ligand is protonated and co-exists with a triflate ion in solution, leading to the dominant resonances observed.
Fig. 5.37 The $^1$H NMR spectra of the reaction of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (22) with 1 equivalent of [Lu(OTf)$_3$] and 1 equivalent of [Sm(OTf)$_3$]. Recorded in anhydrous CD$_3$CN at room temperature.

5.6 Conclusions

A series of pyridyl-based ligands have been synthesised, which are electronically similar yet differ greatly in steric bulk, by lithium-hydrogen exchange with protons of methyl groups attached to oligopyridines. Attempts to lithiate directly adjacent to the nitrogen of such groups were unsuccessful, emphasising the difficulty in metallating increasingly conjugated pyridines, although attempts have lead to the first successful metallation on the 4 and 4’ positions of 2,2’-bipyridine (without a DMG, see Appendix 6). The effect of reaction time and equivalents of reagents on the yield of reaction has been briefly explored.

Exploration of the use of the products as ligands indicates anhydrous conditions are essential for the reaction to occur. Even under anhydrous conditions, crystallisation of uranyl containing products is difficult due to partial hydrolysis with adventitious water mediated by the Lewis acidic nature of the cations employed. The effectiveness of the silylated dimethyl-bipyridines to coordinate to uranyl is uncertain, with NMR spectra of reaction with both uranyl(V) and (VI) producing little to no change in observable resonances. The optical properties of the uranyl(VI) reaction mixtures are uncertain, with maxima observed at uranyl(VI) LMCT regions displaying immeasurably short lifetimes.

The silylated neocuproines prove to be poor ligands for optical spectroscopy with uranyl(VI), although $^1$H NMR spectroscopy suggests the formation of two products in reaction with uranyl(VI) triflate; one of which is identified as co-complex of the protonated
ligand with a triflate ion. The other species is thought to be a uranyl complex, with diffusion-ordered NMR spectroscopy providing insight into how the structures might exist in solution. It is likely that all the silylated neocuproines coordinate to uranyl after a fashion, although the inferred molecular weights from \(^1\)H DOSY-NMR suggest that the silyl arms may be labile, especially for the *bis*-silylated neocuproines. There is also no noticeable trend to how many ligands coordinate to the metal.

Reaction of the silylated neocuproines with uranyl(V) produces two different products by \(^1\)H NMR spectroscopy. The formation of protonated ligand triflate salt is observed; however diffusion-ordered measurements were unable to shed any light on the existence of any potential uranyl complexes. Attempts to observe the emission profile of uranyl(V) result in a uranyl(V) type maximum. However, the short lifetime means it is uncertain if the emission is ligand or uranyl based, similar to the optical properties of uranyl(VI) silylated dimethyl bipyridines. The ligand 2-*tert*-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline has proved its ability to coordinate to spherical ions in reactions with uranium(IV) triflate and europium(III) triflate; in the latter the antennae effect has successfully been employed to show that a ternary complex forms in solution. \(^1\)H NMR spectroscopy additionally suggests that the complexes are in slow exchange with diamagnetic ligand based species in solution on the NMR timescale.

5.7 References

Chapter 6

Transuranic Complexes of Silylated Dimethyl-Bipyridines.
6.1 Introduction

Emission spectroscopy of the curium(III) ion can be utilised to garner information on solution speciation of organic complexants with the metal. Similar to uranyl(VI) (Section 1.9.4), comparison of emission wavelength can provide information on bond strength between the ligand and metal relative to others under the same conditions (solvent, temperature etc.).\[^{1}\] In addition, the long emission lifetimes (Section 1.9.6) mean that there is a large time range over which emission lifetimes can be compared.

Comparison of emission lifetime of the curium aqua ion in H\(_2\)O and D\(_2\)O has resulted in the formulation of an equation to determine how many water molecules are coordinated to the metal by observation of the radiative lifetime of the sample.\[^{2,3}\]

However, different studies on this have resulted in different formulae, despite the similar emission lifetimes observed (Equations 6.1 and 6.2).\[^{2,3}\]

\[
N_{\text{H}_2\text{O}} = 0.65 \times 10^{-3} \ (k_{\text{obs}}) - 0.88.
\]

**Equation 6.1** Determination of the number of water molecules coordinated to a curium ion based on its emission lifetime.\[^{2}\] \(k_{\text{obs}}\) is the inverse of the emission lifetime.

\[
N_{\text{H}_2\text{O}} = 6.12 \times 10^{-4} \ (k_{\text{obs}}) - 0.48
\]

**Equation 6.2** Determination of the number of water molecules coordinated to a curium ion based on its emission lifetime.\[^{3}\] \(k_{\text{obs}}\) is the inverse of the emission lifetime.

Use of either equation gives similar but clearly non-identical results. The values can also be used to determine the coordination of other solvent molecules, but the accuracy is limited.\[^{3}\] This is because these equations do not take into account the presence of a quenching contribution from solvent molecules in the second coordination sphere and only hold if no other quenching processes are active (such as quenching from other X-H oscillators).

Reaction of europium(III) triflate with 6,6’-di-trimethylsilylmethyl-2,2’-bipyridine, 6,6’-di-tert-butylimethylsilylmethyl-2,2’-bipyridine and 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine revealed varying coordination chemistry depending on the silyl group.\[^{4}\] The smallest of the ligands, 6,6’-di-trimethylsilylmethyl-2,2’-bipyridine, decomposes upon reaction with the lanthanide, presumably through hydrolysis (similar to its reaction with \([\text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O}]\), Section 5.3), resulting in a
product incorporating 6,6’-dimethyl-2,2’-bipyridine. This was confirmed by reaction of europium triflate with 6,6’-dimethyl-2,2’-bipyridine.\cite{4}

The interaction of the bulkier ligands with the europium(III) ion (Fig. 6.01) was realised through their ability to sensitise emission of the lanthanide.\cite{4} UV/vis spectroscopy revealed a rising shoulder on the peak of europium(III) absorption profiles that belonged to uncomplexed ligand. Comparison with the determination of coordinated water molecules (via the modified Horrock’s equation)\cite{5} suggested that the bulkiest ligand could accommodate up to a maximum of three ligands around the metal, whilst 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine could potentially fit four.\cite{4} However, the lability of the ligand in methanolic solution and variable coordination number hinder the accuracy of these results.

![Fig. 6.01 Emission maxima of the reaction of europium triflate with two equivalents of 6,6’-di-trimethylsilylmethyl-2,2’-bipyridine, 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine and 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine between 580 and 650 nm. Excitation wavelength = 280 nm. Taken from reference [4].](image)

6.2 Americium(III) Silylated-dimethylbipyridine Reactions

6.2.1 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine

The reaction scheme for the complexation of the silylated dimethylbipyridines to the americium(III) ion followed the corresponding lanthanide scheme;\cite{4} where three equivalents of silylated ligand dissolved in deuterated solvent (MeOD 4:1 CDCl$_3$) were added to one equivalent of a dried sample of americium nitrate (4.1 mmol). The combined solution changes from pink (Americium nitrate in solution) to yellow (Americium silylated dimethylbipyridine complex).\cite{6}
Comparison of the proton spectra between 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine and its reaction with americium(III) nitrate (36) highlights a few changes. These are a slight upfield shift of the protons, noticeable in the aromatic region, and also an increase in the resolution of the proton signals upon complexation (Fig. 6.02). The change in chemical shift is indicative of an interaction between the ligand and the metal on the NMR timescale. Despite having protons on the pyridyl rings that are bound to the Am(III) ion, no drastic change in chemical shift is observed. This highlights the lack of paramagnetic relaxation from the metal. Another minor species is visible in the spectrum of complex 36 that does not correspond to uncomplexed 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine, which is potentially a second complex (36b).

Fig. 6.02 \(^1\)H NMR spectrum of 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine and its reaction with americium nitrate (36) with left a close-up of the aromatic region and right a view of the rest of the spectrum. Both recorded in d\(_4\)-MeOD 5:1 CDCl\(_3\) at 300 K.

\(^1\)H variable temperature NMR spectroscopy shows an increase in coupling resolution at higher temperatures along with a general upfield shift of the proton resonances (Fig. 6.03). At low temperatures, many of the resonances broaden, almost into the baseline by 220 K. The two most downfield resonances appear to coalesce at lower temperature (250 K). The spectra show that resonances assigned to 36b do not increase relative in size to other resonances at any temperature and is thought to be 6,6’-dimethyl-2,2’-bipyridine hydrolysed from 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine (see Section 5.3). This means that the ligand does not dissociate at lower temperature and also that there is one dominant species at most temperatures. Note
that all spectra are referenced to TMS as an internal standard rather than residual protons from the deuterated solvent employed due to their temperature dependent chemical shifts.

Fig. 6.03 Left close-up of the aromatic region and right view of the remainder of the resonances of the variable temperature $^1$H NMR spectra of the americium 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine complex (36) from top 330 K to bottom 220 K. Recorded in d$_4$-MeOD 5:1 CDCl$_3$.

6.2.2 6,6'-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine and 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine

Analysis of the $^1$H NMR spectra of 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine and its americium(III) complex (37) show a broadening of the proton resonances (except for the resonance at 6.92 ppm). Detecting any uncomplexed ligand signals is difficult due to the broadening and number of the resonances and is additionally complicated by couplings in the aromatic region (the presence of the phenyl groups on the silyl arm lead to greater difficulty in interpreting the aromatic region) and minimal shift of alkyl protons. However, the spectrum of 37 is non-identical to the uncomplexed ligand, indicating that there is an interaction occurring between ligand and metal (Fig. 6.04).
Fig. 6.04 $^1$H NMR spectrum of 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine and its reaction with americium(III) nitrate (37) with left a close-up of the aromatic region and right a view of the remaining resonances. Both recorded in d$_4$-MeOD 2:1 CDCl$_3$ at 300 K.

Variable temperature $^1$H NMR spectroscopy (Fig. 6.05) of the proton environments in 37 shows a general trend of a downfield shift of proton resonances upon decreasing the temperature, except at the highest temperatures where there is also a downfield shift. Decreasing the temperature of the sample results in broadening of the signals, potentially hinting at an exchange mechanism for the binding of the ligands.

Fig. 6.05 Left close-up of the aromatic region and right view of the upfield resonances of the variable temperature spectra of the americium 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine complex (37) from top 325 K to bottom 220 K. Recorded in d$_4$-MeOD 2:1 CDCl$_3$.

Variable temperature $^1$H NMR spectroscopy also reveals extra resonances at low temperatures (Fig. 6.06), presenting the possibility of the formation of a second
species, perhaps an analogous complex with a lower ligand coordination number (37b). The resonances increase in size relative to the neighbouring signal, although overlap of signals renders integration of resonance area difficult. The variable temperature plots for 36 and 37 suggest an exchange mechanism of the ligand with the metal ion in solution, with broader resonances observed at low temperature.[7]

In contrast to the two bulkier silylated ligands (tert-butylidiphenyl- and tri-iso-propylsilylated ligands), comparison of the reaction of 6,6′-di-tert-butylidiphenylsilylmethyl-2,2′-bipyridine with americium(III) nitrate (38) and uncomplexed ligand by 1H NMR spectroscopy (Fig. 6.07) depicts very little change in the chemical shift of the proton resonances, questioning whether or not a complex has formed.

Fig. 6.06 Close-up of the aromatic region of the 1H variable temperature spectra of the americium 6,6′-di-tert-butylidiphenylsilylmethyl-2,2′-bipyridine complex (37) from top 325 K to bottom 220 K. Recorded in d$_4$-MeOD 2:1 CDCl$_3$. 
Fig. 6.07 $^1$H NMR spectrum of 6,6'-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine and its reaction with americium(III) nitrate (38) with left a close-up of the aromatic region and right a view of the remaining resonances. Both recorded in d$_4$-MeOD 4:1 CDCl$_3$ at 300 K.

Variable temperature $^1$H NMR spectroscopy follows a similar trend to that observed for 37, in that increasing and decreasing the temperature leads to a downfield shift of most of the resonances (with the exception of the resonance at 7.15 ppm) and resonance broadening (Fig. 6.08). No second species was observed at any temperature in this reaction.

Fig. 6.08 Left close-up of the aromatic region and right view of the other resonances of the variable temperature spectra of the americium 6,6'-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine complex (38) from top 325 K to bottom 220 K. Recorded in d$_4$-MeOD 4:1 CDCl$_3$.

In contrast to 36 and 37, 38 yielded a $^1$H-$^{15}$N 2D NMR correlation spectrum (Fig. 6.09), displaying a nitrogen resonance at approximately 298 ppm when observed
through the protons on the methyl arm of the silylated bipyridine. This suggests that the 6,6'-di-tert-butylidimethylsilylmethyl-2,2'-bipyridine ligand exists in a higher symmetry (C₃-symmetric) environment in solution with americium nitrate[8] or that the existence of uncomplexed ligand with a high degree of conformational freedom is the dominant species in solution.

Fig. 6.09 ¹H-¹⁵N 2D NMR spectrum of the americium 6,6'-di-tert-butylidimethylsilylmethyl-2,2'-bipyridine complex (38). Recorded in d₄-MeOD at 300 K.

6.2.3 $T_1$ relaxation times

Comparison of the $T_1$ values for 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine and 36 reveals a noticeable increase in the relaxation time of the protons upon coordination, almost doubling in some environments (Table 6.1). In contrast, the residual water resonance experiences a decrease in relaxation time.
Table 6.1 \( T_1 \) relaxation times for *above* the americium 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine complex (36) and *below* 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine with *left* a close-up of the aromatic region and *right* the rest of the spectrum. Both recorded in \( d_4 \)-MeOD 5:1 CDCl\(_3\) at 300 K. The errors of the relaxation times are taken from the standard deviation of each \( T_1 \) plot and are quoted in brackets after the respective value.

The relaxation times of the minor species are also calculated as follows: at 8.154 ppm = 3.914 s (1.7 x 10\(^{-2}\)); at 7.873 ppm = 3.669 s (1.0 x 10\(^{-2}\)); at 7.313 ppm = 3.141 s (5 x 10\(^{-3}\)) and at 2.651 ppm = 1.800 s (9 x 10\(^{-3}\)). The resonances of 36b in the region of the silyl groups could not be found. The relaxation times of this minor species are considerably longer than the uncomplexed ligand, and also longer than 36. The higher standard deviation is associated with the lower integration area of the minor species resonances.

The relaxation times recorded for 37 are significantly faster than for the uncomplexed ligand, except for the 1-butyl protons (Table 6.2). No relaxation times are reported for the methyl arm of the ligand due to inaccuracy of the result obtained.
Table 6.2 $T_1$ relaxation times for above the americium 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine complex (37) and below the uncomplexed ligand with left a close-up of the aromatic region and right the rest of the spectrum. Recorded in d$_4$-MeOD 2:1 CDCl$_3$ at 300 K. The errors of the relaxation times are taken from the standard deviation of each $T_1$ plot and are quoted in brackets after the respective value.

The decrease in the $T_1$ relaxation time, compared to that of 36, suggests the existence of the products in a different symmetry$^{[9]}$ and, therefore, possibly a different ligand coordination number to one another. The reaction of americium(III) nitrate with NaTPIP (see Chapter 7) resulted in a similar decrease in $T_1$ relaxation time, therefore 37 may exist in a similar 3:1 ligand to metal geometry.

The $T_1$ relaxation times reported for 38 are of a similar magnitude to those determined for the uncomplexed ligand, where the t-butyl protons have relaxation times within the standard deviation of one another (Table 6.3). No data is reported on the silylmethyl protons due to overlap with the TMS signal. The measured radioactivity and dose rate of the sample indicated that all americium is present in the NMR tube, as also evidenced by the greatly reduced $T_1$ relaxation time of the residual water signal. This means that there is an interaction between water molecules and americium(III) nitrate.
Table 6.3 $T_1$ relaxation times for above the americium 6,6'-di-tert-butyl(dimethyl)silylmethyl-2,2'-bipyridine complex (38) and below 6,6'-di-tert-butyl(dimethyl)silylmethyl-2,2'-bipyridine with left a close-up of the aromatic region and right the rest of the spectrum. Recorded in $d_4$-MeOD 4:1 CDCl$_3$ at 300 K. The errors of the relaxation times are taken from the standard deviation of each $T_1$ plot and are quoted in brackets after the respective value.

The $T_1$ relaxation times suggest a large change in ligand environment for 36 and 37, with the significant difference in the values suggesting complexation (perhaps in exchange). This is supported by the change in chemical shift of the protons in the complex. Conversely, the $T_1$ relaxation times suggest that 6,6'-di-tert-butyl(dimethyl)silylmethyl-2,2'-bipyridine is experiencing no interaction with americium(III) nitrate (that can be observed on the NMR timescale), which is supported by the negligible change in chemical shift of the proton environments in the $^1$H NMR spectrum.

6.3 Curium(III) Silylated-dimethylbipyridine TRLFS
6.3.1 6,6'-di-tri-iso-propyl(dimethyl)silylmethyl-2,2'-bipyridine

Following the study of the silylated dimethylbipyridines on Ln(III) ions by luminescence spectroscopy, the emission properties of the analogous reaction with the Cm(III) ion were investigated by analysing any subsequent bathochromic shifts in subsequent emission maxima and radiative lifetimes. Increasing concentrations of ligand in 2:1 MeOH:CDCl$_3$ solution were added to a 100 nM curium(III) perchlorate
solution (in the same solvent) to monitor the binding of the silylated ligand with the Cm(III) ion.

The emission spectra show the formation of two different species upon increasing concentration of 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine, the first species (39a) is observed to form at 606.3 nm (the curium perchlorate signal is located at 599.7 nm), first observable with a 145 μM solution of 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine, and the second species (39b) is shown to have an emission maxima at 610.9 nm (Fig. 6.10). The second species only forms upon addition of excess ligand (a 1.12 mM solution of 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine), suggesting a Cm(III) ion with a greater number of ligands surrounding it than 39a.

Fig. 6.10 Emission spectrum of the curium perchlorate solution upon incremental addition of 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine in 2:1 MeOH:CDCl₃ (39). Excitation wavelength = 396.6 nm.

Time-resolved emission spectroscopy allows determination of the radiative lifetimes of the two species (Fig. 6.11). The lifetimes determined (233.60 and 258.62 μs for the 39a and 39b respectively) represent an almost doubling of the emission lifetime when compared to the curium perchlorate species (126.04 μs). The lifetimes are also similar
to, but significantly different from one another. This confirms the formation of two species, where one is formed at greater excess of ligand compared to the other.

![Graph](image-url)

**Fig. 6.11** Time resolved emission spectrum (TRES) recorded of the two species formed with a 39.0 mM solution of 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine to curium perchlorate in 2:1 MeOH:CDCl₃ (39). Excitation wavelength = 396.6 nm.

### 6.3.2 6,6’-Di-tert-butyldimethylsilylmethyl-2,2’-bipyridine and 6,6’-di-tert-butyldiphenylsilylmethyl-2,2’-bipyridine complexation

For both ligands, emission from the Cm(III) ion was seen to red-shift upon formation of a complex with the bipyridine-based ligands. For 6,6’-di-tert-butyldiphenylsilylmethyl-2,2’-bipyridine only one species is seen to form (40, at 603.7 nm vs. 600.0 nm for the curium perchlorate emission), first observable after the addition of a 196 μM solution of 6,6’-di-tert-butyldiphenylsilylmethyl-2,2’-bipyridine (Fig. 6.12). Addition of an excess of ligand broadens the signal, indicating the formation of a colloid. The use of 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine as the ligand also produces one major peak (41a) (at 606.0 nm vs. 600.1 nm for the curium perchlorate emission), first observed with a 47 μM solution of 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine (Fig. 6.12). There is a shoulder seen at lower energy (611.0 nm), indicating the formation of a second species (41b).
The emission spectra of a curium(III) perchlorate solution upon addition of *left* 6,6′-di-tert-butyldiphenylsilylmethyl-2,2′-bipyridine (40) and *right* 6,6′-di-tert-butyldimethylsilylmethyl-2,2′-bipyridine (41) in 2:1 MeOH:CDCl₃. Excitation wavelength = 396.6 nm.

![Emission spectra](image1)

**Fig. 6.12** The emission spectra of a curium(III) perchlorate solution upon addition of *left* 6,6′-di-tert-butyldiphenylsilylmethyl-2,2′-bipyridine (40) and *right* 6,6′-di-tert-butyldimethylsilylmethyl-2,2′-bipyridine (41) in 2:1 MeOH:CDCl₃. Excitation wavelength = 396.6 nm.

The lifetime of 40 is 243.34 μs, representing a near doubling of luminescence lifetime when compared to curium(III) perchlorate in solution (126.04 μs) (Table 6.4). Of the two species formed in the reaction of 6,6′-di-tert-butyldimethylsilylmethyl-2,2′-bipyridine, 41a displays a radiative lifetime of 203.10 μs. 41b has an indeterminable lifetime with the current data set obtained – time-resolved emission spectra would have to be obtained with a greater step size. The long lifetime of the species indicates a higher ligand to metal coordination number, and also confirms the maximum is not a ‘hot-band’ arising from a change in crystal field splitting as the symmetry of the Cm(III) species is lowered upon ligand coordination.

From these measurements, it is possible to try and estimate the number of coordinated solvent molecules by use of Equations 6.1 and 6.2. Application of these gives a coordinated number of solvents for the perchlorate sample as 4.3 and 4.4 for
Equations 6.1 and 6.2 respectively, and scaling the derived number up to a coordination number of nine usually provides an estimate of coordination number for non-aqueous solutions.\[^3\] Depending on which equation is used, the number of coordinated solvent molecules may vary slightly. The determined values are presented in Table 6.4.

Table 6.4 Summary of the luminescence lifetimes found for the reaction of silylated dimethylbipyridines with curium(III) perchlorate in 2:1 MeOH:CDCl\(_3\) solution. All fitted to a mono-exponential decay. The emission maximum of the aqua ion varies due to the precision between experiments performed. Estimated accuracy of radiative lifetimes = +/- 10 %, estimated accuracy of \(q\) values +/- 0.5.

<table>
<thead>
<tr>
<th>Curium(III) species</th>
<th>Wavelength /nm</th>
<th>Lifetime /(\mu)s</th>
<th>(q) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curium perchlorate</td>
<td>599.7, 600.0, 600.1</td>
<td>126.04</td>
<td>8.6, 8.8</td>
</tr>
<tr>
<td>Curium + 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine (39) species I</td>
<td>606.3</td>
<td>233.60</td>
<td>4.0, 4.4</td>
</tr>
<tr>
<td>Curium + 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine (39) species II</td>
<td>610.9</td>
<td>258.62</td>
<td>3.4, 3.9</td>
</tr>
<tr>
<td>Curium + 6,6’-di-tert-butyldiphenylsilylmethyl-2,2’-bipyridine (40) species I</td>
<td>603.7</td>
<td>243.34</td>
<td>3.8, 4.2</td>
</tr>
<tr>
<td>Curium + 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine (41) species I</td>
<td>606.0</td>
<td>203.10</td>
<td>4.9, 5.2</td>
</tr>
<tr>
<td>Curium + 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine (41) species II</td>
<td>611.0</td>
<td>unknown</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The emission lifetimes of the first species of the reaction of all three ligands with curium(III) perchlorate are similar, suggesting complexes of similar symmetry (i.e. coordination number), with the choice of alkyl group having only a minimum effect on the lifetime. The \(q\) values offer little insight as to number of coordinated ligands due to the potential for mono- or bi- dentate binding of the ligand and also the lability.
of the ligands in solution, with the inaccuracy suggested by the proposal of the lowest coordination number for the least bulky ligand. The results do infer the varying steric bulk provided by the ligands however.

The wavelength of emission maxima between similar complexes is said to be dependent upon strength of coordination.[1] From this, it can be argued that 6,6’-di-tert-butyldiphenylsilylmethyl-2,2’-bipyridine coordinates weakly to the Cm(III) ion in comparison to the other two ligands, which are of similar strength. 39b and 41b are, in turn, even more strongly coordinated than their predecessors.

6.4 Reactions of Silylated-Dimethylbipyridines with Neptunyl(V)

6.4.1 UV/vis-nIR spectroscopy

Two equivalents of silylated-dimethylbipyridine were dissolved in deuterated solvent (a mixture of d4-MeOD and CDCl3 for solubility) and added to a dried sample of neptunyl(V) chloride.

The UV/vis-nIR spectra of all three green neptunyl silylated dimethyl-bipyridine solutions confirm the neptunyl(V) oxidation state with the principal absorption maximum at 977 nm (Fig. 6.14). No absorption features attributable to neptunyl(VI) around 1200 nm are observed and the spectra remain unchanged after seven days.

![Fig. 6.14 The UV/vis-NIR spectrum of NpV2Cl and 2 equivalents of 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine (42) in MeOH 5:1 CHCl3.](image_url)
6.4.2 Complexation to Np\textsuperscript{V}O\textsubscript{2}Cl – \textsuperscript{1}H NMR spectroscopy

The addition of 6,6’-di-\textit{tert}-butyldimethylsilylmethyl-2,2’-bipyridine to neptunyl(V) (42) chloride resulted in minor shifts in the \textsuperscript{1}H NMR spectrum compared to the uncomplexed ligand along with a loss of resolution of proton-proton coupling (Fig. 6.15). Given the number of unpaired electrons in neptunyl(V) (\(f^2\)), a broader range of paramagnetically shifted proton resonances may be expected, c.f. paramagnetically shifted Ln(III) and U(IV) complexes (Section 1.10.1) This suggests that the ligand is in fast chemical exchange with the metal ion on the NMR timescale.\textsuperscript{[7]}

![Fig. 6.15 \(\textsuperscript{1}H\) NMR spectrum of 6,6’-di-\textit{tert}-butyldimethylsilylmethyl-2,2’-bipyridine and its reaction with neptunyl(V) chloride (42) with left a close-up of the aromatic region and right a view of the remainder of the spectrum. Both recorded in d\textsubscript{4}-MeOD 5:1 CDCl\textsubscript{3} at 300 K.]

Due to time constraints within the placements at INE, 42 was recorded again after three months. The solvent ratio was also changed to mirror that of the reactions of the other silylated dimethylbipyridines with neptunyl(V) chloride (from d\textsubscript{4}-MeOD 5:1 CDCl\textsubscript{3} to d\textsubscript{4}-MeOD 2:1 CDCl\textsubscript{3}). The change in frequency of the proton resonances is more noticeable than in the same experiment three months previously, although there are still no significant paramagnetic shifts (Fig. 6.16). There is also an increase in the number of resonances, suggesting the formation of a second solution species over time (42b).
Fig. 6.16 $^1$H NMR spectrum of 6,6’-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine and its reaction with neptunyl(V) chloride (42) after three months with left a close-up of the aromatic region and right a view of the remaining resonances. Both recorded in d$_4$-MeOD 2:1 CDCl$_3$ at 300 K.

Measurement of the $^1$H spectrum at 325 K and 250 K provides a brief insight into the dependency of the proton environments on temperature, particularly on the coalescence of signals at low temperature (Fig. 6.17). The unequal migration of resonances implies two separate species provide the signals at room temperature which are then observed to revert to their separate chemical shifts upon reheating of the sample. In contrast to studies of the americium(III) silylated-dimethylbipyridine reactions, increasing the temperature did not enhance the resolution of long-distance coupling.

Fig. 6.17 $^1$H variable temperature spectra of the neptunyl(V) 6,6’-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine sample (42) after three months from top 325 K to bottom 250 K. Recorded in d$_4$-MeOD 2:1 CDCl$_3$.

The addition of 6,6’-di-tri-iso-propylsilylmethyl-2,2'-bipyridine to neptunyl(V) (43) chloride resulted in little change in the $^1$H NMR spectrum with only a slight loss in
proton-proton coupling in the spectrum (Fig. 6.18). As with 42, no extreme shift of proton resonances is observed and 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine may not bind to neptunyl(V) under the experimental conditions employed.

Fig. 6.18 $^1$H NMR spectrum of 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine and its reaction with neptunyl(V) chloride (43) with left a close-up of the aromatic region and right a view of the rest of the spectrum. Both recorded in d$_2$-MeOD 2:1 CDCl$_3$ at 300 K.

However, decreasing the temperature from 325 to 250 K results in the migration of the peaks towards one another. The protons upfield in the spectrum are observed to shift downfield and vice-versa (Fig. 6.19) and no resonances appear or disappear in the spectrum. Increasing the temperature results in a slight increase in resolution of proton-proton coupling in the resonances. Together these data suggest that there may be minor paramagnetic contributions to the aromatic proton resonances or that they are in dynamic chemical exchange.

Fig. 6.19 $^1$H variable temperature spectra of the neptunyl(V) 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine (43) from top 325 K to bottom 250 K. Recorded in d$_2$-MeOD 2:1 CDCl$_3$.

Use of the bulkiest of the silylated dimethylbipyridines, 6,6’-di-tert-butylidiphenylsilylmethyl-2,2’-bipyridine, gave the most noticeable change in
chemical shift of the proton signals, combined with a significant broadening of the signals (Fig. 6.20) upon reaction with neptunyl(V) chloride (44). As with the other bipyridine-based ligands, no extreme shift of proton resonances was observed. A noticable quantity of white powder precipitated at the bottom, which may have hindered the shimming process of the NMR measurement. It may also indicate a binding of only one equivalent of the ligand to the neptunyl chloride, although only a visual inspection was available to assess the precipitate and thus the actual quantity is unknown.

**Fig. 6.20** $^1$H NMR spectrum of **6,6’-di-tert-butyldiphenylsilylmethyl-2,2’-bipyridine** and its reaction with neptunyl(V) chloride (44) with left a close-up of the aromatic region and right a view of the rest of the spectrum. Both recorded in d$_4$-MeOD 2:1 CDCl$_3$ at 300 K.

Decreasing the temperature of the NMR experiment results in a broadening of the proton resonances and a slight migration of the peaks towards one another. No other proton resonances belonging to another metal species appear during the experiment (Fig. 6.21). Additionally, the white precipitate did not dissolve during the variable temperature experiment.

**Fig. 6.21** $^1$H variable temperature spectra of the neptunyl(V) **6,6’-di-tert-butyldiphenylsilylmethyl-2,2’-bipyridine** (44) from top 325 K to bottom 250 K. Recorded in d$_4$-MeOD 2:1 CDCl$_3$. 
Increasing the ratio of CDCl$_3$ (from d$_4$-MeOD 2:1 CDCl$_3$ to d$_{14}$-MeOD 5:4 CDCl$_3$) for 44 solubilised the white precipitate. Analysis of the $^1$H NMR spectrum shows no extra resonances present that would be anticipated due to uncomplexed ligand (Fig. 6.22). This suggests either a change in coordination number of the complex upon changing solvent ratio or, more likely, that the ligand is in exchange in solution on the NMR timescale.

![Fig. 6.22 $^1$H NMR spectrum of the neptunyl(V) 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine complex (44) in above d$_4$-MeOD 5:4 CDCl$_3$ and below d$_{14}$-MeOD 2:1 CDCl$_3$ with left a close-up of the aromatic region and right a view of the rest of the spectrum. Both recorded at 300 K.](image)

### 6.4.3 $T_1$ relaxation times

The $T_1$ proton relaxation times measured for 42 show a severe reduction in relaxation time when compared to the ligand (seconds to milliseconds), which unequivocally advocates the interaction of the ligand with the neptunium ion (Table 6.5). In addition, the complex measured after three months still shows an interaction between ligand and metal. This is determined by the fact that all ligand resonances display short $T_1$ relaxation times and the ligand is in interaction with the neptunyl(V) ion in solution. The extra resonances that have formed due to 42b are also due to a neptunyl(V) complex and are not uncomplexed ligand (Table 6.6). Although the solvent ratios are altered between experiments, analysis of the $T_1$ relaxation times in both solvent systems confirms that this does not have a drastic effect on the timescale of the relaxation. The relaxation time of the broad resonance overlapping with residual chloroform in the $^1$H NMR spectrum of the complex could not be calculated.
Table 6.5 $T_1$ relaxation times for the proton environments of *above* the neptunyl(V) 6,6'-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine complex (42) (recorded in d$_4$-MeOD 5:1 CDCl$_3$) and *below* uncomplexed ligand (recorded in d$_4$-MeOD 4:1 CDCl$_3$) with *left* a close-up of the aromatic region and *right* the rest of the spectrum. Recorded at 300 K.
Table 6.6 $T_1$ relaxation times for the proton environments of *above* the neptunyl(V) 6,6'-di-tert-butylidimethylsilylmethyl-2,2'-bipyridine complex (42) after three months and *below* ligand with *left* a close-up of the aromatic region and *right* the rest of the spectrum. Both recorded at 300 K in d$_4$-MeOD 2:1 CDCl$_3$.

The $T_1$ relaxation times for the protons of the two bulkier silylated ligands relax faster when interacting with the neptunyl(V) ion. Although the tri-iso-propyl bearing ligand (Table 6.7) does not relax as fast as the diphenyl-tert-butyl bearing ligand (Table 6.8), which in turn relaxes slower than the ligand with the tert-butyl-dimethyl appendage. In all reactions, the measured times for the relaxation of residual proton resonances of water and methanol are faster than in the uncomplexed ligand samples, suggesting coordination of the solvent to the neptunyl(V) moiety. These relaxation times are also faster than all the ligand protons in the complexes, in some cases by an order of magnitude, indicating exchange of the solvent in solution. The preparation of 43 encountered difficulties in solubilisation of the neptunyl salt, probably through overheating of the sample, and so the minimal change in $T_1$ relaxation time and chemical shift of the protons may be due to a lack of neptunyl(V) in the sample. The relaxation time for the protons on the methyl arm of uncomplexed 6,6'-di-tert-butylidiphenylsilylmethyl-2,2'-bipyridine could not be calculated.
Table 6.7 $T_1$ relaxation times for the proton environments of above the neptunyl(V) 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine complex (43) and below ligand with left a close-up of the aromatic region and right the rest of the spectrum. Both recorded at 300 K in d$_4$-MeOD 2:1 CDCl$_3$. 

<table>
<thead>
<tr>
<th>Above the ligand</th>
<th>Below the ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>1126 ms (1)</td>
<td>1000 ms (1)</td>
</tr>
<tr>
<td>690 ms (1)</td>
<td>809 ms (1)</td>
</tr>
<tr>
<td>822 ms (1)</td>
<td></td>
</tr>
<tr>
<td>884 ms (1)</td>
<td></td>
</tr>
<tr>
<td>43 ms (1)</td>
<td>43 ms (1)</td>
</tr>
<tr>
<td>240 ms (1)</td>
<td>240 ms (1)</td>
</tr>
<tr>
<td>498 ms (1)</td>
<td>498 ms (1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aromatic region</th>
<th>Rest of the spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.038 s (5x 10$^{-3}$)</td>
<td>1.118 s (2x 10$^{-3}$)</td>
</tr>
<tr>
<td>10.523 s (8x 10$^{-3}$)</td>
<td>9.627 s (1x 10$^{-3}$)</td>
</tr>
<tr>
<td>1.480 s (6x 10$^{-3}$)</td>
<td>0.654 s (6x 10$^{-3}$)</td>
</tr>
<tr>
<td>1.672 s (1x 10$^{-3}$)</td>
<td>1.522 s (8x 10$^{-3}$)</td>
</tr>
<tr>
<td>8.552 s (1x 10$^{-3}$)</td>
<td>1.000 s (2x 10$^{-3}$)</td>
</tr>
</tbody>
</table>
Table 6.8 $T_1$ relaxation times for the proton environments of *above* the neptunyl(V) 6,6'-di-tert-butyl diphenylsilylmethyl-2,2'-bipyridine complex (44) and *below* uncomplexed ligand with *left* a close-up of the aromatic region and *right* the rest of the spectrum. Recorded at 300 K. Both recorded in d$_4$-MeOD 2:1 CDCl$_3$.

The $T_1$ relaxation times for 44 recorded after the addition of extra CDCl$_3$ are still notably faster in the neptunyl(V) complex than for the uncomplexed ligand, despite the decrease in relaxation time offered by the increased amount of deuterated chloroform (Table 6.9). The $T_1$ relaxation times still, especially for the solvent protons, encourage the notion that the ligand is in exchange in solution by comparison. The rate of relaxation for water could not be calculated in the sample of the neptunyl(V) complex with this ligand.
Table 6.9 $T_1$ relaxation times for the proton environments of above the neptunyl(V) 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine complex (44) and below uncomplexed ligand with left a close-up of the aromatic region and right the rest of the spectrum. Both recorded at 300 K in $d_4$-MeOD 5:4 CDCl$_3$.

6.4.4 Diffusion-ordered Spectroscopy

Due to the unorthodox solvent mixtures used, hydrated spherical radii are incalculable.

42 gives diffusion coefficients around $8.50 \times 10^{-10}$ m$^2$s$^{-1}$, indicating the presence of only one species and no unbound ligand in solution (Fig. 6.23). Data for the aromatic peak overlapping with the chloroform signal and the methyl groups overlapping with the TMS signal could not be calculated.
Fig. 6.23 Diffusion-ordered spectrum of the $^1$H resonances in the neptunyl(V) 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine complex (42). Recorded in d$_4$-MeOD 5:1 CDCl$_3$ at 300 K.

The DOSY spectrum after three months is incomparable to Fig. 6.23 due to a change in solvent ratios. The spectra indicate the presence of at least two different species in solution, with diffusion coefficients found as (all $\times 10^{-10}$ m$^2$s$^{-1}$): 6.00; 6.15; 6.40; 6.60; 6.80; 7.25; 7.30 and 7.55 (Fig. 6.24). Many of the values adjacent to one another are within error of each other, and overlap of the resonances due to different species in the $^1$H spectrum presents difficulty in obtaining definitive diffusion coefficients for every signal. It can be hypothesised that 42b, compared to the recording three months prior, may represent species that have lost silyl arms on the ligand: NpO$_2$Cl(6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine)$_2$ $M_w = 1128.5$ gmol$^{-1}$, 1.68 times the size of the corresponding complex with no silyl groups on the ligand ($M_w = 672.5$); NpO$_2$Cl(6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine) $M_w = 716.5$ gmol$^{-1}$, 1.47 times the size of the corresponding complex with no silyl groups attached to the ligand. These ratios can correspond to ratios of the diffusion coefficients found by DOSY NMR spectroscopy, i.e. 7.30 vs. 6.15 ($x10^{-10}$ m$^2$s$^{-1}$) gives a molecular weight ratio of 1.67; 7.30 vs. 6.40 ($x10^{-10}$ m$^2$s$^{-1}$) gives a molecular weight ratio of 1.48. Although overlap of signals and error in diffusion measurements (up to +/- 0.20 $x10^{-10}$ m$^2$s$^{-1}$) does not allow for definitive determination of species present in solution, the ratio of diffusion coefficients strongly advocates loss of silyl groups on the ligand over time (42b). This observation mirrors that seen for reactions of the ligand with uranyl(VI) nitrate in non-anhydrous conditions (see Section 5.3).
Fig. 6.24 Diffusion-ordered spectrum of the $^1$H resonances in the neptunyl(V) 6,6'-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine complex (42) after standing for three months. Recorded in d$_4$-MeOD 2:1 CDCl$_3$ at 300 K.

The diffusion-ordered measurements of 43 and 44 present faster diffusing species in solution. Table 6.10 summarises the diffusion measurements found. Measurement of the residual chloroform signal enables comparison between samples, although comparison with 43 is more erroneous.

Despite being the smallest ligand, 6,6'-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine presents the largest diffusion coefficients in solution with neptunyl chloride (near 6.00 x 10$^{-10}$ m$^2$s$^{-1}$). Comparison with 44 supports the previous suggestion that only one 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine ligand is binding to neptunyl(V) chloride in solution (since the latter sample diffuses at a faster rate). However, due to the spread of diffusion coefficient measurements across each sample and the lack of knowledge of at least one species in solution, this hypothesis is hard to prove mathematically. The diffusion coefficients for 43 are much faster and indicate failure of the ligand to bind in solution (due to the low quantity of neptunium in the sample).
Table 6.10 Diffusion coefficients of the proton resonances in the neptunyl(V) silylated dimethylbipyridine complexes. Recorded in d4-MeOD 2:1 CDCl₃ at 300K. Errors in diffusion coefficient (+/-) and spherical radius are given in brackets after values. *Measured after three months.

<table>
<thead>
<tr>
<th>Neptunyl(V) Sample</th>
<th>D / x10⁻¹⁰ m²s⁻¹</th>
<th>CHCl₃</th>
<th>MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>6,6’-di-tert-butyl(dimethyl)silylmethyl-2,2’-bipyridine*</td>
<td>6.00 (0.20), 6.15 (0.15), 6.40 (0.20), 6.60 (0.10), 6.80 (0.15), 7.25 (0.15), 7.30 (0.20), 7.55 (0.15)</td>
<td>21.10 (0.30)</td>
<td>-</td>
</tr>
<tr>
<td>6,6’-di-tri-isopropyl(dimethyl)silylmethyl-2,2’-bipyridine</td>
<td>10.70 (0.20), 11.20 (0.20), 11.30 (0.30)</td>
<td>23.80 (0.20)</td>
<td>21.65 (0.10)</td>
</tr>
<tr>
<td>6,6’-di-tert-butyl(diphenyl)silylmethyl-2,2’-bipyridine</td>
<td>7.55 (0.10), 7.75 (0.10), 7.80 (0.20), 7.85 (0.15), 7.90 (0.10), 8.00 (0.15), 8.10 (0.10), 8.45 (0.15)</td>
<td>20.90 (0.15)</td>
<td>20.40 (0.15)</td>
</tr>
</tbody>
</table>

Analysis of 44 after alteration of the solvent ratio reveals the proton resonances all diffuse at approximately the same rate to one another (between 5.50 and 5.65 (+/- 0.15) x 10⁻¹⁰ m²s⁻¹). If the precipitate was uncomplexed ligand, upon solubilisation there was only one complex present in solution on the NMR timescale. This is in agreement with the previous theory that the change in solvent system has led to a change in coordination number for the complex, or that the ligand is in exchange with the metal centre.

To test the theory that the ligands are in fast exchange with the neptunyl(V) cation under the 2:1 ligand:metal stoichiometries employed, excess ligand added to 42 and 44 should provide additional peaks in the NMR spectrum if uncomplexed ligand forms. The ¹H NMR spectra of 42 (Fig. 6.25) shows a significant change upon addition of excess ligand (with proton signals decreasing in intensity and giving way to a new species), and 44 shows only a minor change in shift of the proton signals (Fig. 6.26).
The diffusion-ordered spectra of the samples are similar to those recorded before the addition of excess ligand. For 44, the diffusion coefficients measured are between 5.10 and 5.30 (+/- 0.10) x 10^{-10} m^2 s^{-1}. The minor discrepancy between this and the measurement before the addition of excess ligand may be attributed to the slight change in diffusion coefficient of the residual chloroform (16.5 vs. 17.6 (+/- 0.30) x 10^{-10} m^2 s^{-1} for the sample with excess ligand and the sample before the addition of excess ligand respectively). This evidence continues to support the prospect of the ligand being in exchange with the neptunyl(V) moiety in solution on the NMR timescale. It is not of sufficient difference to the previous measurement to suggest a change in coordination number.
presents protons with similar diffusion coefficients to the measurement made before the addition of excess ligand, whereby the values are (all $x 10^{-10}$ m$^2$s$^{-1}$): 6.10; 6.35; 6.40; 6.50; 6.95; 7.30; 7.40; 7.75; 7.80 and 8.45 (all +/- 0.20). Despite the significant change in proton environment in the $^1$H NMR spectrum, the diffusion measurements indicate no uncomplexed ligand is present in solution, and the silylated ligand may be in exchange on the NMR timescale in a similar fashion to 44. The observable changes in the $^1$H NMR spectrum of 42, in contrast to 44, is likely due to the presence of multiple species in solution before addition of excess ligand, and therefore, there is a change in ratio of products.

6.4.5 Complexation of 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine to Np$^V$O$_2$(ClO$_4$)

A short study was conducted on the addition of two equivalents of 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine to Np$^V$O$_2$(ClO$_4$) (45). The $^1$H NMR spectrum produced from the reaction changes little over temperature (265 to 325 K) and line broadening occurs at lower temperatures (Fig. 6.27).

![Fig. 6.27 $^1$H variable temperature spectra of the neptunyl(V) 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine complex (45) from top 325 K to bottom 265 K. Recorded in d$_4$-MeOD 8:3 CDCl$_3$.](image)

The UV/vis-NIR spectrum confirms neptunyl exists in the $^+$V oxidation state with the principal absorption maximum at approximately 980 nm. No transitions due to neptunyl(VI) near 1200 nm are observed.

The fast $T_1$ relaxation times (between 5 and 168 ms) hint at a strong paramagnetic interaction between the metal and the ligand protons (Table 6.11). This infers less
chemical exchange for the binding of the ligand to metal vs. reaction with the chloride salt.

Table 6.11 $T_1$ relaxation times for the proton environments of the neptunyl 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine complex (45) with left a close-up of the aromatic region and right the rest of the spectrum. Recorded at 270 K in $d_4$-MeOD 8:3 CDCl$_3$.

Measurement of the diffusion coefficient gives, similarly to the neptunyl(V) chloride measurements for the silylated ligands, one set of diffusion coefficients (Fig. 6.28), suggesting the presence of only one species in solution on the NMR timescale. Lack of data on the viscosity of the solvent mixture present does not allow for calculation of hydrated spherical radii. Additionally, the change in solvent ratio and temperature of measurement prevents comparison with measurements made on the neptunyl(V) chloride systems. All diffusion coefficients are reported as $3.15 \pm 0.15 \times 10^{-10}$ m$^2$s$^{-1}$.

![Diffusion-ordered spectrum of the $^1H$ resonances in the neptunyl perchlorate 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine complex (45). Recorded in $d_4$-MeOD 8:3 CDCl$_3$ at 270 K.](image)

6.5 Conclusions

The coordination chemistry of three bis-trialkyl/aryl substituted silyl dimethyl bipyridine ligands ($R = ^i$BuMe$_2$, $^i$Pr$_3$ and Ph$_2$Bu) with the minor actinides Am(III) and
NpO$_2$(V), has been investigated through a comprehensive 1D and 2D $^1$H NMR spectroscopic study and, in the case of Cm(III), through steady state and time resolved emission spectroscopy. The emission spectra and luminescence lifetimes resolved during titration experiments involving incremental additions of ligand solutions to the Cm(III) ion in solution confirm the interaction of silylated dimethylbipyridines and Cm(III) on the luminescence timescale, similar to NMR investigations of the bulkier silylated ligands (trialkyl groups = $^3$Pr$_3$ and $^3$BuMe$_2$) with Am(III). 6,6′-Di-tert-butyldimethylsilylmethyl-2,2′-bipyridine does not appear to coordinate to americium(III), which is likely as a result of a weaker affinity for binding of this ligand in the presence of the less labile nitrate counterion in the americium(III) sample, compared to the more facile displacement of the perchlorate counterion in the curium(III) experiments. In all cases, one or two distinct Cm(III)-ligand species evolve during the titration and the radiative lifetimes of the final species are all approximately double that of the emission lifetime of the curium perchlorate species in solution. This indicates a significant reduction in competitive non-radiative decay involving energy transfer to closely diffusing O-H oscillators, and therefore suggests that the Cm(III) ions are ligated by at least one ligand. However attempts to realise the coordination number of each ligand produces contrasting information from different results obtained, with calculation of the coordinated number of water molecules resulting in similar products for the ligands. This is in contrast to americium(III) results obtained by calculation of the proton spin-lattice relaxation times. For the Cm(III) species that evolve during the titrations with the three silylated bipyridyl ligands, the combination of the magnitude of the shift of emission maxima to lower energies and the evidence for different binding modes means that the precise nature of the coordination complexes in solution can not be unequivocally unassigned. That the reaction of the Cm(III) ion with 6,6′-di-tert-butyldiphenylsilylmethyl-2,2′-bipyridine does not produce a second species by luminescence investigation indicates that the sterically smaller ligands may have formed a second species with a greater ligand coordination number. The 6,6′-di-tert-butyldiphenylsilylmethyl-2,2′-bipyridine ligand is unable to do this due to its increased steric bulk.

The interaction of the ligands with neptunyl(V) is confirmed by $^1$H NMR spectroscopy (where there is no experimental error), with diffusion measurements confirming that the steric bulk of 6,6′-di-tert-butyldiphenylsilylmethyl-2,2′-
bipyridine influences its coordination, forming a smaller complex than the reaction of 6,6’-di-\textit{tert}-butyldimethylsilylmethyl-2,2’-bipyridine with neptunyl(V) chloride. The proton NMR spectra suggest that all ligands are labile in solution, confirmed by addition of excess ligand to the reaction mixtures. The exchange of the ligands is perhaps unsurprising given the likely competing affinity of the metal for chloride vs. silylated dimethylbipyridine. A short study on the complexation of 6,6’-di-tri-\textit{iso}-propylsilylmethyl-2,2’-bipyridine with the weaker coordinating counterion, perchlorate, has indicated that the ligand can coordinate to neptunyl(V) in the absence of reliable data for reaction with Np\textsuperscript{V}O\textsubscript{2}Cl. The interaction with neptunyl(V) is also stronger than for any ligand with neptunyl(V) chloride. Similar to comparisons between reactions with Am(III) nitrate and Cm(III) perchlorate, the ligands preferentially bind in place of the weaker anion (perchlorate). \textsuperscript{1}H DOSY-NMR spectroscopy also suggests that there is only one neptunyl(V) complex in solution for each sample (except for the presence of hydrolysed product for the smallest ligand).

6.6 References

Chapter 7

Interaction of TPIP with the Minor Actinides Am(III) and Cm(III)
7.1 Introduction
The coordination of TPIP (tetraphenylimidodiphosphinate) to lanthanide(III) ions is documented as following a simple 3:1 ligand to metal geometry,\textsuperscript{[1-3]} generally producing emissive complexes with reasonably long emission lifetimes (Chapter 2). However, the coordination environment of the metal is not completely saturated.\textsuperscript{[4]} Comparison with perfluorinated analogue, F\textsuperscript{3}TPIP, reveals an increase in emissive properties for nIR emitting lanthanides, but a decrease for those that emit in the visible region\textsuperscript{[5,6]} (Chapter 2).

Due to the similar chemistry of the lanthanides and minor actinides, and the ‘hard’ Lewis basic donor atoms of the monoanionic TPIP ligand, similar coordination chemistry may be anticipated for An(III) complexes, and perhaps a similar use of luminescence spectroscopy to characterise the Cm(III) complexes.

7.2 Americium(III) TPIP Reactions
7.2.1 $^1$H and $^{31}$P NMR spectroscopy variable temperature studies
The reaction scheme for the complexation of NaTPIP to the americium(III) ion was derived from the corresponding lanthanide scheme,\textsuperscript{[1-3]} where three equivalents of NaTPIP ligand dissolved in 600 μL of deuterated solvent were added to one equivalent of dried americium nitrate (Scheme 7.1). The combined solution changed from a pink colour (americium(III) nitrate in solution) to yellow/green (americium(III) TPIP complex, \textsuperscript{[7]}) Samples prepared in deuterated methanol resulted in the precipitation of a white product after a short time (\textit{ca.} 30 minutes), which was presumed to be sodium nitrate.
Scheme 7.1 Proposed reaction scheme for the addition of NaTPIP to americium nitrate.

A comparison of the $^1$H NMR spectrum between 46 and NaTPIP shows an upfield shift of the resonances and distinction between the ortho and para protons of the phenyl ring (Fig. 7.01). The $^{31}$P NMR spectrum reveals a large downfield shift of the single phosphorus resonance. The shift of the resonances in both the $^1$H and $^{31}$P NMR spectra, combined with the formation of the white precipitate, indicate the presence of a new species (presumably Am(TPIP)$_3$) and that complete complexation has occurred. Also the $^1$H and $^{31}$P NMR spectra reveal that no uncomplexed NaTPIP remains in solution.

Fig. 7.01 Left $^1$H NMR spectrum and right $^{31}$P-$^1$H NMR spectrum of above Am(TPIP)$_3$ (46) and below NaTPIP, both recorded in d$_4$-MeOD at 300 K.
Variable temperature multinuclear NMR spectroscopy (Fig. 7.02) shows little to no change in the resonances over an 85 K temperature range in both the $^{31}$P and $^1$H NMR spectra. All three proton environments are discernable, but there is a loss of most 3- and 4- bond coupling in the $^1$H NMR spectrum by 240 K.

![Variable temperature spectra](image)

Fig. 7.02 *Left* $^1$H and *right* $^{31}$P-$^1$H variable temperature spectra of the americium(III) TPIP complex (46) *from top* 325 K *to bottom* 240 K. Recorded in d$_4$-MeOD.

At temperatures below 240 K, the $^1$H and $^{31}$P NMR spectra both reveal the formation of a second set of resonances (Fig. 7.03). The proton resonances integrate to a ratio of 3:1 in favour of the ubiquitous resonance from the meta environment of the phenyl ring. The other proton environments are too unresolved to integrate. The formation of yellow-green crystals could also be seen after variable temperature spectroscopy had been performed. However, due to radiological constraints no attempts could be made to perform single crystal X-ray diffraction.
Repetition of the experiment in d$_6$-DMSO allowed higher temperature variable temperature spectra to be recorded. In contrast to the spectra recorded in deuterated methanol, two separate resonances can clearly be seen in the $^{31}$P NMR spectrum (Fig. 7.04) along with a larger number of peaks in the $^1$H NMR spectrum at 300 K. 2D $^1$H-$^{31}$P NMR spectroscopy reveals the phosphorus resonances correlate to separate environments in the $^1$H NMR spectrum. In the measured spectra, the downfield phosphorus resonance (at 52.40 ppm) is observed to couple with only the upfield aromatic proton resonance (at 7.09 ppm), and the upfield phosphorus resonance (at 48.16 ppm) are seen to coupling with the remaining proton environments (7.30, 7.60 and 7.72 ppm), but not with the resonance at 7.09 ppm.
Variable temperature NMR spectroscopy, at both $^1\text{H}$ and $^{31}\text{P}$ frequencies, reflect the observations seen in deuterated methanol – at higher temperatures peaks converge to give spectra that appear to contain one set of peaks (Fig. 7.05). The upfield phosphorus resonance migrates towards the downfield resonance, which only notably alters over the temperature range upon coalescence. It should be noted that the resonances did not take time to appear – heating and cooling the sample immediately produced the displayed resonance(s) even when immediately repeated and measured. The presence of the extra peaks suggest the existence of a second species (47) at lower temperatures.
Fig. 7.05 Left $^1$H and right $^{31}$P-$^1$H variable temperature spectra of the americium(III) TPIP complex (46) from top 370 K to bottom 300 K. Recorded in d$_6$-DMSO.

7.2.2 Ln(III) NMR spectroscopy titrations

Multinuclear NMR spectroscopic titrations performed on Nd(NO$_3$)$_3$, Sm(NO$_3$)$_3$ and Eu(NO$_3$)$_3$ complement the americium(III) TPIP data obtained in the previous section. The $^1$H and $^{31}$P NMR spectra were recorded after the addition of each equivalent of NaTPIP (up to four equivalents). These lanthanide salts have comparable 6-coordinate ionic radii with the Am(III) and Cm(III) ions.$^8$

Each of the three lanthanides show the formation of an intermediate species before the Ln(TPIP)$_3$ complex is formed in deuterated DMSO (Fig. 7.06). Notably samarium(III) appears to form two intermediate species before the final charged-balanced Sm(TPIP)$_3$ species is produced, presumably samarium(III) with one and then two equivalents of TPIP bound. Each experiment also shows the presence of an intermediate alongside Ln(TPIP)$_3$ upon addition of three equivalents of NaTPIP, indicating a competition for the charge-balanced final species, possibly from the solvent. The addition of the fourth equivalent of ligand produced a spectrum with the Ln(TPIP)$_3$ species and unbound ligand present for each lanthanide. No unbound ligand is seen in the spectra with 1, 2 or 3 equivalents of ligand.
Fig. 7.06 Left $^1$H and right $^{31}$P-$^1$H NMR spectra of Ln$^{III}$(TPIP)$x$(NO$_3$)$_y$ with Ln = top Nd, = middle Sm and = bottom Eu. In each set of spectra the bottom spectrum represents NaTPIP and, in ascending order, Ln$^{III}$ with, 1, 2, 3 and 4 equivalents of NaTPIP respectively. All recorded in d$_6$-DMSO at room temperature.

A similar titration of Eu(NO$_3$)$_3$ in deuterated methanol allowed comparison against the titration in deuterated DMSO and vs. the NMR spectra of 46. After addition of the second equivalent of ligand, large amounts of white precipitate formed in the NMR sample. It is thought the final Eu(TPIP)$_3$ complex is largely insoluble in methanol, unlike Am(TPIP)$_3$. Again, the spectra again show the formation of an intermediate species before the final charge-balanced complex (Fig. 7.07). Acquisition of the $^{31}$P NMR spectrum with a high number of scans is necessary in order to observe the Eu(TPIP)$_3$ resonance. Addition of the fourth equivalent of ligand again revealed the formation of uncomplexed ligand, and no complex can be seen in solution (complete
precipitation occurs at this point). The NMR titration in methanol suggests the binding of TPIP to the europium(III) ion proceeds in a 3:1 ratio with less competition from the solvent. Only the final complex was seen after the addition of three equivalents of ligand, albeit weakly with a high number of scans.

Fig. 7.07 Left and middle $^1$H and right $^{31}$P-$^1$H NMR spectra of Eu$^{III}$ (TPIP)$_x$(NO$_3$)$_y$. The bottom spectrum represents NaTPIP and, in ascending order, Eu$^{III}$ with, 1, 2, 3 and 4 equivalents of NaTPIP respectively. All recorded in d$_4$-MeOD at room temperature.

The titrations of NaTPIP to lanthanides in d$_6$-DMSO show incomplete formation of Ln(TPIP)$_3$ after the addition of three equivalents of NaTPIP to Ln(NO$_3$)$_3$. This advocates the theory that the NMR spectra presented earlier in this section for the addition of NaTPIP in d$_6$-DMSO to Am(NO$_3$)$_3$ show the presence of both Am(TPIP)$_3$ and an intermediate complex. The identity of the intermediate is unknown but was found in every titration. In methanol, the intermediate is not found in the spectrum of Am(TPIP)$_3$, a result mirrored in the titration of NaTPIP to europium nitrate in d$_4$-MeOD. This suggests competition in formation of the final complex in DMSO, presumably from the solvent itself. The solvent may play a large role in the displacement of the nitrate counterion in enabling the tris-TPIP complex to form.

The lanthanide titrations also highlight the subtle chemical differences between the lanthanides, with samarium(III) able to form two intermediate species before finishing as Sm(TPIP)$_3$ in DMSO (Equation 7.1).

\[
\begin{align*}
\text{Sm(NO}_3\text{)}_3 & \xrightarrow{\text{NaTPIP}} \text{Sm(NO}_3\text{)}_2(\text{TPIP}) + \text{Na(NO}_3\text{)}_3 \\
\text{NaTPIP} & \xrightarrow{\text{Sm(NO}_3\text{)}_3} \text{Sm(NO}_3\text{)}_2(\text{TPIP}) + 2\text{Na(NO}_3\text{)}_3
\end{align*}
\]

\[
\begin{align*}
\text{NaTPIP} & \xrightarrow{\text{Sm(TPIP)$_3$}} \text{Sm(TPIP)$_3$} + 3\text{Na(NO}_3\text{)}_3 \\
\text{NaTPIP} & \xrightarrow{\text{Sm(TPIP)$_3$}} \text{Sm(TPIP)$_3$} + 3\text{Na(NO}_3\text{)}_3 + \text{NaTPIP}
\end{align*}
\]

Equation. 7.1 Proposed reaction scheme for the stepwise reaction of Sm(NO$_3$)$_3$ with NaTPIP.
The ratio of TPIP to lanthanide (1:1 or 2:1) for the titrations that only show one intermediate complex is unknown.

### 7.2.3 Diffusion-ordered NMR spectroscopy

DOSY-NMR spectroscopy can determine more information upon the formation of multiple species in the sample when performed on multiple nuclei (Fig. 7.08) at a variety of temperatures.

![DOSY-NMR spectrum of the \(^{31}\text{P}\) resonances in the americium(III) TPIP complex](image)

**Fig. 7.08** Diffusion-ordered spectrum of the \(^{31}\text{P}\) resonances in the americium(III) TPIP complex (46). Recorded in \(d_6\)-DMSO at 300 K.

Room temperature \(^{31}\text{P}\) DOSY spectra of the americium TPIP complex in deuterated DMSO reveals a clear distinction in the environment of the two resonances (Fig. 7.08). The spectrum strongly suggests two separate species with a diffusion coefficient of 13.80 (+/- 0.30) x 10\(^{-10}\) m\(^2\)s\(^{-1}\) and 17.20 (+/- 0.30) x 10\(^{-10}\) m\(^2\)s\(^{-1}\) for the upfield (48.16 ppm) and downfield (52.40 ppm) resonances, respectively. Use of Equation 1.7\(^{[9]}\) allows determination of the relative molecular weights of the two species in solution and implies that the larger species, Am(TPIP)\(_3\) (46), has a molecular weight approximately 1.94 times the molecular weight of the species that contributes to the downfield resonance is part of. The molecular weight of Am(TPIP)\(_3\) (1491 gmol\(^{-1}\)) is approximately 1.90 times the molecular weight of Am(TPIP)(NO\(_3\))\(_2\) (783 gmol\(^{-1}\), 47), and thus this is believed to be the identity of the intermediate complex observable in the americium(III) TPIP sample. Solvated DMSO is likely to be in fast exchange with bulk solvent on the NMR timescale.

Measuring the diffusion coefficients of the proton resonances in the same sample reveals all proton environments to be part of the same complex (Fig. 7.09), or part of
multiple complexes which have the same molecular weight, with all proton resonances diffusing at a rate of \(1.60 \pm 0.15 \times 10^{-10} \text{ m}^2\text{s}^{-1}\). This is in contrast to the diffusion ordered spectrum of the \(^{31}\text{P}\) environments, which belong to different proton environments as evidenced by 2D \(^1\text{H}-^{31}\text{P}\) spectroscopy. It is likely that the overlap of proton signals has rendered different diffusion coefficients indistinguishable due to averaging.

![Diffusion-ordered spectrum of the \(^1\text{H}\) resonances in the americium(III) TPIP complex](image)

**Fig. 7.09 Diffusion-ordered spectrum of the \(^1\text{H}\) resonances in the americium(III) TPIP complex (46). Recorded in d$_6$-DMSO at 300 K.**

The diffusion coefficient of the proton environments are presented between 300 and 350 K (Table 7.1). Although comparison between spectra at different temperatures is not possible because of the varied diffusion coefficient of the reference solvents, comparison of the resonances within each spectrum is possible. Analysis of the diffusion coefficients shows little, if any, evidence of a second species in the proton environments at many temperatures, with the greatest difference observed at 330 K (5.95 vs. 6.60 \(\times 10^{-10} \text{ m}^2\text{s}^{-1}\), Table 7.1). Equation 1.7 reveals the slower diffusing complex to be in an environment 1.11 times larger than that of the faster diffusing proton signal. It is also revealed that water does not appear to be interacting with the complex on the NMR timescale.
Table 7.1 Diffusion coefficients of the proton resonances in the americium(III) TPIP complex (46) at varying temperature. Recorded in $d_6$-DMSO. Errors in diffusion coefficient (+/-) are given in brackets after values.

<table>
<thead>
<tr>
<th>T/K</th>
<th>D/x10$^{-10}$ m$^2$s$^{-1}$</th>
<th>Aromatic resonances</th>
<th>H$_2$O</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.60 (0.15)</td>
<td>8.50 (0.15)</td>
<td>6.45 (0.15)</td>
<td></td>
</tr>
<tr>
<td>310</td>
<td>2.50 (0.05), 2.60 (0.05), 2.70 (0.05)</td>
<td>8.45 (0.10)</td>
<td>11.40 (0.15)</td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>3.90 (0.10), 4.00 (0.10), 4.10 (0.10), 4.25 (0.15)</td>
<td>11.10 (0.20)</td>
<td>14.65 (0.20)</td>
<td></td>
</tr>
<tr>
<td>330</td>
<td>5.95 (0.05), 6.45 (0.10), 6.60 (0.15)</td>
<td>15.00 (0.20)</td>
<td>19.70 (0.20)</td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>9.25 (0.10), 9.30 (0.20)</td>
<td>19.30 (0.20)</td>
<td>25.40 (0.20)</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>16.20 (0.20)</td>
<td>28.05 (0.20)</td>
<td>37.10 (0.20)</td>
<td></td>
</tr>
</tbody>
</table>

As with the room temperature measurement, convolution of proton environments has rendered differentiation between diffusion coefficients impossible and the presence of different species is only implied. Equation 1.7\[^{[10]}\] allows hydrodynamic spherical radii of the resonances to be determined; however, hydrated spherical radii can not be obtained at each temperature due to a lack of accurate data for solvent viscosity. Use of the value\[^{[11]}\] 1.3806503 x 10$^{-23}$ m$^3$kgs$^{-2}$K$^{-1}$ for $k_B$ and the value for the solvent viscosity of DMSO at 298 K (1.987 x 10$^{-3}$ mNsm$^{-3}$,\[^{[12]}\] it is not anticipated the value will change significantly over 2 K) gives $r_H = 6.91 (+/- 0.73)$ Å for the resonances measured at 300 K.

### 7.2.4 $T_1$ relaxation times

The $T_1$ relaxation times for the proton environments of the americium(III) TPIP complexes can be determined by inversion recovery measurements and compared to the uncomplexed ligand (Table 7.2).
Table 7.2 $T_1$ relaxation times for top left NaTPIP in d$_4$-MeOD at 300 K, top right TPIP in the americium(III) complex (46) in d$_4$-MeOD at 300 K, bottom left TPIP in the americium(III) complex (46) in d$_6$-DMSO at 300 K and bottom right TPIP in the americium(III) complex (46) in d$_6$-DMSO at 370 K. The errors of the relaxation times are taken from the standard deviation of each $T_1$ plot and are quoted in brackets after the respective value.

The relaxation times of the americium(III) complex are significantly shorter (approximately half) than for NaTPIP, indicating the complexation of the ligand to the americium(III) ion. Changing solvent has a significant effect on the relaxation time of the protons in 46, although not on the timescale of the relaxation. As outlined in the previous section, the sample recorded in d$_6$-DMSO has two complexes with overlapping resonances, and this is likely the reason for the change. In addition, the relaxation times at higher temperature (370 K) increase when compared to the room temperature relaxation times. $^{31}$P NMR spectroscopy shows the presence of only one complex at this temperature, and so it is only this set of resonances which contribute to the relaxation times observable. Due to the migration of peaks, particularly in the sample recorded in d$_6$-DMSO, comparison of relaxation times specific to each resonance is impractical.

Weak paramagnetic contributions from Am(III) to a coordinated ligand can be observed by VT NMR spectroscopy,$^{[13]}$ with resonances expected to experience a
greater change in chemical shift when compared to a non-paramagnetic contribution.\textsuperscript{[13]} In particular, a temperature dependence of the proton resonances with chemical shift at higher temperatures may evidence population of the first spin-orbit \( ^7\text{F}_1 \) excited state in Am(III), which has been estimated to lie approximately 4000 cm\(^{-1}\) above the diamagnetic \( ^7\text{F}_0 \) ground state of the free ion.\textsuperscript{[14]} For a pseudo-contact (dipolar) contribution to paramagnetism, the change in chemical shift with temperature should be proportional to \( 1/T^2 \), whereas for a Fermi contact shift (through bond), the relationship between chemical shift and temperature will approximately equal \( 1/T \).\textsuperscript{[15]} The change in proton resonance frequency, inversely proportional to the inverse of temperature squared, for 46 is presented in Fig. 7.10. The almost non-existent gradients representing the change in chemical shift indicate no paramagnetic contribution to the proton relaxation mechanism. This is likely due to the great distance of the protons from the metal centre and the dependence on distance of paramagnetic effects (Section 1.10.1).\textsuperscript{[13]}

![Fig. 7.10 Plot of change in chemical shift vs. inverse temperature squared. Measured in d\(_4\)-MeOD between 240 and 325 K. m = gradient](image)

The corresponding yttrium complex, \([\text{Y(TPIP)}_3]\) (48), presents relaxation times similar to that of the americium(III) TPIP complex (Table 7.3), indicating a negligible paramagnetic interaction from the \( 5f^6 \) Am(III) ion. The magnitude of the relaxation time is expected to be noticeably different to that of the diamagnetic 48, if
americium(III) were to have a significant paramagnetic contribution to the proton environments.

**Table 7.3** Left $T_1$ relaxation times for the proton environments of $Y$(TPIP)$_3$ (48) and right the $^{31}$P-$\{^1$H$\}$ spectrum. Recorded in $d_6$-DMSO at 300 K. The errors of the relaxation times are taken from the standard deviation of each $T_1$ plot and are quoted in brackets after the respective value.

7.2.5 Fluorinated-TPIP and americium(III)

The reaction Scheme 7.1 was followed for the addition of Na$^{^{19}}$TPIP (Section 2.1) in deuterated methanol to americium(III) nitrate. Due to the inability to decouple the phosphorus nuclei from fluorine, only $^{19}$F NMR spectroscopy were performed at variable temperature and the $^{31}$P NMR spectrum is compared to that of the uncomplexed ligand at room temperature. The change in position of the resonances, upon addition of Na$^{^{19}}$TPIP to Am(III) nitrate are most noticeable in the $^{31}$P NMR spectrum (Fig. 7.11). This indicates the formation of a new species (49) upon addition of the ligand to the americium nitrate, an observation supported by the precipitation of a white solid in the sample, thought to be sodium nitrate. Multinuclear NMR spectroscopy reveals a lack of peaks corresponding to the unbound ligand after addition to americium(III) nitrate. Presumably, the product formed is therefore Am($^{19}$TPIP)$_3$. The phosphorus spectrum hints at the formation of a minor second species downfield to the main one and is a broad resonance at 15 ppm.
Variable temperature $^{19}$F NMR spectroscopy (Fig. 7.12) reflects the observations of the non-fluorinated TPIP reaction in deuterated methanol, where the resonances shift little until a temperature below 240 K is reached and the formation of a second species is apparent (50).

The diffusion coefficients of the fluorine resonances of 49 at 300 K and at 210 K are presented in Fig. 7.13 (chosen because at this temperature the formation of a greater number of fluorine resonances are observed). The two spectra are not directly comparable, but the fluorine environments within each spectrum are. Study of the resonances in both, reveals a similar diffusion coefficient for all fluorine environments in each individual spectrum ($5.10 \times 10^{-10}$ m$^2$s$^{-1}$ at 300 K and $2.50 \times 10^{-10}$ m$^2$s$^{-1}$ at 210 K). It should be noted that small variations in diffusion coefficient...
around each resonance at low temperature are likely caused by the higher error and poorer fit of experimental data associated with the lower temperature measurement, with increased error from increased viscosity of the solvent.\cite{16}

Fig. 7.13 Diffusion-ordered spectrum of the $^{19}$F resonances in the americium(III) $^{5}$TPIP (49) complex above at 300 K and below at 210 K. Recorded in $d_4$-MeOD.\cite{17}

Equation 1.7 presents hydrodynamical spherical radii of the resonances in Table 7.4. The overlap of signals has, as with the americium(III) TPIP experiment, prevented the observation of the separate diffusion coefficients, and therefore complexes at low temperature. As with the hydrogenated derivative, TPIP, these data suggest that $^{5}$TPIP forms a complex (50) with the formula [Am($^{5}$TPIP)(NO$_3$)$_2$], in addition to the major species, 49.

Table 7.4 Hydrodynamic spherical radii of the resonances measured by DOSY-NMR spectroscopy in Am($^{5}$TPIP)$_3$. Measured in $d_4$-MeOD. Values of 3.496 and 0.514 x $10^{-3}$ mNsm$^{-3}$ used for the solvent viscosity.\cite{17}
<table>
<thead>
<tr>
<th>Species</th>
<th>D / x10^{-10} m²s⁻¹</th>
<th>r_H /x10^{-10} m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am⁻⁵⁷TPIP, 300 K</td>
<td>5.10 (0.20)</td>
<td>8.38 (0.53)</td>
</tr>
<tr>
<td>Am⁻⁵⁷TPIP, 210 K</td>
<td>2.50 (0.40)</td>
<td>1.76 (0.33)</td>
</tr>
</tbody>
</table>

7.3 Curium(III) TPIP Time Resolved Laser Fluorescence Spectroscopy (TRLFS)

7.3.1 Curium(III) TPIP titrations

Increasing concentrations of ligand dissolved in methanol were added to a 100 nM curium(III) perchlorate aqueous solution, and the emission spectrum recorded at each step.

The addition of NaTPIP to curium(III) results in the formation of one species, first observable with a 2.53 μM solution of NaTPIP (Fig. 7.14). The emission maximum (609.2 nm) is red-shifted, with respect to the curium(III) perchlorate signal (601.2 nm) in methanol, due to the complexation of TPIP ([51]). The shoulder that arises at higher energy to the emission maxima is assigned as a vibrational ‘hot-band’ as time-resolved emission spectra revealed an equal decrease in signal intensity over time. On complexation, this ‘hot band’ arises due to a large crystal field splitting of the ground \(^8S_{7/2}\) state term (into 4 sub levels) upon a change in coordination environment and ligand-metal bond strength, which is a direct consequence of mixing of the excited states with the ground state term by spin-orbit interactions. Addition of a large excess of NaTPIP (a 4.44 mM solution of NaTPIP) broadens the emission maximum and gives a significant loss of emission intensity, consistent with the formation of colloids (Fig. 7.15)."
Fig. 7.14 Emission spectra of the curium(III) perchlorate solution upon addition of NaTPIP \((51)\) in MeOH 98:2 H₂O. Excitation wavelength = 396.6 nm.

Fig. 7.15 Emission spectra of the curium(III) TPIP species left the final complex formed \((51)\) and right after the addition of great excess of ligand (a 4.44 mM solution of NaTPIP) in MeOH 98:2 H₂O. Excitation wavelength = 396.6 nm.

Use of time-resolved emission spectroscopy enables determination of the emission lifetime for the species present (Fig. 7.16); the lifetime of curium perchlorate in methanol is 128.85 μs. The final complex displays a lifetime of 309.86 μs (Table 7.5), a significant increase compared to curium(III) perchlorate, confirming complexation of the ligand to the Cm(III) ion. Fig. 7.17 depicts an initial red-shift of the emission maxima before the emission peak decreases in intensity, simultaneous to the formation of the final complex peak. This indicates the presence of an intermediate species \((52)\). Use of time-resolved emission spectroscopy before the formation of the
final complex elucidates two separate lifetimes for the two peaks. The intermediate species at 603.7 nm has a radiative lifetime of 251.84 μs and the rising emission profile of the final complex being 261.18 μs, which has shorter than the lifetime of the final complex. The final complex is also found at 610.1 nm in the intermediate solution, slightly red-shifted with respect to its final position. The presence of the intermediate species agrees with the Am(III) ¹H NMR data in section 7.1, which shows the formation of Am(TPIP)(NO₃)₂, before the formation of Am(TPIP)₃. The similarities between the Am(III) ¹H NMR and Cm(III) experiments lead to assignment of the intermediate species in the Cm(III) titration as Cm(TPIP)(O₄Cl)₂ (52) and the final complex as Cm(TPIP)₃ (51).

Fig. 7.16 TRES at the end of the titration of NaTPIP into curium(III) perchlorate (51) (a 1.65 mM NaTPIP solution) in MeOH 98:2 H₂O. Excitation wavelength = 396.6 nm.
Fig. 7.17 Emission spectrum highlighting the final complex (Cm(TPIP)$_3$) (51) and Cm(TPIP)(O$_4$Cl) (52) in a 150 μM NaTPIP solution with curium perchlorate in MeOH 98:2 H$_2$O. Excitation wavelength = 396.6 nm.

Table 7.5 Summary of the emission lifetimes found for the addition of NaTPIP to curium(III) perchlorate. All lifetimes fitted to a mono-exponential decay rate. Estimated error on lifetime measurements = +/- 10%. $N_{H2O}$ values calculated using Equation 6.2,$^{[17]}$ estimated error = ± 0.5.

<table>
<thead>
<tr>
<th>Curium(III) species</th>
<th>Emission Wavelength / nm</th>
<th>Lifetime / μs</th>
<th>$N_{H2O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cm(O$_4$Cl)$_3$</td>
<td>601.2</td>
<td>128.85</td>
<td>8.5</td>
</tr>
<tr>
<td>Cm(TPIP)(O$_4$Cl)</td>
<td>603.4</td>
<td>251.84</td>
<td>3.9</td>
</tr>
<tr>
<td>Cm(TPIP)$_3$</td>
<td>609.2</td>
<td>309.86</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Studies of the same titration in a mixed solvent system gave a different result. Addition of NaTPIP to a curium perchlorate (1:1) MeOH:H$_2$O solution gave rise to the formation of three different peaks (Fig. 7.18). Time-resolved emission spectroscopy reveals a disproportionate decrease in intensity over time for the three peaks. Coupled with the calculation of three different emission lifetimes (Fig. 7.19, Table 7.6), the three bands are identified as different species rather than hot bands.
Fig. 7.18 Emission spectra depicting the formation of three different species upon addition of NaTPIP to curium(III) perchlorate in a 1:1 methanol-water mixture. Excitation wavelength = 396.6 nm.

Fig. 7.19 TRES of the three curium(III)-TPIP species present at the end of the titration with great excess of ligand (a 50.6 mM solution of NaTPIP) in MeOH 1:1 H₂O. Excitation wavelength = 396.6 nm.
Table 7.6 Summary of the emission lifetimes of the species present in the titration of NaTPIP to curium perchlorate in a 1:1 methanol-water solution. Estimated error on lifetime measurements +/- 10%.

<table>
<thead>
<tr>
<th>Curium(III) species</th>
<th>Wavelength / nm</th>
<th>Lifetime / μs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curium(III) perchlorate</td>
<td>593.8</td>
<td>72.2</td>
</tr>
<tr>
<td>Intermediate Complex</td>
<td>598.6</td>
<td>317.64</td>
</tr>
<tr>
<td>Final species I</td>
<td>609.6</td>
<td>304.08</td>
</tr>
<tr>
<td>Final species II</td>
<td>619.5</td>
<td>486.03</td>
</tr>
</tbody>
</table>

The lifetime data show an increase in emission lifetime for all three species with respect to the curium perchlorate solution. Concurrent formation of the final two species indicates that they are of similar stability, which may suggest the involvement of water and methanol in the final complexes on the luminescence timescale when compared to the single species found in the titration in methanolic solution. The initial highest energy peak probably belongs to a species similar to that of the intermediate peak found in the titration of NaTPIP to a methanolic solution of curium perchlorate outlined previously – Cm(TPIP)(O₄Cl)₂.

7.3.2 Curium(III) F⁻TPIP Titration

It was anticipated that the addition of NaF⁻TPIP to curium(III) perchlorate would result in chemistry similar to the NaTPIP titration, but with a longer emission lifetime due to the removal of all C-H oscillators in the ligand. The addition of NaF⁻TPIP to the curium(III) perchlorate solution followed a similar pathway to the corresponding NaTPIP titration – the formation of one final species red-shifted (602.3 nm) (53) with respect to the curium(III) perchlorate emission peak (601.2 nm) (Fig. 7.20). Time-resolved emission spectroscopy also reveals the formation of an intermediate species (54) en route to the final complex (Fig. 7.21, 7.22). In contrast to the NaTPIP titration, the red-shift of 53 is not as severe (1 nm vs. 8 nm), and 54 is found at lower energy to the final complex rather than higher (612.0 nm).

The wavelength of emission maxima between similar complexes is said to be dependent upon strength of coordination.⁴²⁰ Compared to Cm(TPIP)₃, F⁻TPIP appears to coordinate more weakly to Cm(III) in Cm(F⁻TPIP)₃, perhaps due to the electron-withdrawing nature of the fluorine atoms. 54 forms a more stable coordination complex than Cm(F⁻TPIP)₃ under the experimental conditions employed.
Fig. 7.20 Emission spectra of the curium perchlorate solution upon addition of Na\textsuperscript{v}TPIP (53) in MeOH 98:2 H\textsubscript{2}O. Excitation wavelength = 396.6 nm.

Fig. 7.21 TRES of the final Cm\textsuperscript{-v}TPIP species (53) found by titration of the Na\textsuperscript{v}TPIP ligand (a 1.12 mM solution of Na\textsuperscript{v}TPIP) into a Cm(III) perchlorate MeOH 98:2 H\textsubscript{2}O solution. Excitation wavelength = 396.6 nm.
Of note is the considerable increase in emission intensity upon titration of the Na^{4}TPIP ligand, representing an effective decrease in emission quenching from C-H oscillators. However, there is an unexpected smaller increase in emission lifetime of the intermediate (Fig. 7.21, Table 7.7) and final species with respect to the NaTPIP titration, perhaps suggesting an efficient emission deactivation pathway to the ligand at this wavelength. Such an effect was seen in the lanthanides for fluorinated TPIP for complexes that emit near 600 nm (Tb(III), Sm(III) and Eu(III)).\[6\] The calculated N_{H_{2}O} values of approximately 4 for both 53 and 54 in the titration also suggest that the F^{4}TPIP ligand binds more weakly to Cm(III) ions than its hydrogenated TPIP counterpart (where N_{H_{2}O} of the final species is ca. 3). This forms less of a hydrophobic shell around the Cm(III) ions, comparatively encouraging the close approach of donor solvent molecules to the inner coordination sphere of the metal ion (in this case water and/or methanol).

Table 7.7 Summary of the emission lifetimes found for the addition of NaTPIP to curium perchlorate. All fitted to a mono-exponential lifetime in MeOH 98:2 H_{2}O. N_{H_{2}O} values calculated using Equation 6.2,\[17\] estimated error = ± 0.5.

<table>
<thead>
<tr>
<th>Curium(III) species</th>
<th>Wavelength / nm</th>
<th>Lifetime / μs</th>
<th>N_{H_{2}O}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cm(O_{3}Cl)_{3}</td>
<td>601.2</td>
<td>128.85</td>
<td>8.5</td>
</tr>
<tr>
<td>Intermediate species</td>
<td>612.0</td>
<td>258.86</td>
<td>3.8</td>
</tr>
<tr>
<td>Cm(F^{4}TPIP)_{3}</td>
<td>602.3</td>
<td>256.44</td>
<td>3.8</td>
</tr>
</tbody>
</table>
7.4 Conclusions
Multinuclear NMR and TRLFS investigations have been used to study Am(III) and Cm(III) TPIP chemistry respectively. In both cases, a 3:1 ligand to metal complex is determined, similar to corresponding lanthanide chemistry. However, an intermediate structure has been discovered in the formation of the final complexes for both actinides(III) and lanthanides(III), thought to contain one TPIP ligand. In DMSO, this complex is readily observed even upon addition of three equivalents of ligand, presenting competition from the solvent. Curium(III) emission studies also exhibit a solvent-competitive complexation with the TPIP ligands.

Additionally, TRLFS studies suggest a weaker interaction between the curium(III) ion and the perfluorinated ligand vs. the TPIP and a shorter radiative lifetime, concurrent with observations of LnF\textsubscript{3}TPIP\textsubscript{3} complexes.[6]

7.5 References
[8] The Shannon 6 coordinate ionic radii for Am\textsuperscript{3+} = 0.975 Å, Cm\textsuperscript{3+} = 0.97 Å, Nd\textsuperscript{3+} = 0.983 Å, Sm\textsuperscript{3+} = 0.958 Å and Eu\textsuperscript{3+} = 0.947 Å. R.D. Shannon, Acta Crystallogr. A, 1976, 32, 751-767.
Chapter 8

Complexations of TPIP to Neptunyl(V/VI)
8.1 Introduction
Similar to the $f^1$ configuration of uranyl(V), the $f^1$ configuration of neptunyl(VI) confers instability of this ion. It is generally unstable in aqueous solution[1] and prepared neptunyl(VI) samples have to be used almost immediately.[2] Studies of neptunyl(VI) in non-aqueous solvents are less common, mainly due to the industrial focus of aqueous hydrolysis and environmental chemistry. The reasons for the instability of the +VI oxidation state are unclear.

The neptunyl(VI) chloride salt, [NpO$_2$Cl$_2$(THF)]$_n$, prepared by oxidation of a perchloric acid solution of neptunyl,[3] represents a relatively stable neptunyl(VI) salt that can be used as a starting reagent for neptunyl(VI) complex syntheses.[3] Nevertheless, it undergoes partial reduction upon standing in THF for several days to produce a mixed neptunyl(V)-neptunyl(VI) salt (Section 1.7.2).[3] Dissolution of the chloride salt in MeOH immediately results in the formation of neptunyl(V) (Fig. 8.01) due to the reducing nature of the alcohol solvent employed.[4,5]

![UV/vis-NIR absorption spectrum of NpO$_2$Cl$_2$.xH$_2$O in MeOH between 450 and 1300 nm. Taken from references [4] and [5].](image)

It is perhaps surprising, therefore, that the addition of the neutral ligand bis(diphenylphosphino)-methanedioxide (DPPMO) to [NpO$_2$Cl$_2$(THF)]$_n$ in MeOH results in the isolation of a neptunyl crystalline solid, assigned in the +VI oxidation
state by charge-balancing of the X-ray crystal structure.\textsuperscript{[4,5]} The absorption spectrum of the bulk product reveals the presence of neptunium in oxidation states between (IV) and (VI), but this is proposed to be as a result of partial reduction of the neptunyl(VI) chloride salt in MeOH prior to complexation (Fig. 8.01), with resulting coordination to DPPMO stabilising the complex against further reduction.\textsuperscript{[4,5]} The X-ray crystal structure indicates that two [Np\textsuperscript{VI}O\textsubscript{2}(DPPMO\textsubscript{2})\textsubscript{2}Cl\textsubscript{2}] cations are charge balanced by a NpO\textsubscript{2}\textsuperscript{VI}Cl\textsubscript{4} anion.\textsuperscript{[4,5]} Reaction of Ph\textsubscript{3}PNH with the neptunyl(VI) chloride salt results in the formation of [Ph\textsubscript{3}PNH\textsubscript{2}]\textsubscript{2}[NpO\textsubscript{2}Cl\textsubscript{4}] in THF with no suggestion of neptunyl(V) in solution (Fig. 8.02) and the role of [NpO\textsubscript{2}Cl\textsubscript{4}] in stabilising the +VI oxidation state of the neptunyl complex is hypothesised.\textsuperscript{[5]} Reaction of neptunyl(VI) chloride with Ph\textsubscript{3}PO and the [N(CN)\textsubscript{2}]\textsuperscript{-} anion, although uncharacterised, gave neptunyl(V) or neptunyl(VI) compounds by absorption spectrophotometry depending on the choice of solvent; reaction in MeOH gave neptunyl(V) and reaction in THF leading to neptunyl(VI).\textsuperscript{[4]} Therefore, it seems likely that the choice of solvent is crucial in stabilising neptunyl(VI), with non-reducing or aprotic organic solvents seemingly quite useful.\textsuperscript{[4]}

![Fig. 8.02 ORTEP representation of [Ph\textsubscript{3}PNH\textsubscript{2}]\textsubscript{2}[NpO\textsubscript{2}Cl\textsubscript{4}]. Taken from reference [5.]](https://example.com/fig802.png)

Organic solvents do not universally stabilise the +VI oxidation state of neptunium. Reaction of [NpO\textsubscript{2}Cl\textsubscript{2}(THF)]\textsubscript{n} with sterically bulky Schiff-base ligands in THF leads to complete reduction to neptunyl(V) in each case.\textsuperscript{[6]} Dissolution of the solids in pyridine does not alter the oxidation state, neither does contact with diethyl ether.\textsuperscript{[6]} Whilst the multidentate ligands preferentially stabilise neptunyl(V) over (VI),\textsuperscript{[6]} the less sterically bulky Schiff-base ligand salen is able to oxidise neptunyl(V) in MeOH solution.\textsuperscript{[7]}
Therefore, whilst organic solvents are able to stabilise neptunyl(VI) and MeOH favours neptunyl(V), it is clear the choice of ligand and resulting neptunyl coordination environment is the most important factor in determining the stability of the neptunyl cation in a trend that is not yet determined.

8.2 Neptunyl(V/VI) Complexation Studies

The majority of work described in this chapter was performed at the KIT-INE, Karlsruhe as part of the EURACT-NMR programme. The use of neptunium was inhibited by time and radiological constraints.

8.2.1 Neptunyl(VI) TPIP (tetraphenylimidodiphosphinate) solid state structures

Reaction of neptunyl(VI) perchlorate\(^{[3]}\) with two equivalents of NaTPIP followed the same reaction scheme used for uranyl(VI) TPIP complexation (Scheme 8.1).

$$\begin{align*}
\text{Np}^{IV}/\text{NpO}_2^{V/VI} & \xrightarrow{70\%\ \text{HClO}_4} \text{NpO}_2^{VI}(\text{ClO}_4)_2 \quad \text{2 NaTPIP} \\
& \quad \xrightarrow{\text{H}_2\text{O}} "\text{NpO}_2^{VI}(\text{TPIP})_2" \end{align*}$$

Scheme 8.1 The formation of neptunyl(VI) and subsequent reaction with NaTPIP.

Dissolution in water and subsequent filtering left a solid that could be crystallised into different structures using different solvents. Dissolution in DCM and immediate layering with hexane resulted in the formation of single crystals of [NpO\(_2\)(TPIP)\(_2\)(HTPIP)].1/2C\(_6\)H\(_{14}\) (55, Fig. 8.03).
The O=Np=O bond angle is 179.35(13) ° and the Np=O bond lengths are 1.745(2) and 1.758(2) Å. The bond lengths are shorter than almost all of the monomeric uranyl(VI) TPIP bond lengths presented in Section 2.3.1 (statistically indifferent to the [UO$_2$(TPIP)$_2$H$_2$O] shortest U=O bond of 1.761(4) Å). This decrease is expected due to the actinide contraction (see Section 1.7). The structure presents a regular pentagonal bipyramidal geometry with two bidentate TPIP ligands in the equatorial plane. The analogous uranyl(VI) reaction (Section 2.3) yields a trimeric complex with CCl$_3$s, however 55 appears to prefer an uncharged monodentately-bound HTPIP ligand. Presumably, the extra electron on neptunyl(VI) (vs. uranyl(VI)) and slightly shorter neptunyl(VI) Np=O bonds are enough to dissuade the formation of CCl$_3$s. The Np-O$_{_{TPIP}}$ bond length to HTPIP is 2.416(2) Å, longer than three of the Np-O$_{_{TPIP}}$ bonds to the charged ligands (2.314(3) to 2.362(2) Å) yet shorter than one. At 2.442(2) Å, the longest Np-O$_{_{TPIP}}$ bond represents the coordination to the oxygen that is suggested to be hydrogen bound to the imido proton (Fig. 8.03). The shorter lengths of the remaining Np-O$_{_{TPIP}}$ bonds represent the stronger coordination of the charged bidentate TPIP ligands compared to the monodentate HTPIP. The H-O bond length of 2.036 Å is in range for reported (NH)-O bonds.$^8$ It is likely that trace residual acid remaining from the synthetic procedure is the proton source in this reaction.
Reaction of NaTPIP with uranyl(VI) nitrate and crystallisation from benzene produced a trimeric complex (Chapter 2). However, the same reaction with neptunyl(VI) perchlorate resulted in the formation of the complex [NpO$_2$(TPIP)$_2$(HTPIP)].C$_6$H$_6$ (56, Fig. 8.04), which possesses the same connectivity seen in Fig. 8.03 but with a benzene solvent molecule of crystallisation in the asymmetric unit cell. The seeming preference of neptunyl(VI) for the monodentate TPIP ligand is unexpected, the closest structure in uranyl(VI) chemistry is that of {Na[UO$_2$(TPIP)$_2$](μ$_2$-TPIP)}.C$_6$H$_5$CH$_3$ (Section 2.8), where a monodentate TPIP ligand completes the equatorial coordination of uranyl. It is unprotonated and links two uranyl moieties, something not yet seen with neptunium.

![Fig. 8.04 X-ray crystal structure of [NpO$_2$(TPIP)$_2$(HTPIP)].C$_6$H$_6$ (56). Solvent molecules and hydrogen atoms removed for clarity. Thermal ellipsoids set at the 50 % probability level.](image)

The Np=O bond lengths of 1.760(5) and 1.743(4) Å are within error for those seen in 55, although the bond angle of 177.8(3) ° is marginally less linear. Whilst the longest Np-O$_{TPIP}$ bond is to the oxygen orientated closest to the HTPIP nitrogen, it is not certain from the data if the imide is protonated. A hypothetical (NH)-O bond distance of 2.269 Å, whilst > 0.2 Å longer than seen in the hexane solvate, is still within the region of (NH)-O bonds.$^8$
Dissolution in DCM and allowing the sample to stand overnight before layering with hexane resulted in the formation of [NpO₂(TPIP)₂]₂ (57, Fig. 8.05). The crystallographic data is not of good enough quality to determine the position of solvent molecules in the crystal lattice and accurately compare bond lengths and angles, but confirms the analogous connectivity to [UO₂(TPIP)₂]₂ and the +VI oxidation state of the neptunyl ions.

Fig. 8.05 X-ray crystal structure of [NpO₂(TPIP)₂]₂ (57). Represented as a ball and stick diagram. Hydrogen atoms omitted for clarity.

The change in space group (P-1) represents a slight change in geometry for the complex in the solid state (compared to uranyl(VI), C₂ᵥ), with a plane of symmetry through the centre of the two bridging ligands. The two neptunyl(VI) cations are four coordinate in a distorted octahedral geometry with two bridging ligands complementing a capping ligand on each neptunyl(VI) ion.

8.2.2 Neptunyl(VI) TPIP solution chemistry

The absorption spectrum of 56 in benzene exhibits a typical neptunyl(VI) f-f transition at 1215 nm, although weak due to a low quantity of sample. Dissolution of 55 in DCM likely results in the formation of 57, with both giving the same UV/vis-NIR spectrum displaying a principal absorption at 1235 nm. Although of slightly lower energy than 56, the use of different solvents negates comparison. Both spectra display a complete lack of absorption in the 980 nm region for neptunyl(V), even though small fractions are present in the neptunyl(VI) reagent before heating.[4,6] Both display a rising tail in the UV/vis region near the 450 nm region, indicative of
neptunyl(VI) Np=O LMCT bands, which are of much greater intensity and discussed later in this chapter.

Immediate dissolution of neptunyl(VI) perchlorate and two equivalents of NaTPIP in d$_2$-DCM resulted in a $^1$H NMR spectrum (Fig. 8.06) with multiple overlapping resonances in the aromatic region. There is no evidence of resonances at chemical shifts expected for paramagnetic species, however comparison with the lanthanide chemistry of TPIP reveals proton resonances at organic aromatic frequencies for every lanthanide complex.$^{[9-11]}$ It is possible that the protons may be too far from the metal centre to fully experience the effects of paramagnetism. The $^{31}$P NMR spectrum depicts three resonances: one at 23.0 ppm, reminiscent of uncomplexed ligand and two at lower frequency that are considerably broader. The $^{31}$P NMR spectrum suggests that both complexed and uncomplexed TPIP is present in solution, possibility indicating a loss of the HTPIP ligand to form 57 (as seen by crystallisation of the dimeric structure from DCM).

![Fig. 8.06 Left $^1$H NMR spectrum and right $^{31}$P-$[^1$H] NMR spectrum of above [NpO$_2$(TPIP)$_2$]$_2$ (57) and below HTPIP, both recorded in d$_2$-DCM at room temperature.](image)

Proton DOSY-NMR spectroscopy of 57 reveals several diffusion coefficients for the aromatic resonances (Fig. 8.07). Whilst not immediately informative, it does confirm a multiple number of species in solution, suggesting the TPIP ligand is labile in solution. In addition, the fastest diffusion coefficient above 8 ppm (11.00 (+/- 0.50) x $10^{10}$ m$^2$s$^{-1}$) is within error of HTPIP in d$_2$-DCM solution; 10.80 (0.25) x $10^{10}$ m$^2$s$^{-1}$. The slowest diffusion coefficient is approximately 4.90 (+/- 0.30) x $10^{10}$ m$^2$s$^{-1}$, for the
isolated resonance at 6.86 ppm. Use of Equation 1.8 suggests the larger species in the neptunyl(VI) TPIP solution has a molecular mass of 4465 gmol\(^{-1}\) (10.70 x HTPIP), with 2202 gmol\(^{-1}\) required for \([\text{NpO}_2\text{TPIP}]_2\), 5.13 x the size of HTPIP. This implies the fast chemical exchange of the TPIP ligand in solution (presumably the protonated HTPIP ligand) on the NMR timescale with the concurrent formation of at least one aggregated neptunyl(VI) TPIP species in DCM solution, potentially with the formula \([\text{NpO}_2\text{TPIP}]_2\) \((M_r = 4404 \text{ gmol}^{-1})\). However, large deviations from spherical solvates due to chemical exchange will increase the error of the diffusion coefficients measured, alongside decreased \(T_1\) relaxation times arising from the \(f^4\) electronic configuration of the neptunyl(VI) ion.

Fig. 8.07 The \(^1\text{H}\) DOSY-NMR spectrum of the aromatic resonances of \([\text{NpO}_2\text{TPIP}]_2\) \((57)\). Recorded in d\(_2\)-DCM at 295 K.

The \(^1\text{H}\) NMR spectrum of 56 in C\(_6\)D\(_6\) benzene also displays a multitude of aromatic resonances obscured by the residual benzene signal and three phosphorus resonances similar to that seen in Fig. 8.07. Measurement of the \(^1\text{H}\) diffusion coefficients (Appendix 1) exhibits a mixture of species in solution. With overlap near the residual benzene signal, it is difficult to ascertain if there is a resonance due to HTPIP; faster diffusion coefficients may be an average with the solvent peak. The mixture of resonances observed in the \(^1\text{H}\) NMR spectrum, alongside the \(^{31}\text{P}\) NMR spectrum, infer that the TPIP ligand is labile in benzene solution.

8.2.3 \([\text{Np}^{VI}\text{O}_2\text{TPIP}]_2\text{Ph}_3\text{PO}]\) and unusual oxidation state preference

Treatment of neptunyl(V) chloride with two equivalents of NaTPIP and one of Ph\(_3\)PO in CDCl\(_3\) 8:1 d\(_4\)-MeOD in an NMR tube and standing for three months resulted in the
formation of a white salt (presumably sodium perchlorate) and single crystals of the complex [NpO₂(TPIP)₂Ph₃PO] (58, Fig. 8.08).

Fig. 8.08 X-ray crystal structure of [NpO₂(TPIP)₂Ph₃PO] (58). Hydrogen atoms removed for clarity. Thermal ellipsoids set at the 50 % probability level.

Charge balancing suggests a +VI oxidation state for the neptunium cation. The neptunyl(VI) bond lengths of 1.7502(17) and 1.7466(17) Å (bond angle 179.21(8) °) are in the range for previously seen neptunyl(VI) complexes, directly comparable to those in [UO₂(TPIP)₂Ph₃PO] at 1.766(3) and 1.768(3) Å, with the decrease in bond length of between 0.015 and 0.020 Å due to the actinide contraction. The Np-Oₜₐₚ bonds are between 2.3517(16) and 2.3569(16) Å, shorter than the Np-Oₚ₃PO bond length of 2.4081(15) Å. Whilst this indicates a stronger bond to the TPIP ligands, this is in contrast to [UO₂(TPIP)₂Ph₃PO], where all the equatorial bond lengths range between 2.373(3) and 2.401(3) Å and coordination to Ph₃PO is as strong as TPIP, as suggested by the X-ray diffraction data (Section 2.3.1).

UV/vis-nIR spectroscopy confirms the +VI oxidation state with no evidence of neptunyl(V) near 980 nm. The complete oxidation of neptunyl(V) is surprising, with the combination of TPIP and Ph₃PO appearing to prefer the +VI oxidation state of neptunium in this solvent system. Repetition of the reaction in a 1:1 mixture of d₄-MeOD:CDCl₃ resulted in the same complete oxidation to neptunyl(VI) over the same time frame. However, complete dissolution of solid 58 in pure MeOH resulted in
almost complete reduction to the +V oxidation state (Fig. 8.09). The presence of two overlapping peaks at 977 and 987 nm suggest two neptunyl(V) species in solution. Additionally, the maxima at 619 nm suggests the presence of neptunium (IV) (Section 1.81) and there is still evidence of neptunyl(VI) at 1232 nm. Therefore, MeOH does not fully reduce [NpO$_2$(TPIP)$_2$Ph$_3$PO] to the corresponding +V oxidation state. Reaction of a neptunyl(V) chloride sample with NaTPIP in DCM followed the oxidation presented by the reaction with NaTPIP and Ph$_3$PO, so it is the TPIP ligand which is key in the oxidation state stability of neptunyl(VI). Dissolution of the same sample in MeOH returned neptunyl to the +V oxidation state.

This is in contrast to the reactions of Schiff-base ligands in THF.$^{[6]}$ Potentially, the presence of N-donors in the Schiff base ligands means they favour the +V oxidation state, similar to the preference of uranyl(V) for N-donors (Section 1.6). Therefore the use of only oxygen σ-donors in the TPIP ligand may stabilise the +VI oxidation state.

Fig. 8.09 UV/vis-NIR spectrum of [NpO$_2$(TPIP)$_2$Ph$_3$PO] in MeOH between 450 and 1350 nm.

$^1$H NMR spectroscopy displays a series of sharp resonances (Fig. 8.10) amongst broader peaks of lower intensity. The $^{31}$P NMR spectrum is initially misleading, with one sharp resonance at -36.6 accompanied by broad peaks at higher frequency that almost disappear into the baseline. The negative resonance in 57 is centred at -30.0 ppm, and it is likely that these downfield resonances are attributed to coordinated
TPIP ligands. $^1$H DOSY-NMR spectroscopy reveals the broader proton resonances to belong to a smaller, fast diffusing species whilst the sharper resonances to a larger complex (Fig. 8.11). The diffusion coefficient of the larger species is 6.70 ($\pm$ 0.20) x$10^{10}$ m$^2$s$^{-1}$. Use of Equation 1.8 and comparison with 57 suggests a molecular mass of 1747 gmol$^{-1}$ for the larger complex, closest in mass to a hypothetical Np$_2$O$_4$(TPIP)$_3$ species. The comparatively broad resonances of the faster diffusing species are less isolated and thus harder to identify. However, the diffusion coefficient of labile HTPIP in Section 2.2.2 at 11.00 x $10^{10}$ m$^2$s$^{-1}$ is slower than the fast diffusing species in 58 (up to 14.00 x$10^{10}$ m$^2$s$^{-1}$), further implicating the lability of Ph$_3$PO (and not TPIP in this scenario).

Fig. 8.10 Left $^1$H NMR spectrum and right $^{31}$P-($^1$H) NMR spectrum of [NpO$_2$(TPIP)$_2$Ph$_3$PO] (58). Recorded in d$_2$-DCM at 295 K.

Fig. 8.11 The $^1$H DOSY-NMR spectrum of the aromatic resonances of [NpO$_2$(TPIP)$_2$Ph$_3$PO] (58). Recorded in d$_2$-DCM at 295 K.
Comparison of the $^{31}$P NMR spectra of 57, 58 and Ph$_3$PO in CDCl$_3$ is more insightful than in d$_2$-DCM (Fig. 8.12), allowing assignment of the three observed resonances; uncomplexed Ph$_3$PO at 29.2 ppm and neptunyl(VI) TPIP resonances at 20.6 and -28.5 ppm. The $^{31}$P NMR spectra therefore support the findings of the $^1$H DOSY NMR experiment.

![Fig. 8.12 $^{31}$P-$^1$H NMR spectrum of Ph$_3$PO, [NpO$_2$(TPIP)$_2$]$_2$ (57) and [NpO$_2$(TPIP)$_2$Ph$_3$PO] (58). All recorded in CDCl$_3$ at 300 K.]

**8.2.4 Oxidation state stability**

As already shown, 58 can be synthesised from a neptunyl(V) salt in solvents that contain CDCl$_3$ or DCM (Fig. 8.08). However, the use of pure MeOH reduced the neptunyl(VI) complex to neptunyl(V) (Fig. 8.09). This reduction began immediately with the addition of one equivalent of MeOH to a DCM sample of 58; neptunium in both the +V and +VI states can be observed. No change in the absorption spectrum occurs over the course of several days, thus there is not expected to be any major kinetic contribution to the reduction. Whilst complete dissolution in 100 % methanol reduced almost all of the neptunyl(VI), the partial reduction in the presence of a significant molar volume of MeOH (> 20 %) suggests that the initial formation of the +VI oxidation state from neptunyl(V) takes place upon crystallisation in the presence of chlorinated solvent. The neptunyl(V) peak at 988 nm is similar to one of the
maxima observed in Fig. 8.09 (at 987 nm) and is likely to be the same neptunyl(V) species.

Whilst the addition of MeOH resulted in reduction of 58 to a neptunyl(V) species, allowing the solution to stand in 100 % halogenated solvent leaves the complex stable in the +VI oxidation state for an indefinite amount of time (> 9 months at the time of writing by absorption spectroscopy). The same analysis of 57 in DCM over time reveals discrimination between the two complexes (Fig. 8.13). Over the course of three months, the sample showed the appearance of absorption maxima assigned to the +IV and +V (Fig. 8.13) oxidation states of neptunium. Dissolution of the dried sample in benzene revealed no re-oxidation to neptunyl(VI) over time (Fig. 8.13), although no further reduction occurs either. Additionally, layering of the benzene sample with hexane yielded crystals of Np(TPIP)$_4$ (59), confirming the formation of a neptunium TPIP complex in the +IV oxidation state (Fig. 8.14).

59 crystallises with 1.5 benzene solvent molecules in the crystal lattice. The eight co-ordinate metal centre possesses a distorted square anti-prismatic coordination geometry that closely resembles U(TPIP)$_4$ and Th(TPIP)$_4$.[13] Such is the structural resemblance between the three that unit cell parameters are all within 0.2 Å and 0.4 ° of one another.[13] The average Np-O$_{TPIP}$ bond length is 2.355(19) Å (range 2.26(2) – 2.441(15) Å), shorter than the analogous uranium (2.37(3) Å) and thorium (2.41(3) Å) complexes[13] and consistent with the actinide contraction.
Fig. 8.14 X-ray crystal structure of Np(TPIP)$_4$ (59). Hydrogen atoms and solvent molecules removed for clarity. Thermal ellipsoids set at the 50 % probability level.

Reduction of neptunyl(VI) to neptunium(IV) has been observed in the literature for neptunyl(VI) phosphonate chemistry,[14] where reduction of neptunyl(VI) to neptunyl(V) is followed by disproportionation to neptunyl(VI) and neptunium(IV), driven by the precipitation of neptunium(IV).[14] In the above reaction, the solubility of Np(TPIP)$_4$ prevents the reaction going to completion, allowing a mixture of oxidation states to exist in solution. The disproportionation of neptunyl(V) in organic solvents is documented,[15] and suggests a viable pathway for the formation of Np(IV) from neptunyl(V) in this system, presumably by neptunyl(V) CCIs.

The difference in stability between 57 and 58 in solution is subtle, although the solution existence of each is not thought to be related to the solid state structure of each as determined by single crystal X-ray diffraction (Sections 8.2.2 and 8.2.3). Further knowledge of the solution structures of each sample is essential in attempting to understand the origin of the difference in oxidation state stability.

8.2.5 Neptunyl(V) TPIP reactions

Reaction of neptunyl(V) salts with NaTPIP in the presence of halogenated solvents resulted in oxidation to neptunyl(VI), therefore reaction in methanol (Scheme 8.2) is essential to stabilise the +V oxidation state. Due to this, direct comparisons with the neptunyl(VI) derivatives is not be possible.
Scheme 8.2 The reaction of neptunyl(V) with NaTPIP.

\[
\text{NpO}_2^\text{V} \text{(Cl)} + 2 \text{NaTPIP} \xrightarrow{\text{MeOH}} \text{"NpO}_2^\text{V}(\text{TPIP})_2\text{"}
\]

Uranyl(VI) TPIP chemistry (Chapter 2) typically presents a coordination stoichiometry of two ligands to one uranium metal, even when one equivalent of ligand is used in the reaction. With the lower positive charge of neptunyl(V), it may be possible to manufacture a 1:1 ligand to metal complex. Addition of one equivalent of NaTPIP to neptunyl(V) in methanol gave crystals of \([\text{Na(TPIP)(HTPIP)}_2].\text{Et}_2\text{O}\) (60) by layering (Fig. 8.15), suggesting a lack of complexation of the ligand. 60 crystallises with a diethyl ether solvent molecule in the crystal lattice. The crystal structure would be charge unbalanced without protonation of two of the ligands, which are identifiable on two specific TPIP ligands on the difference Fourier map with refinement. The \(^1\text{H}\) and \(^{31}\text{P}\) NMR spectra of NaTPIP and 60 confirm their different solution speciation.

Fig. 8.15 X-ray crystal structure of \([\text{Na(TPIP)}_3].\text{Et}_2\text{O}\) (60). Solvent molecules and hydrogen atoms (bar the imido protons) omitted for clarity.

Reaction of two equivalents of NaTPIP with neptunyl(V) chloride in methanol results in a product (61) which did not produce satisfactory single crystals. NMR spectroscopy instead confirms the presence of a neptunyl(V) TPIP complex (Fig. 8.16). Although the proton resonances are broad and overlap, \(^{31}\text{P}\) NMR spectroscopy
confirms the absence of NaTPIP (and 60). The two resonances found at -21.6 and -161.9 ppm are broad and representative of a strong paramagnetic interaction between neptunyl(V) (2 unpaired $f$ electrons) and phosphorus, with many scans required to see the resonances. Over time, the formation of uncomplexed TPIP ligand is suggested by $^{31}$P NMR spectroscopy, indicating a weaker bond between neptunyl(V) and TPIP compared to neptunyl(VI) (Fig. 8.17). This is perhaps unsurprising given that the PUREX process relies on the preference of a phosphine oxide ligand (TBP, tri-$n$-butyl-phosphate) for early actinides in the +VI (and +IV) oxidation state over +V, with neptunyl(V) not readily complexed by TBP in organic solvents.$^{[3]}$

![Fig. 8.16](image1.png)

**Fig. 8.16** Left $^1$H NMR spectrum and right $^{31}$P-$^1$H NMR spectrum of neptunyl(V) TPIP (61). Recorded in d$_4$-MeOD at 300 K.

![Fig. 8.17](image2.png)

**Fig. 8.17** $^{31}$P-$^1$H NMR spectrum of neptunyl(V) TPIP (61) after one week. Recorded in d$_4$-MeOD at 270 K.
Reaction of neptunyl(V) chloride with two equivalents of NaTPIP and one of Ph₃PO (62) led to the formation of single crystals when layered with diethyl ether (approx. 1:1 ratio). [NpO₂(TPIP)₂Ph₃PO].Et₂O crystallises with a non-coordinative diethyl ether solvent molecule in the crystal lattice. The molecular structure is similar to that of 58 and no sodium atoms can be found in the crystal lattice. This strongly suggests that the neptunyl(V) sample has oxidised to neptunyl(VI) in the presence of the organic solvent diethyl ether. Single crystals could not be grown from a pure methanol sample.

Analysis of the sample in solution by ¹H NMR spectroscopy shows an increase in resolution of resonances compared to the neptunyl(V) TPIP sample (Fig. 8.16), however they are still broad. ³¹P NMR spectroscopy reveals only a single resonance at 32.4 ppm (Fig. 8.18), suggestive of uncoordinated Ph₃PO (32.6 ppm). This may be anticipated due to the poorer affinity of neptunyl(V) for phosphine-oxide ligands (vs. uranyl(VI)).[^3] The remaining phosphorus resonances are again so broad as to be virtually indistinguishable from the baseline at all measurable temperatures.

Absorption spectroscopy in methanol confirms the +V oxidation state of both neptunyl(V) TPIP samples (61 and 62). The spectra of both are similar, with an indication of minor quantities of neptunyl(VI) at 1235 nm. 61 displays a more resolved shoulder at 987 nm, with both samples appearing to consist of two neptunyl(V) species (Fig. 8.19), possibly representing a labile coordination of the ligands. The absorption spectrum of the reaction of neptunyl(V) chloride with one equivalent of NaTPIP is also displayed, showing a prominent peak at 980 nm.

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[^3]: Additional notes or references.
Clearly, neptunyl(V) is stable in MeOH without the TPIP ligands, and the lower energy maxima exhibited by the two complexes indicates the presence of a neptunyl(V) TPIP (Ph₃PO) complex.

Fig. 8.19 UV/vis-NIR spectra of \(\text{(NpO}_2\text{)}^+\), neptunyl(V) TPIP (61) and neptunyl(V) TPIP Ph₃PO (62) in methanol between 800 and 1350 nm.

Comparison between 62 and HTPIP by \(^1\)H DOSY-NMR spectroscopy is not insightful (Fig. 8.20); the wide range of diffusion coefficients displayed by HTPIP (9.00 – 7.25 (+/- 0.10) x 10¹⁰ m²s⁻¹) suggests an extent of aggregation in methanol, with it likely that HTPIP molecules are hydrogen-bonding to one another.[5] The \(^1\)H DOSY spectrum of 62 does provide useful data however, with the presentation of one diffusion coefficient in solution (7.60 (+/- 0.20) x 10¹⁰ m²s⁻¹) suggesting a single complex in solution. The presence of labile ligands would result in separate diffusion coefficients for Ph₃PO and a neptunyl(V) TPIP complex. Whilst this is in contrast to the \(^{31}\)P NMR spectrum (Fig. 8.18), it suggests an exchange mechanism for Ph₃PO where the ligand is in fast exchange between the coordinated and uncoordinated forms, with the slight difference in timescales between \(^1\)H and \(^{31}\)P NMR spectroscopy the reason for the averaged species in the proton NMR spectrum. The lack of spread of diffusion coefficients discourages an argument for averaging of diffusion coefficients. The Stokes-Einstein Equation, Equation 1.7[16] gives sample 62 a hydrated spherical radius of 4.79 (+/- 0.27) Å. The values of 1.3806503 x 10⁻²³ m²kgs⁻²K⁻¹ and 0.593 x 10⁻³ mNsm⁻³ are used for \(k_B\) and \(\eta\) respectively.[17,18]
It was not possible to record a $^1$H DOSY-NMR spectrum for 61 at room temperature due to line broadening. However, comparison of the $^1$H diffusion coefficients between 61 and 62 at 265 K reveals a larger complex when Ph$_3$PO is not present (Fig. 8.21). The diffusion coefficient of $5.95 \pm 0.15 \times 10^{10}$ m$^2$s$^{-1}$ gives a complex 1.7 times the molecular mass of 62 ($D = 7.10 \pm 0.10 \times 10^{10}$ m$^2$s$^{-1}$) using Equation 1.7. With a monomeric NpO$_2$(TPIP)$_2$(Ph$_3$PO) complex being 1.6 times smaller than a dimeric [NpO$_2$(TPIP)$_2$]$_2$ motif, it is possible that 61 exists as ligand bridged dimer in a similar fashion to the solid state neptunyl(VI) TPIP complex. In the absence of structural or additional spectroscopic data it is unclear if CCIs help to assemble the dimeric structure, as may be anticipated for neptunyl(V). Equation 1.8 presents hydrated spherical radii of $3.55 \pm 0.20$ Å for 61 and $2.97 \pm 0.16$ Å for 62. The value of $0.920 \times 10^{-3}$ mNsm$^{-3}$ is used for $\eta$.\[18\]

8.2.6 $T_1$ Relaxation times of paramagnetic neptunyl(V/VI) TPIP samples

The effect of paramagnetism on the protons of TPIP is thought to be minimal, resulting in similar frequencies for the aromatic resonances in the $^1$H NMR spectrum (Section 8.2.2). However, the increased line broadening of the proton resonances in the neptunyl(V) TPIP samples (Fig. 8.18) vs. neptunyl(VI) TPIP (Fig. 8.06) indicates there may be an increased effect of paramagnetism in the neptunyl(V) sample, in
addition to chemical exchange processes on or near the experimental timescale. Such an effect would noticeably decrease the $T_1$ relaxation times of the protons (Section 1.10) and provide an insight into assigning the oxidation state of the neptunyl cation in solution. The $T_1$ relaxation times for neptunyl(V) TPIP samples are displayed in Table 8.1. Resonances in uncomplexed Ph$_3$PO (at 300 K) give relaxation times of 4.279 s ($2 \times 10^{-3}$), 4.389 s ($1 \times 10^{-3}$) and 3.701 s ($1 \times 10^{-3}$) respectively (residual water signal = 8.661 s ($1.5 \times 10^{-2}$) and residual methanol = 7.947 s ($1 \times 10^{-3}$)). Despite the temperature difference, the timescale of the relaxation is significantly different and confirms paramagnetic contribution to spin-lattice relaxation of the ligand protons in solution with neptunium. The $T_1$ relaxation times of the methanol and water resonances are also displayed for comparison and confirm interaction of the solvents with neptunium.

Table 8.1 $T_1$ relaxation times of the proton signals of the left neptunyl(V) TPIP (61) at 260 K and right neptunyl(V) TPIP Ph$_3$PO (62) at 270 K. Recorded in d$_4$-MeOD. The errors of the relaxation times are taken from the standard deviation of each $T_1$ plot and are quoted in brackets after the respective value.

![Image](image_url)

Whilst not measured in the same solvent to preserve the oxidation state of the neptunyl(VI), the $T_1$ relaxation times of 58 in CDCl$_3$ (Fig. 8.22) are on a different timescale to those reported for 61 and 62 (s. vs. ms. respectively), clearly highlighting a significantly reduced paramagnetic interaction between neptunyl(VI) and the TPIP protons compared to neptunyl(V), therefore relaxation times can be used to differentiate between the +V and +VI oxidation states of neptunyl. No spin-lattice relaxation times could be recorded 57 due to the significant overlap of resonances in CDCl$_3$ (Fig. 8.22).
Table 8.2  Left $^1$H NMR spectrum of [NpO$_2$(TPIP)$_2$]$_2$ (57) and right $T_1$ relaxation times of the proton resonances of [NpO$_2$(TPIP)$_2$Ph$_3$PO] (58). Recorded in CDCl$_3$ at 300 K. The errors of the relaxation times are taken from the standard deviation of each $T_1$ plot and are quoted in brackets after the respective value.

8.2.7 Neptunyl(VI) emission spectroscopy
As described in Section 1.8, reports on the emissive properties of neptunyl (both +V and +VI) are rare, particularly in solution. The possibility of analogous LMCT emission to that of uranyl(VI) for neptunyl(VI) remains unexplored. The $\pi$-$\pi^*$ transitions of the phenylic chromophores on TPIP should not significantly overlap with the LMCT excited state of either neptunyl(V) or (VI), providing an opportunity to investigate their emissive properties.

No emission spectra for 62 in methanol or $d_4$-MeOH were observable. Variation of the concentration between 5 mM to 500 $\mu$M and excitation wavelengths used to mirror that of the only previous neptunyl(V) solution emission report (at 393 nm) offered no evidence of emission for 62.$^{[19]}$ In addition, attempts to excite the sample at any wavelength relating to its absorption spectrum (Fig. 8.22) including the entire LMCT region (200-400 nm) were unsuccessful. Excitation at 980 nm did not lead to nIR emission due to $f$-$f$ transitions, either because of facile non-radiative quenching from proximal energy states.$^{[19,20]}$ or due to the sensitivity limit of the nIR detector used (1700 nm, c.f. neptunium(IV) emission reported between 1500 and 2000 nm).$^{[21,22]}$ Therefore, TPIP is not a suitable ligand to observe the emission of neptunyl(V) within current experimental setups.
Dissolution of 58 in DCM between approximately 0.3 and 3 mM did not lead to observable $f$-$f$ based nIR emission (irrespective of excitation wavelength), which has been seen previously in the literature for a neptunyl(VI) polyoxometallate system.\cite{[2]}

The LMCT band (Fig. 8.23) below 400 nm is of high intensity (compared to the neptunyl(VI) $f$-$f$ transition. It is indistinguishable from the absorption maxima of the TPIP ligand (Section 2.6.1), which absorbs below 300 nm, at all visible concentrations.
Excitation into the LMCT absorption band between 310 and 420 nm gives rise to emission between 390 and 525 nm (Fig. 8.24). Changing the excitation wavelength did not alter the emission maxima seen, although excitation can take place past the first emission maxima (410 nm). The excitation bands do not overlap with the TPIP ligand absorption spectrum (Section 2.6.1), therefore excitation may take place into the neptunyl(VI) Np=O LMCT band. The three bands are separated by energy gaps of 1349 and 1489 cm\(^{-1}\). Although Raman spectra were unobtainable for the neptunyl sample(s), the spacing do not correspond to analogous bands seen for the ligand in uranyl complexes (Section 2.4) with no resonances observed in that region of the spectrum.\(^{[23]}\) Literature assignments delegate a band at 1324 cm\(^{-1}\) as N-H δ modes by a process of elimination.\(^{[24]}\) With neptunyl(VI) Raman stretching modes usually seen around 800 cm\(^{-1}\),\(^{[25]}\) the origin of the vibrational fine structure in the emission bands is uncertain, but is close in energy to the calculated P=N bond vibration.\(^{[26]}\) The centre of the emission, approximately 439 nm, is similar to the emission maxima observed for uranyl(V) in solution (centred at 440 nm),\(^{[27]}\) with both existing as 5f\(^1\) species, indicating a similar energy in An=O bond strength between the two and supporting the argument of neptunyl(VI) LMCT emission. It should be noted that computationally predicted vibrational frequencies for the neptunyl(VI) symmetric stretch centre around 800 nm,\(^{[28]}\) at considerably lower energy (over 10,000 cm\(^{-1}\) lower) than the observed spacings in the emission of \([\text{NpO}_2(\text{TPIP})_2\text{Ph}_3\text{PO}])\(^{[58]}\).

Fig. 8.24 The excitation (emission \(\lambda = 438\) nm) and emission (excitation \(\lambda = 320\) nm) spectra of \([\text{NpO}_2(\text{TPIP})_2\text{Ph}_3\text{PO}])\(^{[58]}\) in DCM solution.

The lifetime of emission (Fig. 8.25) is biexponential at 1.31 (95 %) and 5.01 (5 %) ns (\(\chi^2 = 1.37\)), with the short lifetime difficult to measure accurately against a scatterer. The lifetime is significantly shorter than its uranyl(VI) counterparts (Section 2.6) and also uranyl(V) emission in the literature.\(^{[27]}\) However, the only observed solution
emission of neptunyl samples both exhibit short lifetimes that are barely distinguishable from a scatterer,\cite{2,19} although they relate to neptunyl(V) LMCT emission\cite{19} and neptunyl(VI) f-f transitions.\cite{2} The short lifetime for 58 suggests an efficient competition pathway for emission quenching. Overlap of the Np=O LMCT with TPIP absorption in the UV/vis spectrum (Fig. 8.23) means the absorption maxima corresponding to the emission are obscured. This prevents the determination of a quantum yield and the exact origin of the emission.

![Time-resolved emission spectrum (TRES) of [NpO₂(TPIP)₂Ph₃PO] (58) in DCM. Excitation wavelength = 375 nm.](image)

Fig. 8.25 Time-resolved emission spectrum (TRES) of [NpO₂(TPIP)₂Ph₃PO] (58) (approximately 2 mM) in DCM. Excitation wavelength = 375 nm.

Measurement of the mixed oxidation state sample containing 59 (section 8.2.4) led to no emission in benzene. In DCM, emission bands equal in wavelength and lifetime to that seen for 58 were observable, presumably the remaining 57 in solution (Appendix 3). No further bands were discernable.

**8.2.8 Comparison between neptunyl(VI) and uranyl(VI) LMCT emission.**

Addition of \([UO₂(TPIP)₂Ph₃PO]\) into the DCM sample of \([NpO₂(TPIP)₂Ph₃PO]\) resulted in emission of both uranyl(VI) and neptunyl(VI) in the same sample. The neptunyl(VI) emission is more intense and a slight excess of the uranyl(VI) complex is used with a final sample concentration of \([NpO₂(TPIP)₂Ph₃PO]\) ~0.87 mM : 1.47 mM \([UO₂(TPIP)₂Ph₃PO]\). The resulting spectrum (Fig. 8.26) shows the emission of both species in tandem when excited at 330 nm, simultaneously the excitation profile
of both can be seen with emission fixed at a mutually emissive wavelength (500 nm). In both cases the uranyl(VI) maxima are of a lower intensity.

Fig. 8.26 The excitation (emission $\lambda = 500$ nm) and emission (excitation $\lambda = 330$ nm) spectra of a mixture of [NpO$_2$(TPIP)$_2$Ph$_3$PO] (58) and [UO$_2$(TPIP)$_2$Ph$_3$PO] (4) in DCM solution.

Variation of the excitation wavelength results in different emission spectral profiles; neptunyl(VI) emission is only seen when excited between 310 and 420 nm, whilst uranyl(VI) emission is only observed between 280 and 350 nm then again after 410 nm, consistent with the absorption bands of each of these ions; observation of the emission spectrum at wavelengths specific to one actinide e.g. 290 nm for uranyl(VI) and 380 nm for neptunyl(VI), results only in emission due to that species. Similarly, at areas where emission profiles do not overlap (e.g., 438 nm for neptunyl(VI) and 521 nm for uranyl(VI)) the excitation profiles match that seen for each individual actinide (Fig. 8.24 and Section 2.6 for neptunyl(VI) and uranyl(VI) respectively). The individual excitation of each entity is therefore possible, with mutual excitation achieved only at wavelengths each would normally be excited at. This allows for observation of neptunyl(VI), uranyl(VI) emission or both by alteration of excitation wavelength (Fig. 8.27), allowing for the potential for simultaneous detection of different actinides in a mixture and identification of an individual actinide. The capacity to individually excite each actinide also indicates a lack of strong electronic delocalisation coupling and therefore possibly communication between actinyl moieties.
Fig. 8.27 The emission spectra of a mixture of \([\text{NpO}_2\text{(TPIP)}_2\text{Ph}_3\text{PO}]\) (58) and \([\text{UO}_2\text{(TPIP)}_2\text{Ph}_3\text{PO}]\) (4) in DCM solution. **Excitation wavelength = 290 nm, excitation wavelength = 320 nm, excitation wavelength = 380 nm and excitation wavelength = 430 nm.**

The lifetime of the neptunyl(VI) sample is unaltered from that observed for \([\text{NpO}_2\text{(TPIP)}_2\text{Ph}_3\text{PO}]\) (Section 8.2.7), however the emission lifetime of the uranyl(VI) complex is considerably reduced (Fig. 8.28) from 1.66 \(\mu\)s (Section 2.2.6) to match that of the neptunyl(VI) emission on the nanosecond timescale. The lifetime is the same at all emission wavelengths. Similarly, use of a time-gate to try and remove the neptunyl(VI) emission resulted in an equal decrease in uranyl(VI) emission intensity. This indicates communal quenching of the neptunyl(VI) and uranyl(VI) emission, which is perhaps in contrast to the individual excitation wavelengths that can be used to excite the actinyl moieties.
Fig. 8.28 TRES of [UO$_2$(TPIP)$_2$Ph$_3$PO] (1.47 mM) in the mixture of [UO$_2$(TPIP)$_2$Ph$_3$PO] (4) and [NpO$_2$(TPIP)$_2$Ph$_3$PO] (58) in DCM, plotted in logarithmic format, highlight the uranyl(VI) vibronic structure superimposed upon the uranyl(VI) LMCT emission band. Excitation wavelength = 420 nm.

Attempting to better understand the solution chemistry of the mixture of the two actinides is not trivial. Efforts to crystallise the sample led to the isolation of [UO$_2$(TPIP)$_2$Ph$_3$PO] and [NpO$_2$(TPIP)$_2$Ph$_3$PO] along with a solitary crystal of Ph$_3$PO. UV/vis absorption spectrophotometry illustrates that the uranyl(VI) LMCT absorption overlaps with that of neptunyl(VI), albeit at much lower intensity (Fig. 8.29). The maxima are centred at 428 nm, within error of isolated [UO$_2$(TPIP)$_2$Ph$_3$PO] (429 nm) and not within the range of absorption maxima seen for oligomeric uranyl(VI) TPIP complexes (Chapter 2).
Fig. 8.29 The UV/vis absorption spectrum of the DCM mixture of \([\text{UO}_2(\text{TPIP})_2\text{Ph}_3\text{PO}])\) (4) (1.47 mM) and \([\text{NpO}_2(\text{TPIP})_2\text{Ph}_3\text{PO}])\) (58) (~0.87 mM).

$^1\text{H}$ and $^{31}\text{P}$ NMR spectroscopy of the individual complexes suggests that \([\text{UO}_2(\text{TPIP})_2\text{Ph}_3\text{PO}])\) is stable in solution, with no resonance for uncomplexed \(\text{Ph}_3\text{PO}\) observed (Section 2.4). Similarly, the coordination of \(\text{Cy}_3\text{PO}\) to uranyl(VI) TPIP is solution stable.$^{[4]}$ In contrast, \([\text{NpO}_2(\text{TPIP})_2\text{Ph}_3\text{PO}])\) presents a labile \(\text{Ph}_3\text{PO}\) ligand in DCM (Section 8.2.3) and presents unknown topology in solution. Therefore, if communication between the two actinyls takes place it likely revolves around the chemistry of the neptunyl(VI) complex in solution. The $^{31}\text{P}$ NMR spectrum (Fig. 8.30) shows a multitude of resonances, suggesting multiple environments for phosphorus. There is a lack of resonances at negative ppm, with \([\text{NpO}_2(\text{TPIP})_2\text{Ph}_3\text{PO}])\) normally found at -36.6 ppm (Fig. 8.11), whilst the resonance at 27.5 ppm is concurrent with \(\text{Ph}_3\text{PO}\) in DCM and the two broad resonances between 22.5 and 25.5 ppm are typical for uranyl(VI) TPIP in DCM (Section 2.5). The broad resonance at 40.4 ppm is representative of uranyl(VI) coordinated \(\text{Ph}_3\text{PO}\), although the lack of resolution suggests a lability of the ligand. The proton NMR spectrum presents a series of broad resonances with poor spatial resolution.
Fig. 8.30 Left $^1$H NMR spectrum and right $^{31}$P-$^1$H NMR spectrum of the mixture of [AnO$_2$(TPIP)$_2$(Ph$_3$PO)] complexes (An = U, Np). Recorded in d$_2$-DCM at 295 K.

$^1$H DOSY-NMR spectroscopy presents an array of diffusion coefficients associated to the overlapping proton resonances (Fig 8.31). The fastest diffusion coefficient is observable at 11.20 (+/- 0.15) x10$^{10}$ m$^2$s$^{-1}$, similar to HTPIP (Section 2.2.2) and the slowest diffuses at 7.40 (+/- 0.10) x10$^{10}$ m$^2$s$^{-1}$, similar to that of [UO$_2$(TPIP)$_2$H$_2$O] (7.60 (+/- 0.10) x10$^{10}$ m$^2$s$^{-1}$, Chapter 2) and is indicative of a monomeric actinyl moiety. Use of Equation 1.8 vs. HTPIP at 11.20 gives the slower diffusing species a molecular mass of 1446 gmol$^{-1}$, close to [AnO$_2$(TPIP)$_2$(Ph$_3$PO)] at 1380 gmol$^{-1}$ (for An = U) or 1379 gmol$^{-1}$ (for An = Np). Whilst this would initially suggest no communication between the actinyls in solution, Ph$_3$PO is almost certainly labile and no diffusion coefficients are observable that could correspond to such an entity in DCM (Section 8.2.3). It is instead likely that the significant overlap of resonances belonging to many different species in solution results in averaging of resonances so that the relative molecular masses can not be satisfactorily derived.

Fig. 8.31 The $^1$H DOSY-NMR spectrum of the aromatic resonances of [AnO$_2$(TPIP)$_2$Ph$_3$PO] (An = U, Np). Recorded in d$_2$-DCM at 295 K.
Despite these limitations from DOSY NMR spectroscopy, it has been possible to plot a graph of diffusion coefficient against molecular weight, which may serve in aiding the identification of the nuclearity of a TPIP actinyl complex in solution, Fig. 8.32.

Fig. 8.32 Plot of diffusion coefficient against molecular mass for neptunyl(VI) and uranyl(VI) TPIP complexes and HTPIP. Error bars taken from the least accurate measurement ([UO$_2$(TPIP)$_2$], +/- 0.25 x $10^{-10}$ m$^2$s$^{-1}$).

8.3 Conclusions
An investigation into the chemistry of neptunyl(VI) TPIP has revealed a likeness to uranyl(VI) (Chapter 2) with subtle changes in crystallisation conditions and solvent leading to comparatively large changes in structural chemistry. Unlike uranyl(VI), neptunyl(VI) TPIP complexes do not display a tendency to form CCIs, or at least not under analogous conditions. The stability of neptunyl TPIP complexes is easily governed by the use of solvent, with organic solvents favouring the +VI oxidation state and TPIP as a ligand seeming to have slight preference for this oxidation state of neptunium overall. A brief insight into the chemistry of the complexes reveals a subtle difference in stability of different complexes, with [NpO$_2$(TPIP)$_2$]$_2$ producing neptunium in the +IV and +V oxidation states over time, presumably by reduction and then disproportionation. Neptunyl(V) TPIP has not been explored as thoroughly due to the limiting choice of solvents for use and also its seeming inability to crystallise. The emission spectrum of neptunyl(VI) Np=O LMCT has been reported for the first time and compared in solution with uranyl(VI), with mixtures of
\[ \text{[NpO}_2\text{(TPIP)}_2\text{Ph}_3\text{PO}] \text{ and [UO}_2\text{(TPIP)}_2\text{Ph}_3\text{PO]} \text{ resulting in emission from both centres apparently from a connected structure.} \]

The structures of the neptunyl(VI) TPIP complexes in solution appear extended when studied by DOSY-NMR spectroscopy, in comparison to uranyl(VI) (Fig. 8.32). However the minor influence of paramagnetic relaxation may hinder comparison of solution species.

**8.4 References**


Chapter 9

Summary and Conclusions
Investigations into the solution stability of uranyl(VI) fluorinated acetylacetonates (acacs) by emission and diffusion-ordered NMR spectroscopies has revealed that the cation-cation interactions (CCIs) only exist in solution when supported by ligand bridging interactions. Extrapolation of this hypothesis to the trimeric [UO$_2$(TPIP)$_2$)$_3$ (TPIP = tetraphenylimidodiphosphinate) complex presents similar results. Conclusively therefore, uranyl(VI) CCI interactions are not stable in solution unless supported by bridging interactions, which is in contrast to uranyl(V).$^{[1,2]}$ The use of emission spectroscopy in studying aggregated uranyl(VI) structures in this work has also highlighted the sensitivity of the analytical technique to the coordination environment of the uranyl(VI) ion. Resolution of emission maxima and, notably, emission lifetimes are directly affected (broadened and reduced respectively) by the presence of CCIs (in both the solid state and solution). Additionally, the isolation and study of different solvates of [UO$_2$(TPIP)$_2$)$_3$ reveals minor geometrical differences in the solid state which are observable by luminescence spectroscopy, both in the solid state and in solution, confirming the existence of the irregularities in the solution state.

Attempts to produce actinyl(V) complexes of TPIP met with difficulty. Whilst this is unsurprising for uranyl(V), alongside neptunium this indicates that the TPIP ligand may have a preference for the +VI oxidation states of the actinyl ions. Additionally, discrepancies between the stability of different neptunyl(VI) TPIP complexes indicates the role of minor changes of coordination chemistry, supported by varying reduction potentials in the electrochemical investigations of uranyl(VI) TPIP complexes.

The observation of neptunyl(VI) Np=O LMCT emission for the first time has increased understanding of the basic properties of actinide emission. Attempts to understand uranyl(V) emission, from the uranyl LMCT and from $f$-$f$ transitions has met with difficulty, both from a uranyl(V) salt and in the presence of ligands. This is mainly thought to be due to the presence of cations close to the uranyl moiety, quenching the emission. Whilst addition of silylated oligopyridines did result in emission, it is not clear whether this short lived (ns) emission is organic ligand based or from a uranyl(V) excited state.
Attempts to study the actinyl coordination chemistry of silylated oligopyridines proved challenging, with a lack of crystalline material needed for an absolute assignment of coordination species obtained accompanied by inconclusive or non-existent emission spectra. NMR spectroscopy has provided some insight into the solution coordination of the ligands, with coordination to the metal accompanied by co-existence with the anion from the metal salt. For the 2,2’-bipyridine based ligands, there is strong indication that the ligands are labile in solution. Coordination of the ligands is emphasised by diffusion ordered and paramagnetic (for neptunium) observations, with both also confirming the role of the steric bulk of the silyl group in the resulting complex. However, potential lability of the silyl groups and coordination with anions results in no trend of the coordination of one or two ligands in the equatorial plane of the actinyl.

Complexation of the novel series of ligands with lower oxidation state f-elements has been confirmed by NMR and emission spectroscopy. Work on the chemistry of the 2,2’-bipyridine based ligands with the Am(III) and Cm(III) ions has, similar to actinyl chemistry, presented a series of complexes which appear to vary in size/coordination number based on the steric bulk of the ligand, in agreement with preliminary work on lanthanides.[3]

The strongly emissive properties of TPIP complexes, observed for the early actinyl(VI) ions and in lanthanides,[4-6] are mimicked for Cm(III). However, the fluorinated analogue of TPIP, FTPIP has presented reduced emission properties for the visibly emitting actinides (uranyl(VI) and curium(III)) vs. TPIP, and it is likely that there is a more efficient energy overlap between excited states in overlapping UV/visible regions for the fluorinated ligand, similar to that observed in the lanthanide series.[7] The ligand may still enable observation of actinyl nIR f-f based emissive transitions.

In summary, the effect of coordination chemistry on emission spectroscopy has been investigated and shown to be quite significant, whilst analysis of the rate of diffusion of subsequent NMR resonances has proved a useful ally in interpretation of solution speciation. The isolation of stable uranyl(V) complexes has not been successful in this work. Nevertheless, there is ample spectroscopic evidence for the (transient) existence of uranyl(V) complexes with oligopyridine and acac based ligands, whereas
it can be concluded that a non-redox active strong donor, such as TPIP, does not stabilise uranyl(V) (and neptunyl(V) ions) to a great extent.

9.1.2 References

9.2.1 Future Work and Scope of the Project
Extrapolation of actinyl chemistry presented here into further research on transuranics is of interest, although not easy in practice due to the necessary procedural precautions. Certainly, expansion of the TPIP (tetraphenylimidodiphosphinate) chemistry into plutonyl (and perhaps americyl, although difficult to perform) may prove fruitful and could provide insights into a trend for preference of oxidation state, particularly for actinyl ions in the +VI oxidation state. Luminescence properties of such actinyls could then be investigated. Once basic principles of their emission have been established, further effects on photophysical properties due to coordination chemistry, CCIs (cation-cation interactions) etc. could then be investigated. Use of diffusion ordered NMR (DOSY) spectroscopy to aid investigations may become limited due to the increasing paramagnetic relaxation effects of the additional f electrons in transuranic actinyl ions. Such transuranic chemistry may also be applicable for the fluorinated acac ligands.

The chemistry of uranyl(VI) TPIP complexes could be expanded. Whilst complexes with uranyl ions connected by bridging ligands and, in some cases, CCIs exhibit different emissive properties, the variable 5th equatorial coordination site on the uranyl ion has not been utilised fully. Various ligand adducts could be complexed which could lead to
bridging uranyl complexes (Fig. A7.1), and subsequent emission/diffusion properties will provide structural information alongside any solid state structures that may be obtained.

Fig. 9.1 Proposed structures obtainable by use of linking ligands in the 5th equatorial coordination site. TPIP ligands omitted for clarity. By utilising aromatic groups that absorb only in the UV region, the LMCT of the uranyl(VI) unit should be observable at room temperature.

The chemistry of neptunyl(VI) TPIP can perhaps overlap with uranyl(VI); a mixture of neptunyl(VI) and uranyl(VI) salts in the reaction with NaTPIP could lead to a mixed actinide multi-metallic complex. In particular, an analogue of [UO₂(TPIP)₂]₃ could present the first uranyl(VI)-neptunyl(VI) CCIs, and, if elucidated, the first uranyl-neptunyl CCIs to be observed in the solid state for any oxidation state of the actinides.

Future work on the emissive properties of neptunyl(VI) could see the complexation of F⁻TPIP (perfluoro-tetraphenylimidodiphosphinate) to neptunyl(VI); neptunyl(VI) TPIP complexes do not display nIR emission, but use of the fluorinated ligand could result in an
increase in such emissive properties. The solvent-dependent stability of neptunium TPIP complexes could be explored further, with other alcohols perhaps able to stabilise the +V oxidation state. The search for a solvent that stabilises the +IV oxidation state could be of interest. Potentially, a solvent could be identified in which neptunyl(V) and (VI) are soluble but (IV) is not, encouraging the disproportionation and reduction reactions to go to complete formation of neptunium(IV). Coordination of fluorinated acac (acetylacetonates) to neptunyl salts, particularly neptunyl(V), may also be productive, with uranyl(VI) producing much more intense emission with fluorinated acacs (compared to acacs, Chapter 3). Therefore, the report of neptunyl(V) emission coordinated by acac\textsuperscript{1,2} can be built upon.

The elucidation of neptunyl(IV) TPIP presents the possibility, alongside [U(TPIP)\textsubscript{4}],\textsuperscript{[3]} of a series of similar An(IV) structures which could be investigated by luminescence spectroscopy. Potentially the TPIP ligand can reproduce its actinyl(VI) emissive properties for An(IV). Disproportionation and comproportionation reactions could, consequently, be followed \textit{in situ}.

Expanding the database of work performed upon the uranyl(VI) fluorinated acac complexes could revolve around the study of different fluorinated acacs; different acac based ligands lead to different extended frameworks upon sublimation and it is possible that an interesting variety of structural motifs could be discovered. However, decreased fluorination of the ligand increasingly hinders the use of luminescence spectroscopy to study the complexes. The structure of the extended uranyl(VI) aggregates could be studied by $^1$H and/or $^{19}$F DOSY-NMR spectroscopy in an alternative solvent; although DCM proved useful in this study for tta and hfac complexes of the uranyl(VI) cation and benzene could be utilised for the study of aggregates, particularly given its use in attempted reductions. Fluorinated acac structures of uranium in other oxidation states could be expanded with uranyl(V) aggregates compared to uranyl(VI).

In future, further studies of the reduction of uranyl(VI) salts could pave the way to finding a usable uranyl(V) salt as a starting material that does not have uranyl-alkali metal coordination. This would allow for luminescence studies on the salt, and synthesis of complexes that would not bear similar interactions that could potentially hinder emissive properties. Attempts to oxidise U(OTf)\textsubscript{3} to produce [{UO$_2$(py)$_3$}$\{K_3$(OTf)$_3$).py] could provide a useful analogy to the synthesis of [{UO$_2$(py)$_3$}${K_2$(py)$_2$}], which is accessible by either reductive or oxidative routes, and may provide the triflate salt in a more effective
yield \textit{cf.} the oxidation of UI$_3$(THF)$_4$. Further comproportionation studies could see different salts paired together; reaction of uranyl(VI) and uranium(IV) triflates to attempt to produce a uranyl(V) triflate could prove insightful and easier to characterise given the straightforward crystallisation of $\left[\{\text{UO}_2(\text{py})_5\}_2(\text{K}_3(\text{OTf})_5)\cdot\text{py}\right]$. Although AgOTf proved unsuccessful in attempts of one-electron oxidations of uranium(IV), many different oxidising agents could be utilised to this effect.

The comproportionation reaction in Chapter 4, although only partially successful, is nonetheless one of only a few examples of such a reaction.\cite{4} Many factors could affect the comproportionation reaction, such as solvent and coordination chemistry, and further work in this area could provide an insight. In addition, successful comproportionation reactions could potentially provide information about disproportionation reactions; such as if actinyl(VI) and actinide(IV) reagents, which bear resemblance to disproportionation products, can be found to comproportionate with one another.

Future pyridyl ligand synthesis could see the addition of many different SiR$_3$ groups to the neocuproine and 6,6'-dimethyl-2,2'-bipyridine to expand the range of ligands. Further attempts could be made to metallate other oligopyridines, such as the terpyridyl equivalent and perhaps more conjugated systems,\cite{5,6} including those that display multiple potential coordination sites to metals.\cite{7} Attempts to lithiate adjacent to nitrogen positions on the rings could take place potentially by silylation of pyridine, followed by subsequent oligomerisation of the aromatic. Alternatively, the use of DMGs (Directed Metallating Groups) could be considered, with OMe proving useful when combined with iodo leaving groups in 2,2'-bipyridine.\cite{8} Activation of the nitrogen in the pyridyl system\cite{9,10} to produce an N-oxide could lead to an increase in the potential to lithiate next to the nitrogen. A different route to the lithium-halogen exchange mechanism could be employed with synthesis of an Si-Li bond\cite{11} perhaps yielding direct nucleophilic attack to a halogen group on the oligopyridine. Other metallating agents may also find use in metallating the aromatic systems.\cite{12,13} In addition, group other than trialkylsilyl-substituents could be utilised, such as alkyl groups (the nucleophilic attack of alkyllithiums is well documented, Appendix 6) or other novel synthons.

Further work is needed to examine the existence of uranyl silylated oligopyridine complexes. With a contrast in lipophilicity within the ligand itself, a contrast of solvents may be useful in attempting to crystallise a complex. Further luminescence studies are also
needed to interpret the emission spectra observed for reactions with uranyl(V) and (VI) salts. The ligands could be reacted with other uranyl(V) salts, perhaps ones that do not include a U=O-M bond. The destination of the silyl groups that have been decapitated is not always certain, whether there is potential for the activation of the uranyl ion oxygen and if this potential outcome is an issue that should be explored. Ultimately, a wider range of ligands reacted with uranyl(V) could help provide more of an explanation for the products of the reaction of said ligands with uranyl(VI/V) ions.

Although only preliminary work on the reaction of silylated oligopyridines with uranium(IV) and europium(III) salts was started, much further work could be done and the ligands show promise in interactions with such metals.

To complete the study of the coordination of silylated ligands to actinide(III) ions, the neocuproine ligands could be utilised, providing more information via the increased range of ligand choice. From the results obtained, it seems likely that the use of a more labile anion, such as perchlorate, is favourable for the coordination of the ligands, and it would be beneficial to utilise this counterion in future studies. More information on the binding of the 2,2’-bipyridine based ligands studied here could be found from absorption spectra of the samples, along with emissive studies of the americium complexes. However, radiological constraints (among others) will likely prevent this, with such barriers already immediately negating any attempts to perform NMR spectroscopy on curium samples. In addition, there may be slight differences between coordination to americium and curium for the ligands, and a study on more An(III) complexes could help distinguish this (again, radiological/ air sensitive constraints would likely hamper such experimentation).

The results obtained from the coordination of the silylated oligopyridines to neptunyl(V) cations provide only a brief insight into the coordination chemistry of the ligands for this actinyl ion. Ideally, a full study with neptunyl(V) perchlorate would take place with all silylated oligopyridines. The diffusion coefficients obtained could provide an indication of solution steric bulk, in a similar manner to study with uranyl(VI) triflate (Chapter 5). Whether the ligands are suitable for use with neptunyl(V) emission spectroscopy is uncertain, but could also be informative if applicable. Ultimately, the propensity for neptunyl(V) to disproportionate, perhaps in varying solvent systems, in the presence of the ligands would be studied to see if the steric bulk offered by the ligands affects the rate of disproportionation.
Although not directly related to ligands used in this Thesis, the high affinity for pyridine of uranyl(VI) (and other actinides) ions suggests a potential for the use of phosphinine in reactions with uranyl. Although difficult to synthesise,[14] coordination to a uranium salt could provide interesting photophysical and structural comparisons with pyridine analogues.

Many of the studies outlined above are currently in progress in the Natrajan group at The University of Manchester.

9.2.2 References

Chapter 10

Experimental
General Experimental
Mass spectra were obtained using positive electrospray on a Micromass Platform II spectrometer or by MALDI with an ALPHA matrix on a Shimadzu Axima Confidence spectrometer. Accurate mass spectra were recorded on a Waters QTOF. Solutions were made up using DCM, acetonitrile or methanol. Elemental Analyses were performed by the microanalytical services at the University of Manchester using a Carlo ERBA Instruments CHNS-O EA1108 elemental analyzer (C, H and N analysis) and a Fisons Horizon elemental analysis ICP-OED spectrometer for U, P, and halides.

All NMR spectra of organic, uranium and some neptunium samples were recorded on a Bruker Avance 400 spectrometer. NMR spectra of americium and some neptunium samples were recorded on a Bruker Avance III 400 spectrometer with a gradient inverse detection probe used for proton measurements and a broadband observe probe with direct x-magnetisation detection for non-proton measurements. Operating frequencies 400 MHz ($^1$H), 101 MHz ($^{13}$C), 162 MHz ($^{31}$P), 374 MHz ($^{19}$F) and 41 MHz ($^{15}$N), variable temperature unit set at 300 K unless otherwise stated. The NMR machines were controlled remotely using Bruker Topspin 2.1 or 3.1 software. $^1$H Chemical shifts are reported in parts per million relative to TMS and referenced to the residual proton resonances in $d_6$-DMSO, $d_3$-acetonitrile, $d$-chloroform, $d_2$-DCM, $d_5$-pyridine, $d_3$-methanol or $d_6$-benzene. $^{19}$F NMR experiments were referenced to C$_6$F$_6$.

Samples for analysis were transferred into 5mm walled, 8” NMR tubes manufactured by Wilmad-LabGlass. Air sensitive NMR analyses were performed in same model NMR tubes that had been modified with fine-thread Young’s Tap valves by the departmental glassblower. Americium samples were measured in 5mm walled, 8” NMR tubes with Young’s Tap valves purchased from Wilmad-LabGlass. Neptunium samples were transferred to a Teflon insert tube which were subsequently placed into the NMR tubes described above and sealed with ‘Parafilm’.

Steady state emission and excitation spectra were determined using a Perkin-Elmer LS50 B fluorimeter operating in fluorescence mode, or an Edinburgh Instrument FP920 Phosphorescence Lifetime Spectrometer equipped with a 5 watt microsecond pulsed xenon flashlamp (with single 300 mm focal length excitation and emission monochromators in Czerny Turner configuration) and a red sensitive photomultiplier in peltier (air cooled) housing, (Hamamatsu R928P). Lifetime data were recorded.
following excitation with either the flashlamp or an EPL 375 and EPL 405 picosecond pulsed diode laser (Edinburgh Instruments), using time correlated single photon counting (PCS900 plug-in PC card for fast photon counting). Lifetimes were obtained by tail fit on the data obtained or by a reconvolution fit using a solution of Ludox® in water as the scatterer, and quality of fit judged by minimization of reduced chi-squared and residuals squared. Curium samples were studied using an excimer-pumped (EMG 201 MC, Lambda Physics) dye laser system (FL3002, Lambda Physics), excitation wavelength fixed at 396.6 nm. Emission is detected by an optical multichannel analyser using a polychromator (Jobin Yvon 320) with an intensified photodiode array. Specific details on instrumental set-up can be found in the literature.\[1\]

Absorption spectra were recorded in DCM, acetonitrile, benzene, pyridine or methanol on a T60U spectrometer (PG Instruments Ltd.) using fused quartz cells with a path length of 1 cm or on a on a Shimadzu UV-2600. Raman and infrared spectroscopy experiments of uranium containing samples were performed on a Bruker Equinox 55 FTIR/Raman machine equipped with a “Golden Gate” ATR (Attenuated Total Reflectance) attachment (resolution 4 cm\(^{-1}\)), or mixed with nujol to create a mull which was applied to NaCl plates. A Perkin-Elmer Spectrum One FT-IR spectrometer with ATR accessory and Renishaw inVia 1000 micro-Raman Microscope with a 785 nm excitation source were also utilised.

Electrochemical measurements were recorded with AUTOLAB PGSTAT 12 potentiostat/ galvanostat using a platinum disc electrode with a reaction surface of 1 mm\(^2\) as a working electrode. A platinum rod electrode (together with internal referencing vs. [Cp\(_2\)Fe]\(^0\)/+ was used as a reference electrode and a platinum knob electrode as an auxiliary electrode. All electrochemical measurements were recorded in DCM and degassed with nitrogen prior to measurement. The electrolyte used was 0.0625 M [Bu\(_4\)N][BPh\(_4\)].

Single crystal X-Ray diffraction was performed on an Oxford Diffraction Crystals CCD diffractometer at 100 K or an Agilent Technologies SuperNova 4-circle diffractometer at 150 K, both with Mo/ K microfocus source, or with a Bruker X8 Prospector 3-circle diffractometer with a copper microfocus source at 100 K. Data were solved using direct methods with OLEX-2 software.\[2\] The non-H atoms were
refined anisotropically, hydrogen atoms were positioned in idealised sites and were allowed to ride on their parent C or N atoms.

Neptunium crystals suitable for single crystal X-ray diffraction were isolated in fomblin oil in the designated neptunium fumehood in the Centre for Radiochemistry Research (CRR). The crystals were then transported in double containment to the CRR microscope and inserted into a capillary, which was subsequently mounted onto a goniometer which had been designated specifically for use with neptunium crystals.

All air-sensitive manipulations were carried out under argon on a Schlenk line using standard positive pressure techniques attached to a Leybold trivac D4B vacuum pump and using an Innovative Technology pure-lab 2GB glovebox. All glassware was cleaned using a KOH/PrOH/ toluene base bath followed by dilute HCl acid bath, except sinters which were cleaned with dilute nitric acid.

**Origin of Chemicals**

All chemicals were purchased from Sigma Aldrich with the following exceptions:

- Absolute ethanol; Fischer Scientific.
- d$_3$-acetone; Apollo Scientific
- Acetonitrile; Fischer Scientific.
- Bis-(pentfluorophenyl)bromophosphine; Apollo Scientific.
- d$_5$-pyridine; CEA, France.
- Sodium hydroxide; Fischer Scientific.
- Sulphuric acid; Fischer Scientific.
- THF; Fischer Scientific.
- Triphenylphosphineoxide; Alfa Aeser.

- 2,6-Dibromopyridine; Alfa Aeser.
- Dimethylaminoethanol; Acros Organics.
- d$_6$-DMSO; Cambridge Isotope Laboratories Inc.
- Hydrochloric acid; Fischer Scientific.
- Hydrogen peroxide; Fischer Scientific.
- Neocuproine; Acros Organics.
- Nitric acid; Fischer Scientific.
- Pentfluorobromobenzene; Fluorochem.
- d$_5$-pyridine; CEA, France.
- Sodium hydroxide; Fischer Scientific.
- Sulphuric acid; Fischer Scientific.
Solvents for air sensitive reactions (including deuterated solvents) were dried by distilling over potassium, sodium, calcium hydride standard or phosphorus pentoxide under argon and deuterated solvents vacuum transferred before use.

**Radioactive Manipulations**

$^{238}$U, $^{237}$Np, $^{241}$Am and $^{243}$Cm are all high specific activity nuclides and represent a serious internal and/or external hazard. All experiments were performed following the pre-set radiological safety precautions in accordance with the local rules of The University of Manchester, Trinity College Dublin and the KIT-INE, Karlsruhe.

**Synthesis of Uranyl(VI) TPIP Complexes**

**Synthesis of $\left[\text{UO}_2\left(\text{TPIP}\right)_2\text{Py}\right]$.0.5Py**

Method 1 – the preparation of $\left[\text{UO}_2\left(\text{TPIP}\right)_2\text{Py}\right]$.0.5Py

NaTPIP (83 mg, 0.19 mmol) was suspended in absolute ethanol (5 mL) and added to a stirred solution of uranyl nitrate hexahydrate (48 mg, 0.096 mmol) in deionised water (5 mL) to produce a cloudy green solution. After stirring for 1 h. the solution was filtered, rinsed with absolute ethanol and the resulting solid left to air dry. The solid was washed into a sample vial with pyridine (3 mL) and layered with hexane. After several days standing green needles were deposited in the vial (50 mg, 44 %).

UV/vis (DCM): $\lambda_{\text{max}}$/nm ($\epsilon$/cm$^3$/mol$^{-1}$cm$^{-1}$) = 405 (31), 417 (44), 428 (51), 442 (40), 453 (23); UV/vis (py): $\lambda_{\text{max}}$/nm ($\epsilon$) = 398 (24), 406 (36), 418 (49), 429 (57), 443 (43), 454 (25).$^{31}$P-$^1$H NMR (CD$_2$Cl$_2$, 162 MHz) $\delta$ (ppm): 24.1 (s); $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) $\delta$ (ppm): 7.26 – 7.42 (m, 22H, o-CH + pyCH), 7.80 (t, $^3$J$_{HH}$ = 7.5 Hz, 2H, p-CH), 7.98 (m, 11H, m-CH + pyCH), 8.80 (br, 4H, pyCH); $^{13}$C-$^1$H NMR (CD$_2$Cl$_2$, 101 MHz) $\delta$ (ppm): 124.3 (s, pyC), 128.4 (d, $^2$J$_{PC} = 13.5$ Hz, phC), 131.0 (s, ph/pyC), 131.5 (d, $^3$J$_{PC} = 12.0$ Hz, phC), 150.8 (s, pyC). IR (3500-500 cm$^{-1}$, solid sample on ATR cell): 3070 (w), 3052 (w), 2159 (s), 2029 (s), 2008 (sh), 1975 (s), 1599 (w), 1483 (m), 1436 (s), 1308 (w), 1199 (s), 1175 (sh), 1120 (s), 1079 (s), 1059 (s), 1041 (s), 1024 (s), 997 (s), 912 (s), 821 (m), 752 (m), 722 (m), 691 (s), 628 (s), 585 (m), 571 (w), 549 (m), 532 (sh), 510 (m), 486 (m), 455 (w), 439 (w), 415 (m); Raman (solid in glass capillary, 3500 – 50 cm$^{-1}$): 3057 (s), 1592 (s), 1154, (m), 1141 (m), 1029 (m), 1000 (s), 842 (m), 822 (m), 695 (m), 203 (m), 120 (s), 86 (s). Anal.
Calculated for C_{56}H_{58}N_{3}O_{6}P_{4}U_{1}.0.5C_{3}H_{3}N: C, 54.58; H, 3.92; N, 4.01; P, 10.14; U, 19.49. Found: C, 54.58; H, 4.12; N, 4.07; P, 9.83; U, 18.66.

Method 2
NaTPIP (16 mg, 0.036 mmol) was added to a vial containing [UO_2I_2(THF)_3] (13 mg, 0.018 mmol) in an argon glovebox. The mixture of powders was dissolved in anhydrous pyridine (5 mL) to give an orange solution. After stirring overnight the solution was filtered through glass wool and the supernatant layered with anhydrous hexane. Characterisation of the green needles that formed was consistent with that described in method 1 (21 mg, 62 %).

Method 3 – the preparation of [UO_2(TPIP)_2Py].0.5CH_2Cl_2
[UO_2(TPIP)_2Py] (18 mg, 0.015 mmol) was dissolved in anhydrous DCM in an argon glovebox and filtered through glass wool. The supernatant was left to stand overnight before being layered with anhydrous hexane. Green needles were deposited after several days standing.

Method 4
NaTPIP (10 mg, 0.023 mmol) was suspended in absolute ethanol (5 mL) and added to a stirred solution of uranyl nitrate hexahydrate (11 mg, 0.022 mmol) in deionised water (5 mL) to produce a cloudy green solution. After stirring for 1 h. the solution was filtered, rinsed with absolute ethanol and the solid left to dry. The solid was collected in a sample vial, dissolved in pyridine (3 mL) and immediately layered with hexane. After several days standing green needles were deposited in the vial.

Attempted synthesis of [UO_2(TPIP)_2MeCN]
Method 1 – the preparation of [UO_2(TPIP)_2H_2O].2MeCN
NaTPIP (48 mg, 0.11 mmol) was suspended in absolute ethanol (10 mL) and added to a stirred solution of uranyl nitrate hexahydrate (29 mg, 0.058 mmol) in deionised water (10 mL) to produce a cloudy green solution. After stirring for 1 h. the solution was filtered, rinsed with absolute ethanol and the solid left to air dry. The solid was washed into a sample vial with MeCN (5 mL), sonicated and layered with diethyl ether. After several days of standing, green crystals were deposited (54 mg, 83 %). UV/vis (DCM): \( \lambda_{\text{max}}/\text{nm} (\varepsilon/\text{cm}^3\text{mol}^{-1}\text{cm}^{-1}) = 236 (27,830), 267 (6480), 274 (4680), 418 (46), 429 (48), 442 (42), 455 (34).^{31}\text{P-}\{	ext{^1}\text{H}\} \text{NMR (CD}_2\text{Cl}_2, 162 \text{MHz}) \delta (\text{ppm}): 24.9 (s); ^1\text{H NMR (CD}_2\text{Cl}_2, 400 \text{MHz}) \delta (\text{ppm}): 7.33 (br, 24H, \text{pbC}), 8.05 (br, 16H, 

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Method 2 – the preparation of \([\text{UO}_2(\text{TPIP})_2\text{MeCN}]\)

NaTPIP (34 mg, 0.077 mmol) was suspended in absolute ethanol (5 mL) and added to a stirred solution of uranyl nitrate hexahydrate (19 mg, 0.038 mmol) in deionised water (5 mL) to produce a cloudy green solution. After stirring for 1 h, the solution was filtered, rinsed with absolute ethanol and the collected solid left to dry. The solid was taken into an argon glovebox and suspended in anhydrous MeCN (10 mL). After 24 hours, anhydrous DCM (10 mL) was added to produce a pale green solution. Addition of anhydrous hexane resulted in the formation of two layers that were immiscible. Standing for several months resulted in the gradual loss of solvent, yielding large green needles. \(^{31}\text{P}\{-^1\text{H}\}\text{NMR (CD}_2\text{Cl}_2, 162 MHz} \) \(\delta\) (ppm): 25.4 (s); \(^1\text{H}\text{NMR (CD}_2\text{Cl}_2, 400 MHz} \) \(\delta\) (ppm): 1.97 (s, 3H, \(\text{CH}_3\)), 7.07 (m, 6H, \(\text{phCH}\)), 7.2 – 7.5 (br m, 22H, \(\text{phCH}\)), 8.02 (q, \(3^J_{\text{HH}} = 7.0\) Hz, 12H, \(\text{phCH}\)), 8.41 (m, 4H, \(\text{phCH}\)); \(^{13}\text{C}\{-^1\text{H}\}\text{NMR (CD}_2\text{Cl}_2, 101 MHz} \) \(\delta\) (ppm): 128.5 (d, \(2^J_{\text{PC}} = 14.0\) Hz, \(o\)-ph), 131.4 (s, \(p\)-ph), 131.6 (d, \(3^J_{\text{PC}} = 12.5\) Hz, \(m\)-ph).

Synthesis of \([\text{UO}_2(\text{TPIP})_2\text{THF}]\)

NaTPIP (48 mg, 0.11 mmol) was suspended in absolute ethanol (10 mL) and added to a stirred solution of uranyl nitrate hexahydrate (29 mg, 0.058 mmol) in deionised water (10 mL) to produce a cloudy green solution. After stirring for 1 h, the solution was filtered, rinsed with absolute ethanol and the solid left to air dry. The solid was washed into a sample vial with THF (10 mL) and layered with hexane. Standing resulted in the formation of green needles, characterisation of which was consistent with the literature.\(^3\)

Synthesis of \([\text{UO}_2(\text{TPIP})_2\text{Ph}_3\text{PO}]\)
NaTPIP (51 mg, 0.12 mmol) was suspended in absolute ethanol (10 mL) and added to a stirred solution of uranyl nitrate hexahydrate (30 mg, 0.06 mmol) in deionised water (10 mL) to produce a cloudy green solution. After stirring for 1 h, the solution was filtered, rinsed with absolute ethanol and the solid left to air dry. The solid was collected in a sample vial and dissolved in THF (10 mL). Ph₃PO (12 mg, 0.043 mmol) was added to the solution and the sample left to stir over the weekend. Evaporation of the solvent resulted in a precipitate which was dissolved in DCM and layered with hexane. After a couple of days standing pale green needles were deposited in the vial (82 mg, 67%). UV/vis (DCM): λ_{max} / nm (ε / cm³mol⁻¹cm⁻¹) = 404 (33), 417 (35), 429 (37), 442 (34), 454 (27). ³¹P-{¹H} NMR (CD₂Cl₂, 162 MHz) δ (ppm): 24.3 (s, (OP(Ph)₂)₂N), 40.2 (s, Ph₃PO); ¹H NMR (CD₂Cl₂, 400 MHz) δ (ppm): 7.1 – 7.5 (br m, 33H, phCH), 7.6 – 8.3 (br m, 22H, phCH); ¹³C-{¹H} NMR (CD₂Cl₂, 101 MHz) δ (ppm): 128.2 (d, 2J_{PC} = 13.0 Hz, phC), 128.9 (d, 3J_{PC} = 12.5 Hz, phC), 130.7 (s, phC), 131.7 (d, 2J_{PC} = 10.4 Hz, phC), 132.7 (s, phC), 133.2 (d, 3J_{PC} = 9.0 Hz, phC). IR (3500–400 cm⁻¹, solid sample on ATR cell): 3074 (w), 3058 (w), 3043 (w), 2966 (w), 2966 (w), 1969 (w), 1909 (w), 1591 (w), 1521 (w), 1485 (w), 1437 (m), 1286 (w), 1263 (w), 1205 (m), 1180 (m), 1142 (sh), 1121 (s), 1089 (s), 1067 (s), 1048 (m), 1027 (s), 998 (m), 932 (m), 916 (s), 825 (m), 750 (m), 722 (s), 691 (s), 587 (m), 555 (s), 536 (s), 512 (s), 508 (s), 502 (s), 498 (s), 496 (m), 486 (s), 478 (m), 470 (s), 463 (s), 453 (vs), 450 (m), 437 (m), 431 (s), 424 (s), 417 (s), 406 (s); Raman (solid on glass slide, 3500 – 100 cm⁻¹): 3066 (w), 1929 (m), 1574 (w), 1188 (w), 1164 (w), 1114 (w), 1029 (m), 999 (s), 839 (m), 825 (m), 694 (m), 617 (m), 250 (w), 206 (w), 112 (s). Anal. Calculated for C₆₆H₅₄N₂O₇P₅U₁: C, 54.89; H, 3.92; N, 1.91; P, 10.56; U, 16.24. Found: C, 54.18; H, 3.68; N, 1.86; P, 9.94; U, 15.31.

Synthesis of [UO₂(TPIP)₂]₂
NaTPIP (144 mg, 0.33 mmol) was suspended in absolute ethanol (10 mL) and added to a stirred solution of uranyl nitrate hexahydrate (85 mg, 0.17 mmol) in deionised water (10 mL) to produce a cloudy green solution. After stirring for 1 h, the solution was filtered, rinsed with absolute ethanol and the solid left to air dry. The solid was collected in a sample vial and dissolved in DCM (10 mL) and left to stand overnight before layering with hexane. Small green crystals formed after 2 days of standing (138 mg, 37%). UV/vis (DCM): λ_{max} / nm (ε / cm³mol⁻¹cm⁻¹) = 408 (16), 419 (19), 431 (20), 444 (18), 456 (14). ³¹P-{¹H} NMR (CD₂Cl₂, 162 MHz) δ (ppm): 24.9 (s); ¹H NMR (CD₂Cl₂, 400 MHz) δ (ppm): 7.26 (m, 2H, phCH), 7.95 (m, 3H, phCH); ¹³C-
\[^1\text{H}\] NMR (CD$_2$Cl$_2$, 101 MHz) \(\delta\) (ppm): 128.5 (d, \(^2J_{PC} = 13.0\) Hz, \(o\)-ph), 131.4 (s, \(p\)-ph), 131.6 (d, \(^3J_{PC} = 11.5\) Hz, \(m\)-ph). IR (3500–400 cm\(^{-1}\), solid sample on ATR cell): 3055 (m), 3010 (w), 2956 (m), 2922 (m), 2871 (w), 2856 (w), 2360 (m), 2339 (w), 2309 (w), 1958 (w), 1591 (m), 1519 (m), 1483 (m), 1224 (s), 1204 (s), 1179 (m), 1159 (m), 1122 (s), 1085 (s), 1058 (s), 1036 (s), 1020 (s), 994 (s), 915 (s), 853 (m), 746 (s), 724 (s), 689 (s), 616 (w), 599 (w), 586 (w), 514 (s), 500 (sh), 480 (s), 464 (s), 449 (s), 437 (s), 428 (s), 418 (s), 403 (s); Raman (solid in glass capillary, 3500 – 50 cm\(^{-1}\)): 3063 (s), 1592 (s), 1574 (s), 1184 (m), 1160 (m), 1136 (m), 1111 (m), 1029 (m), 1000 (s), 839 (m), 817 (w), 689 (m), 674 (m), 619 (m), 119 (s), 85 (s).

Anal. Calculated for C$_{96}$H$_{80}$N$_{4}$O$_{12}$P$_{8}$U$_{2}$C$_{6}$H$_{14}$: C, 53.46; H, 4.13; N, 2.44; P, 10.81; U, 20.77. Found: C, 53.31; H, 3.83; N, 2.41; P, 10.91; U, 21.06.

**Synthesis of [UO$_2$(TPIP)$_2$]$_3$.0.5C$_6$H$_{14}$**

*Method 1*

NaTPIP (45 mg, 0.10 mmol) was suspended in absolute ethanol (5 mL) and added to a stirred solution of uranyl nitrate hexahydrate (26 mg, 0.052 mmol) in deionised water (5 mL) to produce a cloudy green solution. After stirring for 1 h. the solution was filtered, rinsed with absolute ethanol and the solid left to dry. The solid was collected in a sample vial and dissolved in DCM (5 mL) followed by immediate layering with hexane. Green needles were deposited on the side after a few days. Characterisation of the needles was consistent with previous reports.$[^4]$ UV/vis (DCM): \(\lambda_{\text{max}}/\text{nm (}\varepsilon/\text{cm}^3\text{mol}^{-1}\text{cm}^{-1}) = 410 \text{ (41), 422 \text{ (51), 431 \text{ (59), 444 \text{ (50), 455 \text{ (28).}}}

*Method 2*

NaTPIP (143 mg, 0.33 mmol) was suspended in absolute ethanol (10 mL) and added to a stirred solution of uranyl nitrate hexahydrate (83 mg, 0.17 mmol) in deionised water (10 mL) to produce a cloudy green solution. After stirring for 1 h. the pale green solution was filtered, rinsed with absolute ethanol and the solid left to dry. The solid was collected in a sample vial and dissolved in benzene (5 mL) followed by immediate layering with hexane. Green needles deposited on the side after a few days were characterised as [UO$_2$(TPIP)$_2$]$_3$.0.5C$_6$H$_{14}$ (175 mg, 32 %).

**Synthesis of [UO$_2$(TPIP)$_2$]$_3$.2C$_6$H$_6$**
NaTPIP (45 mg, 0.10 mmol) was suspended in absolute ethanol (5 mL) and added to a stirred solution of uranyl nitrate hexahydrate (26 mg, 0.052 mmol) in deionised water (5 mL) to produce a cloudy green solution. After stirring for 1 h, the solution was filtered, rinsed with absolute ethanol and the solid left to air dry. The solid was collected in a sample vial, dissolved in benzene (5 mL) and left to stand overnight before layering with hexane. Pale green crystals deposited after a few days standing were characterised as [UO$_2$(TPIP)$_2$]$_3$.2C$_6$H$_6$ (51 mg, 30 %). UV/vis (DCM): $\lambda_{\text{max}}$/ nm ($\varepsilon$/ cm$^3$ mol$^{-1}$cm$^{-1}$) = 411 (29), 420 (39), 431 (45), 444 (37), 456 (20). $^{31}$P-$^1$H NMR (CD$_2$Cl$_2$, 162 MHz) $\delta$ (ppm): 25.1 (s); $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) $\delta$ (ppm): 7.32 (m, 2H, o-ph), 7.39 (m, 1H, p-ph), 8.03 (m, 2H, m-ph); $^{13}$C-$^1$H NMR (CD$_2$Cl$_2$) $\delta$ (ppm): 128.5 (d, $^2$J$_{PC}$ = 13.5 Hz, o-ph), 128.7 (s, i-ph), 131.3 (s, p-ph), 131.6 (d, $^3$J$_{PC}$ = 12.0 Hz, m-ph). IR (3500–400 cm$^{-1}$, solid sample on ATR cell): 3057 (w), 3017 (w), 2922 (w), 2969 (w), 1977 (w), 1593 (w), 1486 (w), 1437 (m), 1310 (m), 1290 (m), 1271 (m), 1205 (m), 1178 (m), 1122 (s), 1076 (m), 1057 (s), 1038 (s), 1024 (s), 998 (s), 913 (s), 855 (w), 814 (m), 798 (m), 752 (m), 726 (s), 690 (s), 582 (m), 564 (m), 550 (s), 541 (s), 519 (s), 514 (s), 509 (s), 505 (s), 494 (s), 489 (s), 481 (s), 476 (m), 468 (s), 458 (s), 453 (s), 447 (m), 439 (s), 434 (s), 428 (s), 421 (s), 414 (s), 404 (s); Raman (solid on glass slide, 3500 – 100 cm$^{-1}$): 3065 (w), 1593 (s), 1574 (w), 1186 (w), 1165 (w), 1115 (w), 1029 (m), 999 (s), 836 (m), 816 (m), 698 (m), 689 (m), 617 (m), 247 (m), 201 (m), 111 (s). Anal. Calculated for C$_{144}$H$_{120}$N$_6$O$_{18}$P$_8$U$_3$.2C$_6$H$_6$: C, 54.08; H, 3.84; N, 2.43; P, 10.73; U, 20.61. Found: C, 53.92; H, 3.71; N, 2.42; P, 10.48; U, 19.87.

**Synthesis of [UO$_2$(TPIP)$_2$]$_3$.CH$_2$Cl$_2$**

A powdered sample of [UO$_2$(TPIP)$_2$]$_3$.2C$_6$H$_6$ (50 mg, 0.015 mmol) that had been stored under argon for several months was dissolved in DCM (10 mL) and layered with hexane. Green crystals that formed in the sample vial after 2 days were characterised as [UO$_2$(TPIP)$_2$]$_3$.CH$_2$Cl$_2$. UV/vis (DCM): $\lambda_{\text{max}}$/ nm ($\varepsilon$/ cm$^3$ mol$^{-1}$cm$^{-1}$) = 411 (27), 421 (33), 432 (40), 444 (32), 454 (19). $^1$H NMR (CD$_2$Cl$_2$) $\delta$ (ppm): 7.24 – 7.46 (m, 3H, phC), 8.02 (m, 2H, phC). IR (3500–400 cm$^{-1}$, solid sample on ATR cell): 3057 (w), 3002 (w), 2961 (m), 2294 (m), 2857 (m), 2363 (w), 2329 (w), 1724 (w), 1590 (w), 1479 (w), 1430 (m), 1234 (s), 1200 (s), 1179 (s), 1148 (m), 1120 (s), 1083 (s), 1060 (s), 1025 (s), 1013 (s), 995 (s), 913 (s), 857 (m), 831 (m), 745 (m), 724 (s), 689 (s), 618 (w), 583 (m), 550 (m), 509 (s), 486 (m), 458 (m), 439 (m), 429 (w), 417 (m), 403 (m); Raman (solid in glass capillary, 3500 – 50 cm$^{-1}$): 3058 (s), 1593 (s), 1486 (w), 1437 (m), 1310 (m), 1271 (m), 1205 (m), 1178 (m), 1122 (s), 1076 (m), 1057 (s), 1038 (s), 1024 (s), 998 (s), 913 (s), 855 (w), 814 (m), 798 (m), 752 (m), 726 (s), 690 (s), 582 (m), 564 (m), 550 (s), 541 (s), 519 (s), 514 (s), 509 (s), 505 (s), 494 (s), 489 (s), 481 (s), 476 (m), 468 (s), 458 (s), 453 (s), 447 (m), 439 (s), 434 (s), 428 (s), 421 (s), 414 (s), 404 (s); Raman (solid on glass slide, 3500 – 100 cm$^{-1}$): 3065 (w), 1593 (s), 1574 (w), 1186 (w), 1165 (w), 1115 (w), 1029 (m), 999 (s), 836 (m), 816 (m), 698 (m), 689 (m), 617 (m), 247 (m), 201 (m), 111 (s). Anal. Calculated for C$_{144}$H$_{120}$N$_6$O$_{18}$P$_8$U$_3$.2C$_6$H$_6$: C, 54.08; H, 3.84; N, 2.43; P, 10.73; U, 20.61. Found: C, 53.92; H, 3.71; N, 2.42; P, 10.48; U, 19.87.
1555 (m), 1181 (w), 1159 (m), 1028 (m), 1001 (s), 838 (m), 825 (s), 771 (m), 693 (m), 616 (m), 266 (m), 255 (w), 118 (s), 85 (s). Anal. Calculated for C_{144}H_{120}N_6O_{18}P_8U_3: C, 52.28; H, 3.66; N, 2.54; P, 11.23; U, 21.58. Found: C, 52.80; H, 3.38; N, 2.46; P, 10.90; U, 21.04.

Synthesis of \{Na[UO_2(TPIP)_2]_2(\mu_2\text{-TPIP})\}

NaTPIP (9 mg, 0.021 mol) was suspended in absolute ethanol (5 mL) and added to a stirred solution of uranyl nitrate hexahydrate (5 mg, 0.010 mol) in deionised water (5 mL) to produce a cloudy green solution. After stirring for 1 h, the solution was filtered, rinsed with absolute ethanol and the solid left to dry. The solid was collected in a sample vial and dissolved in toluene (5 mL), sonicated and immediately layered with hexane. Small green crystals deposited on the side were characterised as \{Na[UO_2(TPIP)_2]_2(\mu_2\text{-TPIP})\}. A quantity of uncharacterised pale green powder also precipitated in the base of the sample vial.

Synthesis of \{K[UO_2(TPIP)_2]_2(\mu_2\text{-TPIP})\}

KTPIP (60 mg, 0.13 mmol) was suspended in absolute ethanol (5 mL) and added to a stirred solution of uranyl nitrate hexahydrate (34 mg, 0.068 mmol) in deionised water (5 mL) to produce a cloudy green solution. After stirring for 1 h, the solution was filtered, rinsed with absolute ethanol and the solid left to dry. The solid was collected in a sample vial and dissolved in toluene (10 mL), sonicated and immediately layered with hexane. Small green crystals were deposited on the side. A large quantity of uncharacterised pale green powder also precipitated in the base of the sample vial.

Attempted Synthesis of Uranyl(V) TPIP Complexes

Electrochemical reductions of uranyl(VI) TPIP complexes

Methods 1-4

Bu$_4$NBPh$_4$ (210 mg, 0.374 mmol) in DCM (5 mL) was degassed with nitrogen prior to the addition of uranyl(VI) TPIP complex (0.005 mmol: 1: UO$_2$(TPIP)$_2$THF, 5.5 mg; 2: UO$_2$(TPIP)$_2$Ph$_3$PO, 6.7 mg; 3 [UO$_2$(TPIP)$_2$]$_3$.1/2C$_6$H$_{14}$, 16.3 mg; 4 [UO$_2$(TPIP)$_2$]$_3$.2C$_6$H$_6$, 16.3 mg). Electrochemical measurements were then recorded using a platinum disc working electrode.

Attempted reduction of [UO$_2$(TPIP)$_2$Py]
[UO₂(TPIP)₂Py] (35 mg, 0.030 mmol) and KCp (3 mg, 0.030 mmol) were dissolved in anhydrous pyridine and stirred overnight. Layering of the brown solution with anhydrous hexane led to the formation of crystals of [UO₂(TPIP)₂Py].

**Attempted reduction of [UO₂(TPIP)₂Ph₃PO]**

[UO₂(TPIP)₂Ph₃PO] (14 mg, 0.010 mmol) and KCp (1 mg, 0.010 mmol) were dissolved in anhydrous pyridine and stirred overnight. Layering of the brown solution with anhydrous hexane led to the formation of crystals of [UO₂(TPIP)₂Py].

UV/vis (py): \(\lambda_{\text{max}}/\text{nm} = 341, 352, 416, 428, 440, 550, 671\).

\(^1\)H NMR (C\(_6\)D\(_6\), 400 MHz) \(\delta/\text{ppm}: 6.59-7.07/\text{overlapping peaks}, 7.66/\text{dd}, ^3J_{HH} = 6.0/\text{Hz}, ^4J_{HH} = 2.5/\text{Hz}, 7.76/\text{t}, ^3J_{HH} = 9.0/\text{Hz}, 7.99/\text{br}, 8.26/\text{br}, 8.45-8.56/\text{overlapping signals}, 8.64/\text{br}\).

\(^{31}\)P\{-\(^1\)H\} NMR (C\(_6\)D\(_6\), 162 MHz) \(\delta/\text{ppm}: 15.7/\text{s}, 22.1/\text{br}, 23.2/\text{s}, 25.0/\text{s}, 25.4/\text{s}, 24.7/\text{s}\).

**Attempted reduction of [UO₂(TPIP)₂MeCN]**

[UO₂(TPIP)₂MeCN] (11 mg, 0.010 mmol) and KCp (1 mg, 0.010 mmol) were dissolved in anhydrous MeCN and stirred overnight resulting in a green/brown suspension. UV/vis (MeCN): \(\lambda_{\text{max}}/\text{nm} = 322, 424/\text{sh}, 571, 651\).

**Attempted reduction of [UO₂(TPIP)₂THF]**

**Method 1**

[UO₂(TPIP)₂THF] (25 mg, 0.021 mmol) and KCp (2 mg, 0.021 mmol) were dissolved in anhydrous THF and stirred overnight. Attempts to crystallise the orange solution by layering with anhydrous hexane failed. UV/vis (THF): \(\lambda_{\text{max}}/\text{nm} = 349, 425, 571, 651\).

\(^1\)H NMR (C\(_6\)D\(_6\), 400 MHz) \(\delta/\text{ppm}: 6.74/\text{br}, 6.94/\text{m}, 8.29/\text{br}, 7.99/\text{br}, 8.50/\text{br}, 8.64/\text{br}\).

\(^{31}\)P\{-\(^1\)H\} NMR (C\(_6\)D\(_6\), 162 MHz) \(\delta/\text{ppm}: 22.8/\text{br}\).

**Method 2**

[UO₂(TPIP)₂THF] (12 mg, 0.011 mmol) was dissolved in anhydrous \(d_6\)-benzene (0.7 mL), to which potassium was added (~ 1 mg, 0.026 mmol). The resulting green solution left to stir over the weekend to leave a brown solution with a grey precipitate, The solution was filtered through glass wool.

**Method 3**

[UO₂(TPIP)₂THF] (9 mg, 0.008 mmol) was dissolved in anhydrous \(d_6\)-benzene (0.7 mL), to which KC₈ (1 mg, 0.008 mmol) was added. The green solution was stirred, producing a
cobalt-blue solution after one hour. Filtration through glass wool and layering with anhydrous hexane led to the formation of tiny blue crystals, which were too small to be analysed by single crystal X-ray diffraction. $^{31}$P-$^1$H NMR (C$_6$D$_6$, 162 MHz) $\delta$ (ppm): 29.1 (s), 36.5 (s), 37.6 (br), 38.8 (d, $^3$J$_{PH} = 4.0$ Hz), 39.5 (br), 48.5 (s).

Allowing the solution to stir overnight produced a brown solution with a grey precipitate.

**Method 4**

[UO$_2$(TPIP)$_2$THF] (20 mg, 0.017 mmol) was dissolved in anhydrous $d_5$-pyridine (0.7 mL). To this Cp*$^2$Co (4 mg, 0.012 mmol) was added, resulting in a colour change from yellow to orange/brown. $^{31}$P-$^1$H NMR (C$_6$D$_6$, 162 MHz) $\delta$ (ppm): 24.4 (s), 24.7 (br), 25.9 (s), 31.1 (s), 31.3 (s), 31.4 (s), 31.8 (s). $^1$H NMR (C$_6$D$_6$, 400 MHz) $\delta$ (ppm): 7.30 (m), 7.45 (m), 7.97 (m), 8.15 (m), 8.31 (m).

**Attempted reduction of [UO$_2$(TPIP)$_2$]$_3$**

Reaction of [UO$_2$(TPIP)$_2$]$_3$ (10 mg, 0.003 mmol) with KC$_8$ (1 mg, 0.008 mmol) in anhydrous C$_6$D$_6$ with stirring overnight led to the formation of a brown solution with a grey precipitate.

**Attempted comproportionation reaction**

[UO$_2$(TPIP)$_2$]$_2$ (11 mg, 0.005 mmol) and UI$_4$ (5 mg, 0.005 mmol) were dissolved in anhydrous $d_6$-benzene and stirred overnight. The resulting brown solution was layered in hexane, producing a pale brown precipitate. Raman (solid in glass capillary, 3500 – 50 cm$^{-1}$): 3240 (br), 3059 (s), 1590 (m), 1158 (w), 1092 (w), 999 (s), 118 (s), 86 (s). $^1$H NMR (C$_6$D$_6$, 400 MHz) $\delta$ (ppm): 6.27 (m), 6.74 (s), 6.97 (s), 8.18 (br), 9.15 (br). $^{31}$P-$^1$H NMR (C$_6$D$_6$, 162 MHz) $\delta$ (ppm): 26.53 (s).

**Reaction of uranyl(V) triflate with NaTPIP**

**Method 1**

{[UO$_2$(py)$_3$]$_2$[K$_3$(OTf)$_3$].Py} (80 mg, 0.036 mmol) and NaTPIP (16 mg, 0.036 mmol) were dissolved in anhydrous pyridine and stirred overnight. Layering of the brown solution with hexane led to the isolation of [UO$_2$(TPIP)$_2$]Py. UV/vis (pyridine): $\lambda_{max}$/nm = 405 (br), 677, 845. $^1$H NMR (C$_6$D$_6$, 400 MHz) $\delta$ (ppm): 6.66 (br, 2H, o-ph), 6.96 (br, 1H, p-ph), 8.55 (br, 2H, m-ph).
**Method 2**

\[
\{\text{UO}_2(\text{py})_5\}\{\text{K}_3(\text{OTf})_3\}\cdot\text{Py} \quad (10 \text{ mg, 0.004 mmol}) \text{ and NaTPIP (4 mg, 0.009 mmol) were dissolved in anhydrous pyridine and stirred overnight. Layering of the brown solution with hexane led to the isolation of [UO}_2(\text{TPIP})_2\text{Py}]. \text{ UV/vis (pyridine): } \lambda_{\text{max}}/\text{nm} = 405 \text{ (br), 424 (sh), 641, 850.} \]

\[1^H \text{ NMR (C}_6\text{D}_6, 400 \text{ MHz}) \delta (ppm): 6.67 (dd, 3J_{HH} = 7.0 \text{ Hz, } 4J_{HH} = 2.0 \text{ Hz, 2H, o-ph}, 6.99 (t, 3J_{HH} = 8.0 \text{ Hz, 1H, p-ph}), 7.65 (dd, 3J_{HH} = 6.0 \text{ Hz, } 4J_{HH} = 2.5 \text{ Hz, 0.02H}), 7.99 \text{ (br, 0.03H), 8.53 (br, 2H, m-ph).} \]

\[31^P-{^1H} \text{ NMR (C}_6\text{D}_6, 162 \text{ MHz}) \delta (ppm): 16.0 \text{ (br), 24.67 (s).} \]

\[13^C-{^1H} \text{ NMR (C}_6\text{D}_6, 101 \text{ MHz}) \delta (ppm): 123.5 \text{ (s, o-ph), 135.2 (s, p-ph), 150.4 (s, m-ph).} \]

**Method 3**

\[\text{[UO}_2(\text{OTf})_\text{THF})_{1.5}] \quad (7 \text{ mg, 0.013 mmol}) \text{ and NaTPIP (15 mg, 0.034 mmol) were dissolved in anhydrous THF and stirred for an hour. Layering the yellow/brown solution with hexane led to single crystals of [Na}_3(\text{TPIP})_2(\text{OTf})(\text{THF})_3].\text{THF.} \]

**Synthesis of Tetraphenylimidodiphosphinates.**

**Synthesis of NaTPIP**

**Method 1**

The synthesis was performed as described in the literature.\[^5\]

**Method 2**

The synthesis was performed as described in the literature\[^5\] except that after addition of hexamethyldisilazane (1.25 mL, 6.00 mmol), the solution was sonicated for 5 min. and all volatiles were removed under reduced pressure. The sample was transferred to the glovebox and filtered with anhydrous hexane. The white solid was re-dissolved in anhydrous toluene and removed from the glovebox. 3-Chloroperbenzoic acid (475.5 mg, 2.76 mmol) was dissolved in chloroform and added dropwise with the resulting solution left to stir for 5 days. Saturated sodium hydrogen carbonate was then added and all volatiles removed under reduced pressure. Washing with water lead to a white solid identified as HTPIP (284 mg, 0.69 mmol). Dissolution in methanol was followed by the addition of NaOH (27 mg, 0.68 mmol) with stirring for 2 h. All solvents were removed under reduced pressure and the product washed with hexane and DCM before being recrystallised from ethanol to yield NaTPIP (160 mg, 10 %). Characterisation was consistent with the literature.\[^5\]
Synthesis of KTPIP
The synthesis was performed as described in the literature.[5]

Synthesis of NaF_TPIP from FPh_2PBr

Method 1 – the preparation of HP(C_6F_5)_2
The synthesis was performed as described in the literature.[6] However, attempts to isolate HN(OP(C_6F_5)_2)_2 yielded HP(C_6F_5)_2. ^1^H NMR (d_6-DMSO, 400 MHz) δ (ppm): 5.76 (s, 1H, HP). ^3^P-^1^H NMR (d_6-DMSO, 162 MHz) δ (ppm): -11.0 (s, HP).

Stirring in methanol (5 mL) with KOH (92 mg, 1.64 mmol) resulted in an unidentified potassium salt of the phosphine oxide. ^3^P-^1^H NMR (d_6-DMSO, 162 MHz) δ (ppm): -14.7 (s). ^1^3^C-^1^H NMR (d_6-DMSO, 101 MHz) δ (ppm): 116.3 (dm, ^2^J_FC = 110.5 Hz, i-ph), 136.6 (dm, ^1^J_FC = 258.5 Hz), 140.8 (dm, ^1^J_FC = 242.5 Hz), 146.1 (dm, ^1^J_FC = 253.0 Hz) ^1^9^F NMR (d_6-DMSO, 374 MHz) δ (ppm): -165.13 (tm, ^3^J_FF = 24.5 Hz, p-ph), -156.06 (tm, ^3^J_FF = 21.5 Hz, m-ph), -136.88 (dm, ^2^J_FF = 25.5 Hz, o-ph). Anal. Found: C, 32.85; H, 0.00; N, 0.36, K, 7.12; P, 6.95.

Method 2
The synthesis was performed as described in the literature[6] except that after addition of hexamethyldisilazane (0.50 mL, 2.40 mmol), the solution was refluxed for 5 days and all volatiles were removed under reduced pressure. The sample was transferred to the glovebox and filtered with anhydrous hexane. The white solid was redissolved in anhydrous toluene and removed from the glovebox. 3-Chloroperbenzoic acid (100 mg, 0.58 mmol) was dissolved in chloroform and added dropwise with the resulting solution left to stir for 5 days. Saturated sodium hydrogen carbonate was then added and all volatiles removed under reduced pressure. Washing with water led to a white solid identified as F_TPIP (150 mg, 0.19 mmol). Dissolution in methanol was followed by the addition of NaOH (12 mg, 0.30 mmol) with stirring for two hours. All solvents were removed under reduced pressure and the product washed with hexane and DCM before being recrystallised from ethanol to yield NaF_TPIP (66 mg, 4 %). Characterisation was consistent with the literature.[6]

Synthesis of NaF_TPIP from FPhBr

Method 1
The synthesis was performed as described in the literature. However, upon attempts to separate \((C_6F_5)PCl_2\), \((C_6F_5)_2PCl\) and \((C_6F_5)_3P\) by fractional distillation, the low volatility of the products led to the contamination of the desired \((C_6F_5)_2PCl\) with the first product. The literature procedure was followed therein for the combined products. After washing of the oxidised product, \(\textsuperscript{31}P\) NMR spectroscopy confirmed the failure of the reaction. \(\textsuperscript{31}P\) NMR (\(d_6\)-DMSO, 162 MHz) \(\delta\) (ppm): -4.8 (br), -14.8 (s).

**Method 2**

\(PCl_2NEt_2\) was synthesised as described in the literature. To a separate flamed out Schlenk tube, bromopentafluorobenzene (0.7 mL, 5.62 mmol) was dissolved in anhydrous diethyl ether (10 mL). The solution was cooled in an acetone-N\(_2\)(l) bath and turned yellow upon dropwise addition of \(^9\)BuLi (4 mL, 1.6 M). The solution was left to stir for 1 hour, after which time \(PCl_2NEt_2\) (0.4 mL, 2.74 mmol) was added dropwise via cannula. The resulting prismatic series of colour changes leave a brown/purple solution which was left to stir overnight and then quenched with propan-2-ol/toluene. The solution was filtered incompletely via cannula and filter funnel into an empty flamed out Schlenk tube. The supernatant was cooled in an acetone-N\(_2\)(l) bath and \(HCl\) (1.45 mL) in anhydrous THF (17 mL) was added dropwise and the solution left to stir overnight. Removal of all volatiles under reduced pressure led to the isolation of unidentified products. \(^1H\) NMR (\(d_6\)-DMSO, 400 MHz) \(\delta\) (ppm): 1.85 (q, \(^3J_{HH} = 6.0\) Hz, CH\(_2\)), 3.75 (t, \(^3J_{HH} = 6.0\) Hz). \(\textsuperscript{31}P\)-\(^1H\) NMR (\(d_6\)-DMSO, 162 MHz) \(\delta\) (ppm): 4.0 (m), 12.1 (m), 25.4 (m), 26.0 (m), 26.5 (m), 27.0 (m), 28.5 (br), 32.2 (m). \(\textsuperscript{19}F\) NMR (\(d_6\)-DMSO, 374 MHz) \(\delta\) (ppm): -160.69 – -159.03 (overlapping signals), -155.59 (t, \(^2J_{FF} = 21.0\) Hz), -154.97 (dt, \(^2J_{FF} = 20.5\) Hz, \(^4J_{FF} = 6.0\) Hz), -151.46 – -148.58 (overlapping signals), -140.88 – -137.97 (overlapping signals), -137.92 – -136.17 (overlapping signals), -132.53 – -126.91 (overlapping signals).

**Method 3**

\(PCl_2NEt_2\) and \(P(NEt_2)_3\) were synthesised as described in the literature. Pentafluorobromobenzene (3.3 mL, 26.5 mmol) was dissolved in anhydrous benzonitrile (5 mL) in a flamed out Schlenk tube. Trimethylsilylchloride (3.3 mL, 26.0 mmol) was added and the solution freeze-thaw degassed. The solution was cooled to -35°C and \(P(NEt_2)_3\) (7.3 mL, 26.6 mmol), was added dropwise with stirring with the resulting yellow solution stirred overnight. After vacuum sublimation, the
clear distillate was cannula transferred dropwise to a suspension of silver fluoride (1.32 g, x mmol) in anhydrous propionitrile (30 mL) with stirring. After 3 hours of stirring the suspension was cooled in an acetone-N₂(l) bath and a mixture of PCl₂NEt₂ (0.71 mL, 10.4 mmol) in anhydrous propionitrile (2 mL) was transferred to the solution dropwise over 20 minutes. The resulting orange solution/suspension was stirred over a weekend. The product was filtered over celite and all solvents were removed under reduce pressure to leave a brown/orange residue. The residue was dissolved in anhydrous toluene (5 mL) and cooled in an acetone-N₂(l) bath. HCl (1.00 mL) in anhydrous THF (12 mL) was added dropwise and the solution left to stir overnight, followed by cannula filtration of the solution at -78 °C. ³¹P-{¹H} NMR (CDCl₃, 162 MHz) δ (ppm): 4.2 (br), 6.4 (br).

**Synthesis of a Uranyl(VI) F₅TPIP Complex**

**Synthesis of UO₂(F₅TPIP)₂Py**
Na⁵TPIP (23 mg, 0.029 mmol) was suspended in absolute ethanol (5 mL) and added to a stirred solution of uranyl nitrate hexahydrate (7 mg, 0.014 mmol) in deionised water (5 mL) to produce a cloudy green solution. After stirring for 1 h the solution was filtered, rinsed with absolute ethanol and the solid left to dry. The solid was washed into a sample vial with pyridine (3 mL) and immediately layered with hexane. UV/vis (DCM): λ_{max}/nm = 236, 266 (sh), 298 (sh), 419, 490 (br). ³¹P-{¹H} NMR (CD₂Cl₂) δ (ppm): -12.5 (br); ¹⁹F NMR (CD₂Cl₂) δ (ppm): -137.88 (br), -136.47 (br), -134.35 (br).

**Synthesis of Uranyl(VI) Fluorinated acac Complexes**

**Synthesis of [UO₂(hfac)₂Et₂O]**
Following the literature procedure,[¹⁰] the sublimination of [UO₂(hfac)₂H₂O] at 50 °C at 0.06 mbar led to the deposition of yellow crystals. UV/vis (DCM): λ_{max}/nm = 267, 298, 363, 417, 429, 444, 456, 484, 502. ¹H NMR (CD₂Cl₂, 400 MHz) δ (ppm): 1.62 (br, 6H, CH₃), 4.89 (br, 4H, CH₂), 6.74 (s, 2H, CH); ¹⁹F NMR (CD₂Cl₂, 374 MHz) δ (ppm): -78.26 (s, 9F, CF₃), -78.05 (s, 9F, CF₃). IR (3500-600 cm⁻¹, solid sample on ATR cell): 3143 (w), 2923 (vs), 2853 (vs), 2359 (m), 2339 (m), 1653 (s), 1599 (m), 1457 (vs), 1376 (s), 1255 (s), 1211 (s), 1163 (s), 1031 (m), 948 (m), 899 (w), 804 (m), 776 (m), 742 (m), 668 (m), 658 (m).
Synthesis of \([\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}]\)

\([\text{UO}_2(\text{hfac})_2\text{H}_2\text{O}]\) was used as prepared by D. Whittaker.\[^{[11]}\]

Synthesis of \([\text{UO}_2(\text{hfac})_2]_4\)

\([\text{UO}_2(\text{hfac})_2]_4\) was used as prepared by D. Whittaker\[^{[11]}\] and A. Formanuik.\[^{[12]}\]

Synthesis of \([\text{UO}_2(\text{hfac})_2\text{THF}]\)

\([\text{UO}_2(\text{hfac})_2\text{THF}]\) (50 mg, 0.019 mmol) was dissolved in anhydrous THF 1:1 diethyl ether (5 mL) and removed from the glovebox. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz) \(\delta\) (ppm): 2.41 (s, 4H, THF), 5.01 (s, 4H, THF), 6.64 (s, 2H, (OCCH); \(^19\)F NMR (CD\(_2\)Cl\(_2\), 374 MHz) \(\delta\) (ppm): -74.39 (s), 74.84 (s), 75.89 (s), 76.02 (s), 78.91 (s).

Synthesis of \([\text{UO}_2(\text{hfac})_2\text{Et}_2\text{O}][\text{UO}_2(\text{hfac})_2]_4\)

\([\text{UO}_2(\text{hfac})_2\text{THF}]\) was sublimed following the literature procedure,\[^{[10]}\] leading to the formation of yellow-orange crystals.

Synthesis of \([\text{UO}_2(\text{tta})_2\text{MeOH}]\)

\([\text{UO}_2(\text{tta})_2\text{MeOH}]\) was used as prepared by K. Tucker.\[^{[13]}\]

Synthesis of \([\text{UO}_2(\text{tta})_2]_2\)

\([\text{UO}_2(\text{tta})_2]_2\) was used as prepared by K. Tucker\[^{[13]}\] and A. Formanuik.\[^{[12]}\]

Synthesis of \([\text{U(tta)}_4]\)

\([\text{U(tta)}_4]\) (10 mg, 0.007 mmol) was dissolved in DCM (2 mL) and layered with hexane (0.7 mL). Over the course of a year, small red crystals deposited. UV/vis (DCM): \(\lambda_{max}\) nm = 285, 336, 378. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz) \(\delta\) (ppm): 6.88 (br, 4H), 7.34 (br, 4H), 7.89 (br, 4H), 8.23 (br, 4H), 12.62 (s, 4H, (OCCH); \(^19\)F NMR (CD\(_2\)Cl\(_2\), 374 MHz) \(\delta\) (ppm): -79.86 (s, 6F), -77.23 (t, 34.0 Hz, 6F).

**Attempted Synthesis of Uranyl(V) Fluorinated acac Complexes**

**Attempted reduction of \([\text{UO}_2(\text{hfac})_2]_4\)**

*Method 1*
[UO₂(hfac)₂]₄ (17 mg, 0.006 mmol) and KCp (3 mg, 0.028 mmol) were dissolved in C₆D₆ (1 mL) and stirred overnight to leave an orange solution with brown precipitate. ¹H NMR (C₆D₆, 400 MHz) δ (ppm): 5.59 (br), 5.73 (br), 5.92 (br), 6.11 (br), 6.16 (br), 6.24 (br), 6.46 (s, [UO₂(hfac)₂]₄), 6.50 (br), 7.68 (br), 8.10 (br); ¹⁹F NMR (C₆D₆, 374 MHz) δ (ppm): -81.23 (s), -77.57 (br, [UO₂(hfac)₂]₄), -73.84 (s), -73.11 (s), -68.06 (s), -67.11 (s), -64.50 (s).

Method 2
[UO₂(hfac)₂]₄ (16 mg, 0.006 mmol) and K (1 mg, 0.026 mmol) were dissolved in C₆D₆ (1 mL) and stirred overnight to leave an orange solution with brown precipitate. ¹H NMR (C₆D₆, 400 MHz) δ (ppm): 6.43 (s, [UO₂(hfac)₂]₄), 6.48 (s), 6.51 (s), 6.67 (s), 8.32 (s), 10.36 (s), 10.58 (s), 11.46 (s); ¹⁹F NMR (C₆D₆, 374 MHz) δ (ppm): -87.11 (br), -86.48 (br), -85.99 (s), -85.02 (br), -84.60 (br), -83.66 (br), -81.74 (br), -81.39 (s), -79.62 (s), -77.64 (s), -77.54 (s, [UO₂(hfac)₂]₄), -77.46 (s, [UO₂(hfac)₂]₄), -75.08 (s), -75.53 (s), -74.94 (s), -74.82 (br), -73.50 (s).

Attempted reduction of [UO₂(tta)₂]₂
Method 1
[UO₂(tta)₂]₂ (10 mg, 0.007 mmol) and KCp (1 mg, 0.009 mmol) were dissolved in C₆D₆ (1 mL) and stirred overnight to yield an orange solution. ¹H NMR (C₆D₆, 400 MHz) δ (ppm): 5.18 (br), 5.42 (br), 6.09 (br), 6.13 (br), 6.36 (br), 6.57 (br), 6.84 (br, [UO₂(tta)₂]₂), 6.97 (m), 7.74 (br), 8.54 (br), 9.11 (br), 12.35 (s); ¹⁹F NMR (C₆D₆, 374 MHz) δ (ppm): -81.38 (br), -77.28 (s), -75.90 (br), -74.22 (s), -73.87 (s), -73.10 (br), -71.98 (br, [UO₂(tta)₂]₂).

Method 2
[UO₂(tta)₂]₂ (15 mg, 0.011 mmol) and K (1 mg, 0.026 mmol) were dissolved in C₆D₆ (1 mL) and stirred overnight to yield a blue solution. ¹H NMR (C₆D₆, 400 MHz) δ (ppm): 5.18 (br), 5.42 (br), 6.09 (br), 6.36 (br), 6.54 (br), 6.84 (s, [UO₂(tta)₂]₂), 6.88 (br), 7.73 (br), 8.50 (br), 9.10 (br), 12.35 (s); ¹⁹F NMR (C₆D₆, 374 MHz) δ (ppm): -81.29 (br), -77.26 (s), -75.90 (br), -74.21 (s), -73.93 (br), -73.10 (br), -71.98 (br, [UO₂(tta)₂]₂).

Synthesis of Uranyl Salts

Synthesis of [UO₂Cl₂(THF)₃]
The synthesis was performed as described in the literature.[¹⁴]
Synthesis of $[\text{UO}_2(\text{OTf})_2(\text{THF})_3]$

The synthesis was performed as described in the literature.\[^{[15]}\]

Synthesis of $[\text{UO}_2\text{I}_2(\text{THF})_3]$

The synthesis was performed as described in the literature.\[^{[16]}\]

**Attempted reduction of $[\text{UO}_2\text{Cl}_2(\text{THF})_3]$**

*A Method 1*

$\text{UO}_2\text{Cl}_2(\text{THF})_3$ (41 mg, 0.074 mmol) and KCp (8 mg, 0.077 mmol) were dissolved in anhydrous pyridine (5 mL) and stirred overnight to leave a yellow/brown solution. Layering with hexane yielded crystals of $\text{UO}_2\text{Cl}_2(\text{py})_3$. UV/vis (py): $\lambda_{\text{max}}/\text{nm} = 347, 356, 393, 405, 417, 429, 443, 460, 476, 665$.

*B Method 2*

$\text{UO}_2\text{Cl}_2(\text{THF})_3$ (41 mg, 0.074 mmol) and KC$_8$ (5 mg, 0.037 mmol) were dissolved in anhydrous pyridine (5 mL) and stirred overnight to leave a yellow/brown solution. Layering with hexane yielded crystals of $\text{UO}_2\text{Cl}_2(\text{py})_3$.

Synthesis of $\{[\text{UO}_2(\text{py})_5]_2\{\text{K}_3(\text{OTf})_5\}\text{py}\}_n$

The synthesis was performed as described in the literature.\[^{[17]}\] $\text{UO}_2(\text{OTf})_2(\text{THF})_3$ (196 mg, 0.250 mmol) and KCp (37 mg, 0.360 mmol) were dissolved in anhydrous pyridine (3 mL) and stirred overnight to leave a brown solution. The solution was filtered through celite before being recrystallised from hexane. The crystals were washed with copious amounts of anhydrous toluene to yield $\{[\text{UO}_2(\text{py})_5]_2\{\text{K}_3(\text{OTf})_5\}\text{py}\}_n$ (200 mg, 35%). UV/vis (py): $\lambda_{\text{max}}/\text{nm} (\varepsilon/\text{cm}^3\text{mol}^{-1}\text{cm}^{-1}) = 456 (1632), 611, 740, 834, 839$. IR (1500-600 cm$^{-1}$, nujol mull): 1456 (vs), 1376 (s), 1260 (m), 1213 (w), 1172 (m), 1164 (sh), 1096 (m), 1032 (m), 976 (w), 895 (w), 807 (m), 727 (m).

Synthesis of $[\text{UO}_2(\text{OTf})(\text{py})_{1.3}]$

The synthesis was performed as described in the literature.\[^{[17]}\]

Synthesis of $\{[\text{UO}_2(\text{py})_5]\{\text{KI}_2(\text{py})_2\}\}_n$

The synthesis was performed as described in the literature.\[^{[17]}\]
**Synthesis of UCl₄**
UCl₄ was used as synthesised by C. de la Fontaine.[19]

**Reaction of UCl₄ with AgOTf**

*Method 1*
UCl₄ (8 mg, 0.021 mmol) and AgOTf (44 mg, 0.171 mmol) were dissolved in anhydrous THF (5 mL) and stirred over a weekend in the dark to leave a silvery gelatinous mush.

*Method 2*
UCl₄ (8 mg, 0.021 mmol) and AgOTf (43 mg, 0.167 mmol) were dissolved in anhydrous MeCN (5 mL) and stirred in the dark overnight. Recrystallisation from anhydrous THF and anhydrous hexane produced UO₂(OTf)₂(THF)₃.

**Synthesis of UI₄(Et₂O)₂**
UI₄(Et₂O)₂ was used as synthesised by S. Randall.[20]

**Synthesis of UI₃**
UI₃ was used as synthesised by S. Randall.[20]

**Synthesis of [{UO₂(py)₂₂(μ₂-O)₂(μ₃-O)(μ₂-I)}I₂(py)]₂**
UI₃ (21 mg, 0.034 mmol) and KI (4 mg, 0.024 mmol) were suspended in anhydrous pyridine* (1 mL). PyNO (2 mg, 0.021 mmol) was dissolved in anhydrous pyridine* (1 mL) and added to the first mixture to yield a brown solution. After 7 days standing an orange/yellow solution formed. Layering with hexane yielded crystals of [{UO₂(py)₂₂(μ₂-O)₂(μ₃-O)(μ₂-I)}I₂(py)]₂. *The pyridine transpired to be insubstantially anhydrous.

**Attempted synthesis of [{UO₂(py)₅}{KI₂(py)₂}]ₙ from UI₃**
The synthesis was performed as described in the literature[21] except that UI₃ (34 mg, 0.055 mmol) was used instead of UI₃(thf)₄. The solution remained yellow/brown after several weeks standing and single crystals of [{UO₂(py)₅}{KI₂(py)₂}]ₙ could not be obtained.

**Attempted comproportionation reaction of [UO₂I₂(THF)₃] and UI₄(Et₂O)₂**
UO₂I₂(THF)₃ (12 mg, 0.016 mmol), UI₄(Et₂O)₂ (14 mg, 0.016 mmol) and KI (3 mg, 0.018 mmol) were dissolved in anhydrous pyridine (3 mL) and the resulting red solution stirred over a weekend to yield an orange solution. Layering with anhydrous hexane rendered an
orange precipitate. IR (1500-600 cm\(^{-1}\), nujol mull): 1381 (vs), 1310 (s), 1262 (s), 1171 (m), 1158 (m), 1039 (w), 1008 (w), 974 (w), 894 (w), 852 (w), 810 (m), 778 (w), 726 (s), 700 (m).

**Silylation Reactions of Oligopyridines.**

**Synthesis of 6,6’-dibromo-2,2’-bipyridine and 6,6’’-dibromo-2,2’:6’,2’’-terpyridine**

The synthesis was performed as described in the literature.[22] The resulting white crystals were analysed as a mixture of 6,6’-dibromo-2,2’-bipyridine and 6,6’’-dibromo-2,2’:6’,2’’-terpyridine, from which the latter was preferentially crystallised from DCM at room temperature (yield 0.47 g, 3 %, characterisation was consistent with the literature[22]). 6,6’-Dibromo-2,2’-bipyridine was crystallised at -18 °C (yield 0.59 g, 3 %, characterisation was consistent with the literature[23]).

**Attempted silylation of 6,6’-dibromo-2,2’-bipyridine via lithium-halogen exchange**

*Method 1*
6,6’-Dibromo-2,2’-bipyridine (69 mg, 0.22 mmol) was added to a flamed out Schlenk tube under argon and dissolved in anhydrous THF (5 mL). The solution was cooled in an acetone-N₂(l) bath for 10 min. followed by the dropwise addition of nBuLi (0.50 mL, 1.6 M) via syringe with stirring. The resulting black solution was left to warm to room temperature and stirred for one hour. tert-Butyldimethylsilylchloride (138 mg, 0.92 mmol) was added to a second flamed out Schlenk tube under argon and dissolved in anhydrous THF (3 mL). The tert-butyldimethylsilylchloride solution was transferred with the use of a cannula to the lithiated 6,6’-dibromo-2,2’-bipyridine solution that had been re-cooled by an acetone-N₂(l) bath and the resulting mixture left to warm to room temperature with stirring. The reaction was quenched with deionised water. All organic solvents were removed under reduced pressure and the remaining aqueous solution was partitioned with DCM. The organic layer was collected, dried over magnesium sulphate and filtered. All volatiles were removed under reduced pressure and the residue was dissolved in diethyl ether. The solution was then filtered through celite to produce a black solid upon removal of all volatiles. 

**Method 2**

6,6’-Dibromo-2,2’-bipyridine (0.20 g, 0.64 mmol) was added to a flamed out Schlenk tube under argon and dissolved in anhydrous THF (5 mL). nBuLi (0.80 mL, 1.6 M) was added to the solution by syringe at -78°C to produce a black solution. At this point TMEDA (0.70 mL, 4.67 mmol) was added into the solution via syringe. All solvents were removed under reduced pressure and the unknown lithiated product was transferred to the glovebox.

**Method 3**

LHMDS (116 mg, 0.69 mmol) was added to a Schlenk tube in an Ar glovebox. To flamed out Schlenk tubes, 6,6’-dibromo-2,2’-bipyridine (80 mg, 0.25 mmol) and tert-butyldimethylsilylchloride (117 mg, 0.78 mmol) were added separately under argon. All three were dissolved in anhydrous THF (10 mL). The LHMDS solution was cooled in an acetone-N₂(l) bath and the 6,6’-dibromo-2,2’-bipyridine solution transferred via cannula, resulting in a pale yellow solution which was left to stir for 2 h. The solution was re-cooled in an acetone-N₂(l) bath before the addition of the tert-
butyldimethylsilylchloride solution by cannula. The reaction mixture was left to stir overnight. Absolute ethanol was then added to the mixture via syringe and the pale yellow contents of the Schlenk were transferred to a round bottomed flask, all solvents removed under reduced pressure and washed with saturated sodium hydrogen carbonate solution. The mixture was then separated into ethyl acetate and dried over magnesium sulphate. The solution was filtered and the ethyl acetate removed under reduced pressure to yield white crystals. Characterisation was consistent with the literature for 6,6’-dibromo-2,2’-bipyridine.[23]

**Method 4 – the preparation of 4,5’-di-tert-butyldimethylsilyl-6,6’-dibromo-2,2’-bipyridine**

Di-iso-propylamine (0.20 mL, 1.40 mmol) was added to a flamed out Schlenk tube under argon and dissolved in anhydrous THF (5 mL). The contents of the Schlenk were cooled in an acetone-N₂(1) bath and "BuLi (0.70 mL, 1.6 M) added by syringe to form an LDA solution. The solution was allowed to stir for 10 min. before warming to room temperature. 6,6’-Dibromo-2,2’-bipyridine (99 mg, 0.32 mmol) was added to a flamed out Schlenk tube under argon and dissolved in anhydrous THF (5 mL). The same was done for tert-butyldimethylsilylchloride (193 mg, 1.28 mmol). The 6,6’-dibromo-2,2’-bipyridine solution was then transferred via cannula to the re-cooled LDA solution, producing a black solution which was left to stir for 1 h. The tert-butyldimethylsilylchloride solution was then transferred via cannula and the solution was warmed to room temperature before quenching with a 5:2 mixture of iPrOH/toluene. The solvents were removed under reduced pressure and the powder washed with saturated sodium hydrogen carbonate solution. The product was partitioned into ethyl acetate and dried over magnesium sulphate. Ethyl acetate was removed under reduced pressure to yield 4,5’-di-tert-butyldimethylsilyl-6,6’-dibromo-2,2’-bipyridine (95 mg, 56%).
ES^+ MS (DCM) m/z 562 (90%), 563 (80%), 564 (100%), 566 (30%). ^1H NMR (CDCl₃, 400 MHz) δ (ppm): 0.31 (s, 6H, C₂Si(CH₃)₂), 0.44 (s, 6H, C₈Si(CH₃)₂), 0.97 (s, 18H, 2x SiC(CH₃)₃), 6.90 (d, ^4J_HH = 3.0 Hz, 1H, H7), 7.70 (d, ^4J_HH = 3.0 Hz, 1H, H6), 7.79 (d, ^3J_HH = 8.0 Hz, 1H, H3), 8.41 (d, ^3J_HH = 8.0 Hz, 1H, H4). ^13C-{^1H} NMR (CDCl₃, 101 MHz) δ (ppm): -3.4 (C₈Si(CH₃)₂), -6.2 (C₂Si(CH₃)₂), 17.0 (2 x SiC(CH₃)₃), 26.8 and 27.2 (2 x SiC(CH₃)₃), 105.9 (C9), 117.0 (C7), 119.0 (C4), 135.1 (C₈) 146.9 (C3), 158.9 (C5), 163.9 (C₆).

**Method 5**

tert-Butyldimethylsilylchloride (143 mg, 0.95 mmol) and 6,6'-dibromo-2,2'-bipyridine (97 mg, 0.31 mmol) were added to separate flamed out Schlenk tubes under argon. nBuLi (0.70 mL, 1.6 M) was added to a third flamed out Schlenk tube under argon and all three were dissolved in anhydrous THF (10 mL). The nBuLi solution was cooled with the use of a methanol-N₂(l) bath. The tert-butyldimethylsilylchloride solution was transferred by cannula, immediately followed by the addition of the 6,6'-dibromo-2,2'-bipyridine solution, also by cannula. The reaction mixture was quenched with absolute ethanol after being left to stir overnight. The mixture was transferred to a round bottomed flask followed by washing with saturated sodium hydrogen carbonate solution. The aromatic products were separated into ethyl acetate and dried with magnesium sulphate before filtration. The solvent of the supernatant was removed under reduced pressure to produce white crystals. Characterisation was consistent with the literature for 6,6'-dibromo-2,2'-bipyridine.^[23]

**Attempted silylation of 2,2'-bipyridine via lithium-hydrogen exchange**

![Diagram of 2,2'-bipyridine with R-Li reagent]

**Methods 1 and 2**
2,2’-Bipyridine (1: 53 mg, 0.34 mmol; 2: 54 mg, 0.35 mmol) was added to a flamed out Schlenk tube and dissolved in 1: anhydrous THF (10 mL) and 2: anhydrous toluene (10 mL). 2-Dimethylaminoethanol (0.10 mL, 0.10 mmol) was added to a flamed out Schlenk tube and dissolved in 1: anhydrous hexane (5 mL) and 2: anhydrous toluene (5 mL), to which was added n-BuLi (1.6M: 1: 1.25 mL; 2: 1.30 mL) via syringe at 0 °C before the solution was allowed to warm to room temperature. The 2,2’-bipyridine solution was cannula transferred to the re-cooled (in an acetone-N₂(l) bath) solution of lithiated 2-dimethylaminoethanol and left to stir for 1 h. tert-Butyldimethylsilylchloride (145 mg, 0.96 mmol) was added to a flamed out Schlenk tube, dissolved in anhydrous THF (10 mL) and cannula transferred to the mixture. After an hour stirring, the solution was allowed to warm to room temperature and the reaction quenched with absolute ethanol. All solvents were removed under reduced pressure and the solution washed with saturated sodium hydrogen carbonate solution, separated into ethyl acetate and dried over magnesium sulphate. The solution was filtered and the supernatant reduced to dryness to produce white crystals. Characterisation of the crystals as 2,2’-bipyridine was consistent with the literature.[24]

**Method 3**

LHMDS (175 mg, 1.05 mmol) was weighed out in an Ar glovebox and added to a Schlenk tube. tert-Butyldimethylsilylchloride (144 mg, 0.96 mmol) and 2,2’-bipyridine (55 mg, 0.35 mmol) were added to separate flamed out Schlenk tubes under argon. All three were dissolved in anhydrous diethyl ether (10 mL) and the 2,2’-bipyridine solution was cannula transferred to the acetone-N₂(l) bath cooled LHDMS solution. The resulting mixture was left to stir for 2 h. after which time the tert-butyldimethylsilylchloride solution was added by cannula and the solution left to stir overnight. Quenching with absolute ethanol was followed by removal of all solvents under reduced pressure to yield white crystals, characterisation of which was consistent with the literature for 2,2’-bipyridine.[24]

**Methods 4 and 5 – the preparation of 4-tert-butyldimethylsilyl-2,2’-bipyridine and 4,4-di-tert-butyldimethylsilyl-2,2’-bipyridine**

2,2’-Bipyridine (1: 110 mg, 0.71 mmol; 2: 55 mg, 0.36 mmol), tert-butyldimethylsilylchloride (1: 288 mg, 1.91 mmol; 2: 145 mg, 0.96 mmol) and di-isopropylamine (1: 0.40 mL, 2.80 mmol; 2: 0.20 mL, 1.40 mmol) were added to separate
flamed out Schlenk tubes and dissolved in 1: anhydrous THF (10 mL) and 2: anhydrous diethyl ether (10 mL). The di-iso-propylamine solution was cooled in an acetone-N\(_2\)(l) bath and \(^n\)BuLi (1.6 M: 1: 3.50 mL; 2: 0.80 mL) was added to it via syringe. After 15 min. of stirring the solution was allowed to warm to room temperature before being re-cooled in an acetone-N\(_2\)(l) bath. The 2,2'-bipyridine solution was cannula transferred to the LDA solution and the mixture left to stir for 1 h. The solution of tert-butylidemethylsilylchloride was then transferred via cannula to the black lithiated 2,2'-bipyridine reaction mixture and left to stir overnight, after which it was quenched with absolute ethanol. Removal of all solvents under reduced pressure and washing with saturated sodium hydrogen carbonate solution was followed by separation into ethyl acetate and drying over magnesium sulphate. Filtration of the solution and removal of the solvent of the supernatant under reduced pressure led to an orange/brown mixture. The use of a gradient elution of hexane/ethyl acetate (from a ratio of 100:0 to 0:100 of hexane:ethyl acetate) in silica gel column chromatography led to the separation of three products.

The first fraction was isolated as a yellow/brown oil of 4,4'-di-tert-butylidemethylsilyl-2,2'-bipyridine (1: 67 mg, 35%; 2: 32 mg, 24%). Accurate MS (ESI\(^+\)): \(m/z\) calculated: 385.2490; found: 385.2484. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(δ\) (ppm): 0.33 (s, 6H, C\(_3\)Si(CH\(_3\))\(_2\)), 0.35 (s, 6H, C\(_8\)Si(CH\(_3\))\(_2\)), 0.90 (s, 9H, C\(_3\)SiC(CH\(_3\))\(_3\)), 0.92 (s, 9H, C\(_8\)SiC(CH\(_3\))\(_3\)), 7.40 (td, \(^3\)J\(_{HH}\) = 5.0 Hz, \(^4\)J\(_{HH}\) = 1.0 Hz, 1H, H\(_9\)), 7.92 (td, \(^3\)J\(_{HH}\) = 7.0 Hz, \(^4\)J\(_{HH}\) = 2 Hz, 1H, H\(_2\)), 8.35 (ddd, \(^7\)J\(_{HH}\) = 11.0 Hz, \(^7\)J\(_{HH}\) = 8.0 Hz, \(^7\)J\(_{HH}\) = 1.0 Hz, 1H, H\(_9\)), 8.50 (dt, \(^7\)J\(_{HH}\) = 13.0 Hz, \(^4\)J\(_{HH}\) = 1.0 Hz, 1H, H\(_1\)), 8.77 (dq, \(^7\)J\(_{HH}\) = 10.0 Hz, \(^4\)J\(_{HH}\) = 1.0 Hz, 1H, H\(_7\)\)), 8.64 (td, \(^3\)J\(_{HH}\) = 5.0 Hz, \(^4\)J\(_{HH}\) = 1.0 Hz, 1H, H\(_{10}\)), 8.77 (dq, \(^7\)J\(_{HH}\) = 10.0 Hz, \(^4\)J\(_{HH}\) = 1.0 Hz, 1H, H\(_7\)\)). \(^{13}\)C-{\(^1\)H} NMR (CDCl\(_3\), 101 MHz) \(δ\) (ppm): -6.3 (2 x Si(CH\(_3\))\(_2\)), 16.9 (2 x
SiC(CH₃)₃, 26.6 (2 x SiC(CH₃)₃), 121.5 (C₁), 123.7 (C₀), 126.8 (C₇), 129.6 (C₂), 132.3 (C₃), 147.7 (C₁₀), 149.4 (C₄), 149.6 (C₈), 154.5 (C₆), 156.6 (C₅).

The second fraction was isolated as a brown oil of 4-tert-butyldimethylsilyl-2,2’-bipyridine (1: 134 mg, 50%; 2: 45 mg, 48%). Accurate MS (ESI⁺): m/z calculated: 271.1626; found: 271.1626. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 0.36 (s, 6H, Si(CH₃)₂), 0.92 (s, 9H, SiC(CH₃)₃), 7.30 (ddd, ³J_HH = 8.0 Hz, ³J_HH = 5.0 Hz, ⁴J_HH = 1.0 Hz, 1H, H₀), 7.41 (dd, ³J_HH = 4.5 Hz, ⁴J_HH = 1.0 Hz, 1H, H₂), 7.81 (td, ³J_HH = 8.0 Hz, ⁴J_HH = 1.0 Hz, 1H, H₈), 8.37 (dt, ³J_HH = 8.0 Hz, ⁴J_HH = 1.0 Hz, 1H, H₇), 8.50 (t, ³J_HH = 5.0 Hz, ⁴J_HH = 1.0 Hz, ¹H, H₁₀). ¹³C NMR (CDCl₃, 101 MHz) δ (ppm): -6.3 (Si(CH₃)₂), 16.9 (SiC(CH₃)₃), 26.6 (SiC(CH₃)₃), 121.5 (C₇), 123.6 (C₀), 126.7 (C₄), 129.5 (C₂), 137.0 (C₈), 147.9 (C₁), 149.1 (C₃), 149.4 (C₁₀), 154.7 and 156.8 (C₅ and C₆).

The third fraction was isolated as 2,2’-bipyridine, characterisation was consistent with the literature.[²⁴]

Methods 6 and 7
2,2’-Bipyridine (1: 110 mg, 0.71 mmol; 2: 52 mg, 0.33 mmol), tert-butyldimethylsilylchloride (1: 290 mg, 1.92 mmol; 2: 143 mg, 0.95 mmol) and di-isopropylamine (1: 0.40 mL, 2.80 mmol; 2: 0.20 mL, 1.40 mmol) were added to separate flamed out Schlenk tubes and dissolved in 1: anhydrous THF (10 mL) and 2; anhydrous diethyl ether (10 mL). The di-isopropylamine solution was cooled in an acetone-N₂(l) bath and °BuLi (1.6 M: 1: 3.50 mL; 2: 0.80 mL) was added to it via syringe. After 15 min. of stirring the solution was allowed to warm to room temperature before being re-cooled in an acetone-N₂(l) bath. The 2,2’-bipyridine solution was cannula transferred to the LDA solution and the mixture left to stir for 1
h. The solution of tert-butyldimethylsilylchloride was then transferred via cannula to the black lithiated 2,2'-bipyridine reaction mixture and left to stir for 2 hours, after which it was quenched with absolute ethanol. Removal of all solvents under reduced pressure and washing with saturated sodium hydrogen carbonate solution was followed by separation into ethyl acetate and drying over magnesium sulphate. Filtration of the solution and removal of the solvent of the supernatant under reduced pressure led to white crystals, which were characterised as 2,2'-bipyridine.\[24\]

**Attempted silylation of 6,6''-dibromo-2,2':6',2''-terpyridine via lithium-halogen exchange**

![Chemical structure](image)

6,6''-Dibromo-2,2':6',2''-terpyridine (100 mg, 0.26 mmol), tert-butyldimethylsilylchloride (150 mg, 1.00 mmol) and di-iso-propylamine (0.18 mL, 1.26 mmol) were added to separate flamed out Schlenk tubes and dissolved in anhydrous THF (10 mL). The di-iso-propylamine solution was cooled in an acetone-N\(_2\)(l) bath and \(^9\)BuLi (0.50 mL, 1.6 M) was added to it via syringe. After 15 min. of stirring the solution was allowed to warm to room temperature before being re-cooled in an acetone-N\(_2\)(l) bath. The 6,6''-dibromo-2,2':6',2''-terpyridine solution was cannula transferred to the LDA solution to produce a green-black solution. The mixture was left to stir for 1 h. The solution of tert-butyldimethylsilylchloride was then transferred via cannula to the lithiated 6,6''-dibromo-2,2':6',2''-terpyridine reaction mixture and left to stir overnight, after which time it was quenched with absolute ethanol. Removal of all solvents under reduced pressure and washing with saturated sodium hydrogen carbonate solution was followed by separation into ethyl acetate and drying over magnesium sulphate. Filtration of the solution and removal of the solvent of the supernatant under reduced pressure led to white crystals, which were characterised as 6,6''-dibromo-2,2':6',2''-terpyridine.\[22\]

**Attempted silylation of 2,2':6',2''-terpyridine via lithium-hydrogen exchange**
2,2’:6’,2”-Terpyridine (49 mg, 0.21 mmol), tert-butyldimethylsilylchloride (94 mg, 0.62 mmol) and di-iso-propylamine (0.19 mL, 1.33 mmol) were added to separate flamed out Schlenk tubes and dissolved in anhydrous diethyl ether (10 mL). The di-iso-propylamine solution was cooled in an acetone-N\(_2\) bath and \(^n\)BuLi (0.75 mL, 1.6 M) was added to it via syringe. After 15 min. of stirring the solution was allowed to warm to room temperature before being re-cooled in an acetone-N\(_2\) bath. The 2,2’:6’,2”-terpyridine solution was cannula transferred to the LDA solution and the mixture left to stir for 1 h. The solution of tert-butyldimethylsilylchloride was then transferred via cannula to the green-black lithiated 2,2’:6’,2”-terpyridine reaction mixture and left to stir overnight, after which it was quenched with absolute ethanol. Removal of all solvents under reduced pressure and washing with saturated sodium hydrogen carbonate solution was followed by separation into ethyl acetate and drying over magnesium sulphate. Filtration of the solution and removal of the solvent of the supernatant under reduced pressure led to white crystals, which were characterised as 2,2’:6’,2”-terpyridine.\(^{[25]}\)

**Attempted silylation of 1,10-phenanthroline via lithium-hydrogen exchange**

1,10-Phenanthroline (100 mg, 0.56 mmol), tert-butyldimethylsilylchloride (310 mg, 2.06 mmol) and di-iso-propylamine (0.40 mL, 2.80 mmol) were added to separate flamed out Schlenk tubes and dissolved in THF (10 mL). The di-iso-propylamine...
solution was cooled in an acetone-N₂(l) bath and sBuLi (1.25 mL, 1.6 M) was added to it via syringe. After 30 min. of stirring the solution was allowed to warm to room temperature before being re-cooled in an acetone-N₂(l) bath. The 1,10-phenanthrolone solution was cannula transferred to the LDA solution dropwise and the resulting black mixture left to stir for 2 h. The solution of tert-butyldimethylsilylchloride was then transferred via cannula to the lithiated 1,10-phenanthroline reaction mixture and left to stir overnight, after which it was quenched with absolute ethanol. Removal of all solvents under reduced pressure and washing with saturated sodium hydrogen carbonate solution was followed by separation into ethyl acetate and drying over magnesium sulphate. Filtration of the solution and removal of the solvent of the supernatant under reduced pressure led to white crystals, which were characterised as 1,10-phenanthroline.[26]

Silylation reactions of 2,9-dimethyl-1,10-phenanthroline via lithium-hydrogen exchange

Methods 1-3 – the preparation of 2,9-di-tert-butyldimethylsilylmethyl-1,10-phenanthroline and 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline

Neocuproine hemihydrate (1 and 3: 353 mg, 1.63 mmol; 2: 200 mg, 0.92 mmol) was added to a flamed out Schlenk tube, gently heated with the use of a heat gun under vacuum and left to dehydrate for an hour. tert-Butyldimethylsilylchloride (1: 685 mg, 4.55 mmol; 2: 221 mg, 1.47 mmol) and di-iso-propylamine (0.60 mL, 4.20 mmol) were added to separate Schlenk tubes under argon. All three were dissolved in anhydrous THF (15 mL). The di-iso-propylamine solution was cooled in an acetone-N₂(l) bath and sBuLi (1.6 M: 1 and 3: 2.40 mL; 2: 2.00 mL) was added via syringe. The resulting LDA solution was left to stir for 30 min. before warming to room temperature and subsequent re-cooling. The neocuproine solution was transferred to the LDA solution by cannula, immediately producing a black solution. This was left to stir for 1 and 2: 1 hour; 3: overnight before the tert-butyldimethylsilylchloride solution was added rapidly by cannula. The black solution was stirred for 1 and 2: 20 minutes; 3: overnight before being warmed to room temperature. Absolute ethanol was added slowly via syringe to the solution to quench it, resulting in a vivid series of colour changes. The black solution changed to dark blue, to a lighter blue and then becoming cloudy blue. It then changed to a cloudy green before going from dark to light green, changing to a bright yellow before settling for a duller yellow. The product was transferred to a round bottom flask and the solvent was removed under
reduced pressure followed by washing with saturated sodium hydrogen carbonate solution. The mixture was partitioned into ethyl acetate and dried over magnesium sulphate, followed by filtration. The solvent of the supernatant was removed under reduced pressure, yielding a yellow precipitate. The use of a gradient elution of hexane/ethyl acetate (from a ratio of 100:0 to 0:100 of hexane:ethyl acetate) in silica gel column chromatography led to the separation of three products.

The first fraction was isolated as 2,9-di-tert-butyldimethylsilylmethyl-1,10-phenanthroline (1: 81 mg, 11%; 2: 145 mg, 36%; 3: 275 mg, 37%). Characterisation was consistent with the literature.\[^{26}\]

The second fraction was isolated as a pale yellow powder of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (1: 303 mg, 55%; 2: 310 mg, 60%; 3: 181 mg, 33%). M.p. 144-146 °C. Accurate MS (ESI\(^+\)): m/z calculated: 323.1931; found: 323.1939. UV/vis (DCM): \(\lambda_{max}/\) nm (\(\epsilon/\text{cm}^3\text{mol}^{-1}\text{cm}^{-1}\)) = 235 (35,771), 275 (24,394), 332 (1012), 348 (370). IR (3500-500 cm\(^{-1}\), solid sample on ATR cell): 2954 (m), 2934 (sh), 2924 (m), 2894 (w), 2879 (w), 2853 (m), 1616 (m),
1607 (m), 1590 (s), 1504 (s), 1490 (s), 1462 (m), 1403 (m), 1358 (s), 1296 (m), 1260 (s), 1218 (m), 1134 (s), 1076 (w), 1007 (m), 931 (m), 853 (s), 835 (s), 823 (s), 806 (s), 747 (s), 714 (m), 662 (m), 642 (m), 624 (m).

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$(ppm): 0.03 (s, 6H, Si(CH$_3$)$_2$), 0.96 (s, 9H, SiC(CH$_3$)$_3$), 2.79 (s, 2H, CH$_2$), 2.90 (s, 3H, CH$_3$), 7.31 (d, $^3$J$_{HH}$ = 8.0 Hz, 1H, H$_2$), 7.44 (d, $^3$J$_{HH}$ = 8.0 Hz, 1H, H$_9$), 7.62 (d, $^3$J$_{HH}$ = 8.0 Hz, 1H, H$_3$), 8.06 (d, $^3$J$_{HH}$ = 8.0 Hz, 1H, H$_8$).

$^{13}$C-$^1$H NMR (CDCl$_3$, 101 MHz) $\delta$(ppm): -8.1 (SiC(CH$_3$)$_3$), 15.0 (SiC(CH$_3$)$_3$), 23.8 (CH$_3$), 24.5 (Si(CH$_3$)$_2$), 25.3 (CH$_2$), 120.9 (C$_2$), 121.0 (C$_9$), 122.5 (C$_5$), 123.3 (C$_6$), 123.8 (C$_4$), 124.7 (C$_7$), 133.5 (C$_3$), 133.8 (C$_8$), 143.5 (C$_{12}$), 143.6 (C$_{11}$), 156.8 (C$_1$), 160.3 (C$_{10}$).

The third fraction was characterised as neocuproine.$^{[26]}$

**Method 4**

Neocuproine hemihydrate (194 mg, 0.90 mmol) was added to a flamed out Schlenk tube under argon and gently heated with the use of a heat gun under vacuum. tert-Butyldimethylsilylchloride (430 mg, 2.86 mmol) was added to a second flamed out Schlenk tube under argon. After the neocuproine had been left under vacuum for 1 h., the contents of both Schlenk tubes were dissolved in anhydrous diethyl ether (10 mL) and the neocuproine solution was cooled in an acetone-N$_2$(l) bath. $^1$BuLi (1.50 mL, 1.9 M) was added dropwise via syringe with stirring and the purple-black solution left to stir for 2 h. The solution was recooled and the contents of the second Schlenk tube were transferred rapidly by cannula. The solution was stirred for 30 min. before warming to room temperature. The addition of absolute ethanol (10 mL) via syringe resulted in a prismatic series of colour changes, from scarlet through to yellow. All solvents were removed from a round-bottomed flask under reduced pressure followed by washing in water with saturated potassium hydrogen carbonate solution. The product was separated into ethyl acetate, dried over magnesium sulphate and filtered. Removal of the solvent supernatant yielded a powder characterised as neocuproine.$^{[26]}$

**Method 5**

Neocuproine hemihydrate (353 mg, 1.63 mmol) was added to a flamed out Schlenk, gently heated with the use of a heat gun under vacuum and left to dehydrate for an hour. Trimethylsilylchloride (0.58 mL, 4.90 mmol) and di-iso-propylamine (0.60 mL, 4.20 mmol) were added to separate Schlenk tubes under argon. All three were
dissolved in anhydrous THF (15 mL). The di-iso-propylamine solution was cooled in an acetone-N$_2$(l) bath and $^t$BuLi (2.50 mL, 1.6 M) was added via syringe. The resulting LDA solution was left to stir for 30 min. before warming to room temperature and subsequently re-cooled. The neocuproine solution was transferred to the LDA solution by cannula, immediately producing a black solution. This was left to stir for 1 h. before the trimethylsilylchloride solution was added rapidly by cannula, resulting in a prismatic series of colour changes. The yellow solution was stirred for 20 min. before being warmed to room temperature. Absolute ethanol was added slowly via syringe to the solution to quench it. The product was transferred to a round bottom flask and all solvents removed under reduced pressure followed by washing with saturated sodium hydrogen carbonate solution. The mixture was separated into ethyl acetate and dried over magnesium sulphate, followed by filtration. The solvent of the supernatant was removed under reduced pressure, yielding a yellow-white precipitate. Characterisation was consistent with the literature for neocuproine.\[26\]

**Method 6 – the preparation of 2,9-di-tri-iso-propylsilylmethyl-1,10-phenanthroline and 2-tri-iso-propylsilylmethyl-9-methyl-1,10-phenanthroline**

Neocuproine hemihydrate (350 mg, 1.61 mmol) was added to a flamed out Schlenk tube, gently heated with the use of a heat gun under vacuum and left to dehydrate for an hour. Tri-iso-propylsilylchloride (1.02 mL, 4.86 mmol) and di-iso-propylamine (0.72 mL, 5.04 mmol) were added to separate Schlenk tubes under argon. All three were dissolved in anhydrous THF (10 mL). The di-iso-propylamine solution was cooled in an acetone-N$_2$(l) bath and $^t$BuLi (3.50 mL, 1.6 M) was added via syringe. The resulting LDA solution was left to stir for 30 min. before warming to room temperature and subsequently re-cooled. The neocuproine solution was transferred to the LDA solution by cannula, immediately producing a black solution. This was left to stir for 1 h. before the tri-iso-propylsilylchloride solution was added rapidly by cannula. The black solution was stirred for 20 min. before being warmed to room temperature. Absolute ethanol was added slowly via syringe to the solution to quench it, resulting in a vivid series of colour changes. The yellow product was transferred to a round bottom flask and the solvent was removed under reduced pressure followed by washing with saturated sodium hydrogen carbonate solution. The mixture was partitioned into ethyl acetate and dried over magnesium sulphate, followed by filtration. The solvent of the supernatant was removed under reduced pressure,
yielding a yellow precipitate. The use of a gradient elution of hexane/ethyl acetate (from a ratio of 100:0 to 0:100 of hexane:ethyl acetate) in silica gel column chromatography led to the separation of three products.

The first fraction was isolated as a yellow powder of 2,9-di-tri-iso-propylsilylmethyl-1,10-phenanthroline (410 mg, 49%). M.p. 97-98 °C. Accurate MS (ESI⁺): m/z calculated: 521.3742; found 521.3749. UV/vis (DCM): \( \lambda_{\text{max}} \) nm (\( \varepsilon / \text{mol} \cdot \text{cm}^{-1} \)) = 236 (46,905), 282 (28,127), 338 (1366). IR (3500-500 cm⁻¹, solid sample on ATR cell): 2957 (w), 2938 (m), 2886 (w), 2862 (s), 1588 (m), 1519 (m), 1503 (s), 1488 (m), 1360 (m), 1300 (m), 1244 (m), 1207 (m), 1146 (m), 1072 (w), 1002 (m), 882 (s), 846 (s), 801 (w), 745 (s), 714 (m), 648 (s). \(^1\)H NMR (CDCl₃, 400 MHz) δ(ppm): 1.03 (d, \( ^3J_{\text{HH}} = 7.0 \) Hz, 36H, SiCCH₃), 1.16 (sept., \( ^3J_{\text{HH}} = 7.0 \) Hz, 6H, SiCH), 2.83 (s, 4H, CH₂), 7.34 (d, \( ^3J_{\text{HH}} = 8.0 \) Hz, 2H, H₂), 7.58 (s, 2H, H₅), 7.97 (d, \( ^3J_{\text{HH}} = 8.0 \) Hz, 2H, H₃). \(^{13}\)C-\(^1\)H NMR (CDCl₃, 101 MHz) δ(ppm): 11.2 (SiCH), 18.7 (SiCCH₃), 24.4 (CH₂), 122.9 (C₂), 124.7 (C₃), 125.9 (C₄), 135.4 (C₅), 145.6 (C₆), 162.4 (C₁).
The second fraction was isolated as an orange-yellow oil of 2-tri-isopropylsilylmethyl-9-methyl-1,10-phenanthroline (106 mg, 18%). Accurate MS (ESI⁺): m/z calculated: 365.2408; found 365.2407:365.2408. UV/vis (DCM): \( \lambda_{\text{max}} \) nm (\( \epsilon \) cm\(^3\) mol\(^{-1}\) cm\(^{-1}\)) = 241 (22,659), 275 (29,681), 333 (1638), 349 (622). IR (3500-500 cm\(^{-1}\), sample on ATR cell): 3041 (w), 2941 (vs), 2887 (m), 2863 (vs), 1618 (s), 1611 (s), 1590 (s), 1574 (m), 1547 (s), 1504 (s), 1492 (vs), 1463 (m), 1462 (m), 1421 (m), 1360 (m), 1301 (m), 1281 (m), 1241 (m), 1220 (w), 1207 (m), 1142 (m), 1118 (w), 1076 (w), 1016 (w), 1001 (w), 929 (w), 912 (w), 881 (s), 848 (s), 769 (w), 745 (w), 718 (w), 700 (w), 655 (s), 633 (s). \(^1\)H NMR (CDCl\(_3\) 400 MHz) \( \delta \) (ppm): 1.08 (d, \( J_{\text{HH}} = 6.5 \) Hz, 18H, SiC\(_3\)H\(_3\)), 1.15 (sept., \( J_{\text{HH}} = 6.5 \) Hz, 3H, SiCH), 2.86 (s, 2H, CH\(_2\)), 2.88 (s, 3H, CH\(_3\)), 7.38 (d, \( J_{\text{HH}} = 8.0 \) Hz, 1H, H\(_2\)), 7.44 (d, \( J_{\text{HH}} = 8.0 \) Hz, 1H, H\(_3\)), 7.61 (d, \( J_{\text{HH}} = 8.5 \) Hz, 1H, H\(_5\)), 7.64 (d, \( J_{\text{HH}} = 8.5 \) Hz, 1H, H\(_6\)), 8.00 (d, \( J_{\text{HH}} = 8.0 \) Hz, 1H, H\(_3\)), 8.07 (d, \( J_{\text{HH}} = 8.0 \) Hz, 1H, H\(_8\)). \(^{13}\)C-{\(^1\)H} NMR (CDCl\(_3\), 101 MHz) \( \delta \) (ppm): 11.5 (SiCH), 16.8 (SiC\(_3\)H\(_3\)), 24.4 (CH\(_2\)), 25.9 (CH\(_3\)), 123.1 (C9), 123.3 (C2), 124.6 (C3), 125.5 (C6), 128.0 (C7), 128.7 (C4), 135.5 (C3), 135.9 (C8), 146.5 (C11), 146.5 (C12), 159.6 (C10), 163.6 (C1). The third fraction was characterised as neocuproine.\(^{[26]}\)

**Method 7 - the preparation of 2,9-di-tert-butyldiphenylsilylmethyl-1,10-phenanthroline and 2-tert-butyldiphenylsilylmethyl-9-methyl-1,10-phenanthroline**

Neocuproine hemihydrate (100 mg, 0.46 mmol) was added to a flamed out Schlenk tube, gently heated with the use of a heat gun under vacuum and left to dehydrate for an hour. tert-Butyldiphenylsilylchloride (0.38 mL, 1.44 mmol) and di-iso-propylamine (0.21 mL, 1.47 mmol) were added to separate Schlenk tubes under argon. All three were dissolved in anhydrous THF (5 mL). The di-iso-propylamine solution was cooled in an acetone-N\(_2\)(l) bath and \(^{8}\)BuLi (0.81 mL, 1.6 M) was added via syringe. The resulting LDA solution was left to stir for 30 min. before warming to room temperature and subsequently re-cooled. The neocuproine solution was transferred to the LDA solution by cannula, immediately producing a black solution. This was left to stir for 1 h. before the tert-butyldiphenylsilylchloride solution was added rapidly by cannula. The black solution was stirred for 20 min. before being warmed to room temperature. Absolute ethanol was added slowly via syringe to the solution to quench it, resulting in a vivid series of colour changes. The yellow product was transferred to a round bottom flask and the solvent was removed under reduced
pressure followed by washing with saturated sodium hydrogen carbonate solution. The mixture was partitioned into ethyl acetate and dried over magnesium sulphate, followed by filtration. The solvent of the supernatant was removed under reduced pressure, yielding a yellow/orange oily precipitate. The use of a gradient elution of hexane/ethyl acetate (from a ratio of 100:0 to 0:100 of hexane:ethyl acetate) in silica gel column chromatography led to the separation of four products. The first product was characterised as tert-butyldiphenylsilylchloride.\[26\]

The second fraction was isolated as an orange oil of 2,9-di-tert-butyldiphenylsilylmethyl-1,10-phenanthroline (21 mg, 7 %). Accurate MS (ESI\(^+\)): \(m/z\) calculated: 685.3434; found 685.3429. UV/vis (DCM): \(\lambda_{\text{max}}\) nm (\(\varepsilon\) cm\(^{-1}\) mol\(^{-1}\) cm\(^{-1}\)) = 230 (49,059), 279 (24,301), 333 (1338). IR (3500-500 cm\(^{-1}\), sample on ATR cell): 3373 (br), 3071 (m), 3046 (m), 2957 (s), 2929 (s), 2980 (s), 2855 (s), 2361 (m), 2338 (m), 1609 (w), 1589 (s), 1546 (w), 1505 (m), 1490 (m), 1470 (m), 1426 (s), 1391 (m), 1361 (m), 1303 (w), 1284 (w), 1261 (m), 1242 (m), 1208 (m), 1157 (m), 1106 (s), 1027 (m), 1006 (m), 997 (m), 936 (m), 850 (s), 820 (s), 762 (m), 735 (s), 699 (vs), 637 (m), 606 (s), 588 (m), 577 (m), 503 (s). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) (ppm): 1.08 (s, 9H, SiC\(_2\)H\(_3\)), 1.12 (s, 9H, SiC\(_2\)H\(_3\)), 3.50 (s, 4H, CH\(_2\)), 6.74 (d, \(^3\)J\(_{\text{HH}}\) = 8.5 Hz, 2H, H\(_2\)), 7.29-7.42 (m, 12H, m-ph and p-ph), 7.47 (s, 2H, H\(_5\)), 7.68 (d, \(^3\)J\(_{\text{HH}}\) = 8.5 Hz, 2H, H\(_3\)), 7.72 (m, 8H, o-ph). \(^{13}\)C-{\(^1\)H} NMR (CDCl\(_3\), 101 MHz) \(\delta\) (ppm): 19.0 and 19.1 (2 x SiC\(_2\)H\(_3\)), 26.2 (CH\(_2\)), 26.7 (SiC\(_2\)H\(_3\)), 28.0 (SiC\(_2\)H\(_3\)), 123.2 (C\(_2\)), 124.9 (C\(_3\)), 127.7, 127.9, 129.3 and 129.8 (m- and p-ph), 134.8 (i-ph), 134.9 (o-ph), 135.2 (i-ph), 135.3 (C\(_3\)), 136.5 (o-ph), 145.1 (C\(_4\)), 160.8 (C\(_6\)), 160.9 (C\(_1\)).
The third fraction was isolated as orange-white flakes of 2-tert-butyldiphenylsilylmethyl-9-methyl-1,10-phenanthroline (113 mg, 55 %). M.p. decomposes over 210 °C. Accurate MS (ESI\(^{+}\)): \( m/z \) calculated: 447.2252; found 447.2241. UV/vis (DCM): \( \lambda_{max}/ \text{nm} (\epsilon/ \text{cm}^3\text{mol}^{-1}\text{cm}^{-1}) = 232 (39,726), 275 (22,001), 331 (2428), 349 (1268). IR (3500-500 cm\(^{-1}\), solid sample on ATR cell): 3064 (m), 3044 (m), 2960 (s), 2923 (s), 2852 (s), 2361 (m), 2337 (m), 1735 (vw), 1612 (w), 1587 (m), 1546 (w), 1504 (m), 1493 (s), 1462 (m), 1426 (s), 1358 (m), 1283 (w), 1260 (s), 1242 (m), 1223 (m), 1206 (m), 1151 (m), 1101 (vs), 1081 (vs), 1020 (vs), 933 (m), 859 (s), 814 (s), 801 (vs), 767 (s), 747 (s), 738 (s), 717 (w), 699 (vs), 676 (s), 632 (s), 602 (s), 575 (vs), 1081 (vs), 1020 (vs), 933 (m), 859 (s), 814 (s), 801 (vs), 767 (s), 747 (s), 738 (s), 717 (w), 699 (vs), 676 (s), 632 (s), 602 (s), 575 (m), 561 (s), 547 (m), 537 (m), 527 (m), 502 (m). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta/\text{ppm} \): 1.12 (s, 9H, SiCH\(_3\)), 2.98 (s, 3H, CH\(_3\)), 3.44 (s, 2H, CH\(_2\)), 6.77 (d, \( ^3\)J\(_{HH} = 8.5 \text{ Hz}, 1H, H_2 \)), 7.31 (m, 6H, m-ph and p-ph), 7.46 (d, \( ^3\)J\(_{HH} = 8.0 \text{ Hz}, 1H, H_0 \)), 7.53 (d, \( ^3\)J\(_{HH} = 8.5 \text{ Hz}, 1H, H_5 \)), 7.59 (d, \( ^3\)J\(_{HH} = 8.5 \text{ Hz}, 1H, H_6 \)), 7.70 (d, \( ^3\)J\(_{HH} = 8.5 \text{ Hz}, 1H, H_3 \)), 7.76 (dd, \( ^3\)J\(_{HH} = 8.0 \text{ Hz}, ^4\)J\(_{HH} = 1.80 \text{ Hz}, 4H, o-H)), 8.06 (d, \( ^3\)J\(_{HH} = 8.0 \text{ Hz}, 1H, H_8 \)). \(^{13}\)C-\{\(^1\)H\} NMR (CDCl\(_3\), 101 MHz) \( \delta/\text{ppm} \): 18.9 (SiC\(_3\)H\(_3\)), 26.0 (CH\(_3\)), 26.2 (CH\(_2\)), 28.0 (SiC\(_4\)H\(_4\)), 123.2 (C\(_9\)), 123.5 (C\(_2\)), 124.8 (C\(_6\)), 125.5 (C\(_5\)), 127.6 (m-ph), 129.2 (m-ph), 134.2 (i-ph), 135.2 (C\(_3\)), 136.0 (C\(_8\)), 144.5 (C\(_4\)), 145.1 (C\(_7\)), 158.9 (C\(_{10}\)), 160.8 (C\(_1\)), 170.7 (C\(_{11}\) and C\(_{12}\)).

The fourth fraction was characterised as neocuproine.\(^{[26]}\)

**Attempted silylation of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline via lithium-hydrogen exchange**

2-tert-Butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (50 mg, 0.16 mmol) was added to a Schlenk tube in an argon glovebox. Tri-iso-propylsilylchloride (0.10 mL, 0.46 mmol) and di-iso-propylamine (0.10 mL, 0.70 mmol) were added to
separate Schlenk tubes under argon. All three were dissolved in anhydrous THF (5 mL). The di-iso-propylamine solution was cooled in an acetone-N_2(l) bath and nBuLi (0.35 mL, 1.6 M) was added via syringe. The resulting LDA solution was left to stir for 30 min. before warming to room temperature and subsequent re-cooling. The neocuproine solution was transferred to the LDA solution by cannula, immediately producing a black solution. This was left to stir for 1 h. before the tri-iso-propylsilylchloride solution was added rapidly by cannula. The black solution was stirred for 30 min. before being warmed to room temperature. Absolute ethanol was added slowly via syringe to the solution to quench it, resulting in a vivid series of colour changes. The yellow product was transferred to a round bottom flask and the solvent was removed under reduced pressure, followed by washing with saturated sodium hydrogen carbonate solution. The mixture was partitioned into ethyl acetate and dried over magnesium sulphate, followed by filtration. The solvent of the supernatant was removed under reduced pressure, yielding an orange oil.

Silylation of 6,6’-dimethyl-2,2’-bipyridine via lithium-hydrogen exchange

Method 1 – the preparation of 6,6’-di-tert-butyldiphenylsilylmethyl-2,2’-bipyridine

6,6’-Dimethyl-2,2’-bipyridine (100 mg, 0.54 mmol), tert-butyldiphenylsilylchloride (1.42 mL, 5.38 mmol) and di-iso-propylamine (0.95 mL, 6.65 mmol) were added to separate Schlenk tubes under argon. All three were dissolved in anhydrous THF (15 mL). The di-iso-propylamine solution was cooled in an acetone-N_2(l) bath and nBuLi (3.00 mL, 1.6 M) was added via syringe. The resulting LDA solution was left to stir for 30 min. before warming to room temperature and then re-cooled. The 6,6’-dimethyl-2,2’-bipyridine solution was transferred to the LDA solution by cannula, immediately producing a purple-black solution. This was left to stir for 2 h. before the tert-butyldiphenylsilylchloride solution was added rapidly by cannula. The black solution was stirred for 30 min. before being warmed to room temperature. Absolute ethanol was added slowly via syringe to the solution to quench it, resulting in a vivid series of colour changes. The yellow product was transferred to a round bottom flask and the solvent removed under reduced pressure, followed by washing with saturated sodium hydrogen carbonate solution. The mixture was partitioned into ethyl acetate and dried over magnesium sulphate, followed by filtration. The solvent of the supernatant was removed under reduced pressure to yield a white precipitate. Washing with hexane led to the isolation of white crystals of 6,6’-di-tert-butyldiphenylsilylmethyl-2,2’-bipyridine (197 mg, 55%).
M.p. 150 °C. Accurate MS (ESI⁺): m/z calculated: 661.3429; found 661.3429. UV/vis (DCM): λmax nm (ε cm⁻³ mol⁻¹ cm⁻¹) = 230 (28,280), 251 (9789), 301 (15,849), 312 (11,854), 342 (666). IR (3500-500 cm⁻¹, solid sample on ATR cell): 3068 (w), 3042 (w), 3012 (w), 2955 (m), 2931 (m), 2881 (m), 2855 (m), 2364 (vw), 2154 (vw), 2020 (vw), 1960 (vw), 1569 (s), 1488 (w), 1465 (m), 1431 (s), 1404 (w), 1390 (w), 1360 (w), 1325 (m), 1264 (m), 1241 (s), 1194 (w), 1152 (s), 1101 (s), 1083 (w), 1029 (w), 1010 (w), 999 (w), 990 (w), 934 (w), 903 (w), 854 (w), 837 (s), 819 (s), 801 (s), 763 (s), 748 (w), 735 (s), 695 (vs), 634 (w), 619 (w), 607 (w), 590 (s), 550 (vw), 542 (vw), 525 (s). ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 1.06 (s, 18H, SiC(CH₃)₂), 3.01 (s, 4H, CH₂), 6.57 (d, 3JHH = 7.5 Hz, 2H, H₂), 7.26-7.37 (m, 14H, H₄, o-ph and p-ph), 7.59-7.64 (m, 10H, H₃ and m-ph). ¹³C-¹H NMR (CDCl₃, 101 MHz) δ (ppm): 18.8 (Si(CH₃)), 24.6 (CH₂), 28.0 (SiC(CH₃)), 117.0 (C₃), 123.1 (C₂), 127.5 (o-ph), 129.1 (p-ph), 134.6 (i-ph), 136.5 (m-ph), 155.5 (C₄), 159.0 (C₁), 159.3 (C₅).

Method 2 – the preparation of 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine

6,6’-Dimethyl-2,2’-bipyridine (250 mg, 1.35 mmol), tert-butyldimethylsilylchloride (610 mg, 4.05 mmol) and di-iso-propylamine (0.65 mL, 4.55 mmol) were added to separate Schlenk tubes under argon. All three were dissolved in anhydrous THF (10 mL). The di-iso-propylamine solution was cooled in an acetone-N₂(l) bath and nBuLi (2.4 mL, 1.6 M) was added via syringe. The resulting LDA solution was left to stir for 30 min. before warming to room temperature and then re-cooled. The 6,6’-dimethyl-2,2’-bipyridine solution was transferred to the LDA solution by cannula, immediately producing a purple-black solution. This was left to stir for 2 h. before the tert-butyldimethylsilylchloride solution was added rapidly by cannula. The black solution was stirred for 30 min. before being warmed to room temperature. Absolute
ethanol was added slowly via syringe to the solution to quench it, resulting in a vivid series of colour changes. The yellow product was transferred to a round bottom flask and the solvent removed under reduced pressure, followed by washing with saturated sodium hydrogen carbonate solution. The mixture was partitioned into ethyl acetate and dried over magnesium sulphate, followed by filtration. The solvent of the supernatant was removed under reduced pressure to yield a white precipitate. Washing with hexane led to the isolation of a white powder of 6,6'-di-tert-butylmethylsilylmethyl-2,2'-bipyridine. Characterisation was consistent with the literature.[27]

Method 3 – the preparation of 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine

6,6'-Dimethyl-2,2'-bipyridine (103 mg, 0.56 mmol), tri-iso-propylsilylchloride (0.35 mL, 1.63 mmol) and di-iso-propylamine (0.30 mL, 2.10 mmol) were added to separate Schlenk tubes under argon. All three were dissolved in anhydrous THF (10 mL). The di-iso-propylamine solution was cooled in an acetone-N₂/l bath and ²BuLi (1.0 mL, 1.6 M) was added via syringe. The resulting LDA solution was left to stir for 30 min. before warming to room temperature and then re-cooled. The 6,6'-dimethyl-2,2'-bipyridine solution was transferred to the LDA solution by cannula, immediately producing a purple-black solution. This was left to stir for 2 h. before the tri-iso-propylsilylchloride solution was added rapidly by cannula. The black solution was stirred for 30 min. before being warmed to room temperature. Absolute ethanol was added slowly via syringe to the solution to quench it, resulting in a vivid series of colour changes. The yellow product was transferred to a round bottom flask and the solvent removed under reduced pressure, followed by washing with saturated sodium hydrogen carbonate solution. The mixture was partitioned into ethyl acetate and dried over magnesium sulphate, followed by filtration. The solvent of the supernatant was removed under reduced pressure to yield a white precipitate. Washing with hexane led to the isolation of white crystals of 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine. Characterisation was consistent with the literature.[27]

Complexation Reactions of Silylated-Oligopyridines.

Reaction of 6,6'-dimethyl-2,2'-bipyridine with uranyl(VI) nitrate

[UO₂(NO₃)₂].6H₂O (29 mg, 0.058 mmol) and 6,6'-dimethyl-2,2'-bipyridine (22 mg, 0.120 mmol) were dissolved in absolute ethanol (5 mL) and stirred overnight. Slow
evaporation of the solution led to the co-crystallisation of the two reagents. \(^1\)H NMR (MeOD, 400 MHz) \(\delta\) (ppm): 2.74 (s, 6H, CH\(_2\)), 7.56 (d, \(^3J_{HH} = 7.5\) Hz, 2H, H\(_5\)), 8.08 (dd, \(^3J_{HH} = 7.5\) Hz, \(^3J_{HH} = 8.0\) Hz, 2H, H\(_4\)), 8.19 (d, \(^3J_{HH} = 8.0\) Hz, 2H, H\(_3\)).

**Reaction of 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine with uranyl(VI) nitrate**

[UO\(_2\)(NO\(_3\))\(_2\)]\(\cdot\)6H\(_2\)O (4 mg, 0.008 mmol) and 6,6’-di-tert-butyldimethyl-2,2’-bipyridine (10 mg, 0.024 mmol) were dissolved in deuterated methanol (1 mL). Slow evaporation of the solvent resulted in the co-crystallisation of uranyl nitrate and 6,6’-dimethyl-2,2’-bipyridine. \(^1\)H NMR (MeOD, 400 MHz) \(\delta\) (ppm): 0.01 (s, 12H, SiCH\(_3\)), 0.97 (s, 18H, SiCCH\(_3\)), 2.65 (s, 4H, CH\(_2\)), 7.38 (d, \(^3J_{HH} = 8.0\) Hz, 2H, H\(_5\)), 7.97 (dd, \(^3J_{HH} = 8.0\) Hz, \(^3J_{HH} = 8.0\) Hz, 2H, H\(_4\)), 8.07 (d, \(^3J_{HH} = 8.0\) Hz, 2H, H\(_3\)). UV/vis (MeOH:1:1 DCM): \(\lambda_{\text{max}}\) nm = 433.

**Reaction of 6,6’-di-trimethylsilylmethyl-2,2’-bipyridine with uranyl(VI) nitrate**

[UO\(_2\)(NO\(_3\))\(_2\)]\(\cdot\)6H\(_2\)O (2 mg, 0.004 mmol) and 6,6’-di-trimethylsilylmethyl-2,2’-bipyridine (3 mg, 0.009 mmol) were dissolved in deuterated methanol (1 mL). \(^1\)H NMR (MeOD, 400 MHz) \(\delta\) (ppm): 0.11 (s, 18H, SiCH\(_3\)), 2.73 (m, 4H, CH\(_2\)), 7.57 (d, \(^3J_{HH} = 7.5\) Hz, 2H, H\(_5\)), 8.09 (dd, \(^3J_{HH} = 8.0\) Hz, \(^3J_{HH} = 7.5\) Hz, 2H, H\(_4\)), 8.21 (d, \(^3J_{HH} = 8.0\) Hz, 2H, H\(_3\)). UV/vis (MeOH:1:1 DCM): \(\lambda_{\text{max}}\) nm = 433.

**Reaction of 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine with uranyl(VI) nitrate**

[UO\(_2\)(NO\(_3\))\(_2\)]\(\cdot\)6H\(_2\)O (3 mg, 0.006 mmol) and 6,6’-di-tri-iso-propylsilylmethyl-2,2’-bipyridine (6 mg, 0.012 mmol) were dissolved in deuterated methanol (1 mL). \(^1\)H NMR (MeOD, 400 MHz) \(\delta\) (ppm): 1.08 (d, \(^3J_{HH} = 7.0\) Hz, 36H, SiCCH\(_3\)), 1.14 (sept., \(^3J_{HH} = 7.0\) Hz, 6H, SiCH), 2.61 (s, 4H, CH\(_2\)), 7.38 (d, \(^3J_{HH} = 8.0\) Hz, 2H, H\(_5\)), 7.83 (br, 2H, H\(_4\)), 8.06 (d, \(^3J_{HH} = 8.0\) Hz, 2H, H\(_3\)). UV/vis (MeOH:1:1 DCM): \(\lambda_{\text{max}}\) nm = 432.

**Reaction of 6,6’-di-tert-butyldiphenylsilylmethyl-2,2’-bipyridine with uranyl(VI) nitrate**

[UO\(_2\)(NO\(_3\))\(_2\)]\(\cdot\)6H\(_2\)O (4 mg, 0.008 mmol) and 6,6’-di-tert-butyldiphenyl-2,2’-bipyridine (9 mg, 0.014 mmol) were dissolved in deuterated methanol (1 mL). \(^1\)H NMR (MeOD, 400 MHz) \(\delta\) (ppm): 1.08 (s, 18H, SiCCH\(_3\)), 3.06 (s, 4H, CH\(_2\)), 6.86
(br, 2H, H₂), 7.22-7.38 (m, 14H, H₄, o-ph and p-ph), 7.42-7.59 (m, 10H, H₃ and m-ph). UV/vis (MeOH 1:1 DCM): λ_{max} nm = 434.

**Reaction of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline with uranyl(VI) nitrate**

[UO₂(NO₃)₂].6H₂O (10 mg, 0.020 mmol) and 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (14 mg, 0.043 mmol) were dissolved in acetonitrile, resulting in a foggy yellow solution. Layering of the solution with diethyl ether resulted in the formation of a yellow precipitate. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 0.08 (s, SiCH₃), 0.09 (s, SiCH₃), 0.93 (s, SiCCH₃), 1.03 (s, SiCCH₃), 3.01(s, CH₂), 3.03 (s, CH₂), 7.60 (d, ³JHH = 8.5 Hz), 7.65 (d, ³JHH = 8.5 Hz), 7.80 (s), 7.85 (d, ³JHH = 9.0 Hz), 7.92 (d, ³JHH = 9.0 Hz), 8.15 (m), 6.26 (dd, ³JHH = 8.5 Hz, ⁴JHH = 4.0 Hz) 8.50 (d, ³JHH = 9.0 Hz), 8.91 (d, ³JHH = 8.5 Hz).

**Reaction of 2,9-di-tri-iso-propylsilylmethyl-1,10-phenanthroline with uranyl(VI) nitrate**

[UO₂(NO₃)₂].6H₂O (10 mg, 0.020 mmol) and 2,9-di-tri-iso-propylsilylmethyl-1,10-phenanthroline (21 mg, 0.040 mmol) were dissolved in acetonitrile, resulting in a foggy yellow solution. Layering of the solution with diethyl ether resulted in the formation of a yellow precipitate. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 2.96 (s, CH₂, 6H), 7.52 (d, ³JHH = 8.5 Hz, 2H), 7.73 (s, 2H), 8.16 (d, ³JHH = 8.5 Hz, 2H).

**Reaction of 6,6'-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine with uranyl(VI) triflate**

[UO₂(OTf)₂(THF)]₃ (4 mg, 0.005 mmol) and 6,6'-di-tert-butyldimethyl-2,2'-bipyridine (5 mg, 0.012 mmol) were dissolved in CDCl₃ (1 mL) to give a yellow solution. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): -0.01 (s, 12H, SiCH₃), 0.94 (s, 18H, SiCCH₃), 2.42 (s, 4H, CH₂), 6.97 (d, ³JHH = 7.0 Hz, 2H, H₃), 7.62 (br, 2H, H₄), 8.09 (d, ³JHH = 7.0 Hz, 2H, H₃). UV/vis (MeCN): λ_{max} nm = 246, 331.

**Reaction of 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine with uranyl(VI) triflate**

[UO₂(OTf)₂(THF)]₃ (3 mg, 0.004 mmol) and 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine (4 mg, 0.008 mmol) were dissolved in CDCl₃ (1 mL) to give a yellow solution. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 1.06 (d, ³JHH = 6.5 Hz, 36H, SiCCH₃), 349
1.13 (sept., \( ^3J_{HH} = 6.5 \) Hz, 6H, SiCH), 2.50 (s, 4H, CH\(_2\)), 7.04 (d, \( ^3J_{HH} = 8.0 \) Hz, 2H, H\(_3\)), 7.59 (dd, \( ^3J_{HH} = 8.0 \) Hz, \( ^3J_{HH} = 8.0 \) Hz, 2H, H\(_4\)), 8.12 (d, \( ^3J_{HH} = 8.0 \) Hz, 2H, H\(_3\)).

UV/vis (MeCN): \( \lambda_{\text{max}}/\text{nm} = 238, 346, 417 \).

**Reaction of 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine with uranyl(VI) triflate**

\[ [\text{UO}_2(\text{OTf})_2(\text{THF})_3] \text{ (2 mg, 0.003 mmol)} \] and 6,6'-di-tert-butyldiphenyl-2,2'-bipyridine (4 mg, 0.006 mmol) were dissolved in CDCl\(_3\) (1 mL) to give a yellow solution. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) (ppm): 1.07 (s, 18H, SiCCH\(_3\)), 3.03 (s, 4H, CH\(_2\)), 6.59 (d, \( ^3J_{HH} = 7.5 \) Hz, 2H, H\(_2\)), 7.22-7.40 (overlapping signals, 14H, H\(_4\), o-ph and p-ph), 7.63 (m, 10H, H\(_3\) and m-ph). UV/vis (MeCN): \( \lambda_{\text{max}}/\text{nm} = 250, 336 \).

**Reaction of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline with uranyl(VI) iodide**

\[ [\text{UO}_2(\text{I})_2(\text{THF})_3] \text{ (12 mg, 0.016 mmol)} \] and 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (10 mg, 0.031 mmol) were dissolved in THF to give an orange/red solution. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) (ppm): -0.23 (s, SiCCH\(_3\)), -0.15 (s, SiCCH\(_3\)), 0.04 (s, SiCH\(_3\)), 0.77 (s, SiCCH\(_3\)), 0.96 (s, SiCCH\(_3\)), 2.82 (s, CH\(_2\)), 2.92 (s, CH\(_2\)), 3.03 (s, CH\(_2\)), 7.36 (d, \( ^3J_{HH} = 8.0 \) Hz), 7.48 (d, \( ^3J_{HH} = 8.0 \) Hz), 7.66 (d, \( ^3J_{HH} = 9.0 \) Hz), 7.69 (d, \( ^3J_{HH} = 9.0 \) Hz), 7.90 (br), 8.02 (br), 8.09 (dd, \( ^3J_{HH} = 8.0 \) Hz) 8.11 (d, \( ^3J_{HH} = 8.0 \) Hz), 8.45 (d, \( ^3J_{HH} = 8.5 \) Hz), 8.52 (d, \( ^3J_{HH} = 8.5 \) Hz), 14.57 (s, NH).

**Reaction of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline with uranyl(VI) triflate**

\[ [\text{UO}_2(\text{OTf})_2(\text{THF})_3] \text{ (12 mg, 0.015 mmol)} \] and 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (10 mg, 0.031 mmol) were dissolved in THF (5 mL) to give a yellow solution. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) (ppm): -0.23 (s, SiCCH\(_3\)), 0.04 (s, SiCH\(_3\)), 0.77 (s, SiCCH\(_3\)), 0.97 (s, SiCCH\(_3\)), 2.85 (s, CH\(_2\)), 2.93 (s, CH\(_2\)), 7.36 (d, \( ^3J_{HH} = 8.0 \) Hz), 7.49 (d, \( ^3J_{HH} = 8.0 \) Hz), 7.68 (s), 7.91 (m), 8.11 (m), 8.43 (d, \( ^3J_{HH} = 8.5 \) Hz), 8.53 (d, \( ^3J_{HH} = 8.5 \) Hz), 14.75 (s, NH). UV/vis (MeCN): \( \lambda_{\text{max}}/\text{nm} = 233, 275 \).

Layering the solution with hexane yielded single crystals of \( [2\text{-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline}][\text{OTf}]. \)
Reaction of 2,9-di-tert-butyldimethylsilylmethyl-1,10-phenanthroline with uranyl(VI) triflate

[UO₂(OTf)₂(THF)₃] (2 mg, 0.003 mmol) and 2,9-di-tert-butyldimethylsilylmethyl-1,10-phenanthroline (2 mg, 0.005 mmol) were dissolved in CDCl₃ (1 mL) to give a yellow solution. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): -0.15 (s, SiCH₃), 0.01 (s, SiCH₃), 0.81 (s, SiCCH₃), 0.97 (s, SiCCH₃), 2.80 (br, CH₂), 3.85 (br, CH₂), 7.33 (br), 7.68 (br), 7.93 (m), 8.06 (br), 8.43 (d, J_HH = 8.5 Hz), 8.47 (br), 14.45 (s, NH). UV/vis (MeCN): λ_max/ nm = 234, 285.

Reaction of 2-tri-iso-propylsilylmethyl-9-methyl-1,10-phenanthroline with uranyl(VI) triflate

[UO₂(OTf)₂(THF)₃] (2 mg, 0.003 mmol) and 2-tri-iso-propylsilylmethyl-9-methyl-1,10-phenanthroline (1 mg, 0.003 mmol) were dissolved in CDCl₃ (1 mL) to give a yellow solution. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 0.85 (d, J_HH = 8.0 Hz, SiCCH₃), 1.02 (d, J_HH = 8.0 Hz, SiCCH₃), 1.04-1.28 (overlapping signals, SiCH), 2.88 (s, CH₂), 2.99 (s, CH₂), 7.64 (m), 7.78 (d, J_HH = 8.5 Hz), 7.83 (d, J_HH = 8.5 Hz), 7.93 (s), 7.99 (d, J_HH = 8.5 Hz), 8.13 (d, J_HH = 8.5 Hz), 8.29 (br), 8.41 (d, J_HH = 8.5 Hz), 8.49 (br), 8.54 (d, J_HH = 8.5 Hz), 13.27 (s, NH). UV/vis (MeCN): λ_max/ nm = 233, 275.

Reaction of 2,9-tri-iso-propylsilylmethyl-1,10-phenanthroline with uranyl(VI) triflate

[UO₂(OTf)₂(THF)₃] (2 mg, 0.003 mmol) and 2,9-tri-iso-propylsilylmethyl-1,10-phenanthroline (3 mg, 0.006 mmol) were dissolved in CDCl₃ (1 mL) to give a yellow solution. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 0.93 (s, SiCCH₃), 1.16 (s, SiCCH₃), 3.00 (s, CH₂), 3.55 (s, CH₂), 7.00 (br), 7.30 (m), 7.52-7.82 (overlapping
signals), 8.04 (d, $^3J_{HH} = 8.5$ Hz), 8.11 (d, $^3J_{HH} = 8.5$ Hz), 8.18 (br), 8.46 (d, $^3J_{HH} = 8.5$ Hz), 13.90 (s, NH). UV/vis (MeCN): $\lambda_{\text{max}}$/nm = 233, 275.

**Reaction of 2,9-di-tert-butylidiphenylsilylmethyl-1,10-phenanthroline with uranyl(VI) triflate**

[UO$_2$(OTf)$_3$(THF)$_3$] (2 mg, 0.003 mmol) and 2,9-di-tert-butylidiphenylsilylmethyl-1,10-phenanthroline (3 mg, 0.004 mmol) were dissolved in CDCl$_3$ (1 mL) to give a yellow solution. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): 1.08 (s, SiCCH$_3$), 1.14 (s, SiCCH$_3$), 2.89 (s, CH$_2$), 3.30 (s, CH$_2$), 7.16-7.46 (overlapping signals), 7.51 (d, $^3J_{HH} = 7.0$ Hz), 7.61 (s), 7.72 (br), 8.06 (br), 8.24 (br).

**Reaction of 2,9-tri-isopropylsilylmethyl-1,10-phenanthroline with uranyl(VI) triflate**

[O$_2$(OTf)$_3$(THF)$_3$] (2 mg, 0.003 mmol) and 2,9-tri-isopropylsilylmethyl-1,10-phenanthroline (3 mg, 0.004 mmol) were dissolved in CDCl$_3$ (1 mL) to give a yellow solution. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): 1.08 (s, SiCCH$_3$), 1.14 (s, SiCCH$_3$), 2.89 (s, CH$_2$), 3.30 (s, CH$_2$), 7.16-7.46 (overlapping signals), 7.51 (d, $^3J_{HH} = 7.0$ Hz), 7.61 (s), 7.72 (br), 8.06 (br), 8.24 (br).

**Layering the solution with hexane yielded single crystals of [2-tert-butylidimethylsilylmethyl-9-methyl-1,10-phenanthroline]$^+[\text{OTf}]^-$.

**Reaction of 2,9-di-tert-butylidimethylsilylmethyl-9-methyl-1,10-phenanthroline with uranyl(V) triflate**

[O$_2$(OTf)$_3$(THF)$_3$] (2 mg, 0.003 mmol) and 2,9-di-tert-butylidimethylsilylmethyl-9-methyl-1,10-phenanthroline (3 mg, 0.004 mmol) were dissolved in CDCl$_3$ (1 mL) to give a yellow solution. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): 1.08 (s, SiCCH$_3$), 1.14 (s, SiCCH$_3$), 2.89 (s, CH$_2$), 3.30 (s, CH$_2$), 7.16-7.46 (overlapping signals), 7.51 (d, $^3J_{HH} = 7.0$ Hz), 7.61 (s), 7.72 (br), 8.06 (br), 8.24 (br).

**Reaction of 2,9-tri-isopropylsilylmethyl-1,10-phenanthroline with uranyl(V) triflate**

[O$_2$(OTf)$_3$(THF)$_3$] (2 mg, 0.003 mmol) and 2,9-tri-isopropylsilylmethyl-1,10-phenanthroline (3 mg, 0.004 mmol) were dissolved in CDCl$_3$ (1 mL) to give a yellow solution. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): 1.08 (s, SiCCH$_3$), 1.14 (s, SiCCH$_3$), 2.89 (s, CH$_2$), 3.30 (s, CH$_2$), 7.16-7.46 (overlapping signals), 7.51 (d, $^3J_{HH} = 7.0$ Hz), 7.61 (s), 7.72 (br), 8.06 (br), 8.24 (br).

**Layering the solution with hexane yielded single crystals of [2-tert-butylidimethylsilylmethyl-9-methyl-1,10-phenanthroline]$^+[\text{OTf}]^-$.

**Reaction of 2,9-di-tert-butylidimethylsilylmethyl-2,2’-bipyridine with uranyl(V) triflate**

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\[\{\text{UO}_2(\text{py})_3\}\{\text{K}_3(\text{OTf})_3\}\cdot\text{py}\}_{\text{n}}\) (18 mg, 0.008 mmol) and 6,6’-di-tert-butyldimethyl-2,2’-bipyridine (7 mg, 0.017 mmol) were dissolved in d_6-benzene (1 mL) to yield a brown solution. \(^1\text{H}\) NMR (C\textsubscript{6}D\textsubscript{6}, 400 MHz) \(\delta\) (ppm): 0.04 (s, SiCH\textsubscript{3}), 0.92 (s, SiCCH\textsubscript{3}), 2.40 (s, CH\textsubscript{2}), 6.66 (br), 6.97 (br), 7.16 (br), 7.30 (br), 8.54 (br), 8.60 (br). UV/vis (C\textsubscript{6}D\textsubscript{6}): \(\lambda_{\text{max}}\) nm = 652.

Reaction of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline with uranium(IV) triflate

[U(OTf)\textsubscript{4}] (26 mg, 0.031 mmol) and 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (10 mg, 0.031 mmol) were dissolved in d\textsubscript{5}-pyridine (1 mL) to give a dull green solution. \(^1\text{H}\) NMR (C\textsubscript{5}D\textsubscript{5}N, 400 MHz) \(\delta\) (ppm): 0.82 (br), 1.63 (br), 1.93 (br), 3.46 (br), 7.93 (br), 8.25 (br), 8.58 (br), 8.98 (br), 9.58 (br), 15.60 (br), 19.51 (br), 41.16 (br), 42.42 (br), 43.02 (br), 52.87 (br), 54.54 (br), 57.51 (br), 58.62 (br), 62.80 (br), 67.99 (br), 71.38 (br).

Reaction of 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline with europium (III) triflate

[Eu(OTf)\textsubscript{3}].6H\textsubscript{2}O (5 mg, 0.008 mmol) and 2-tert-butyldimethylsilylmethyl-9-methyl-1,10-phenanthroline (3 mg, 0.009 mmol) were dissolved in d\textsubscript{3}-MeCN (1 mL). \(^1\text{H}\) NMR (CD\textsubscript{3}CN, 400 MHz) \(\delta\) (ppm): 0.00 (s, 6H, SiCH\textsubscript{3}), 0.96 (s, 9H, SiCCH\textsubscript{3}), 2.81 (s, 3H, CH\textsubscript{3}), 2.84 (s, 2H, CH\textsubscript{2}), 7.55 (d, \(^3\)J\textsubscript{HH} = 8.5 Hz, 1H, H\textsubscript{3}), 7.64 (d, \(^3\)J\textsubscript{HH} = 9.0 Hz, 1H, H\textsubscript{6}), 7.86 (s, 2H, H\textsubscript{5} + H\textsubscript{6}), 8.33 (d, \(^3\)J\textsubscript{HH} = 8.5 Hz, 1H, H\textsubscript{4}), 8.14 (d, \(^3\)J\textsubscript{HH} = 9.0 Hz, 1H, H\textsubscript{7}).

Transuranic Complexations of Silylated Dimethyl-Bipyridines

**Reaction of Am(NO\textsubscript{3})\textsubscript{3} with 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine**

A solution containing Am(III) (1 mg, 4.1 mmol) in 0.5 M HNO\textsubscript{3} was heated to dryness by Dr A. Geist. A 600 μL (MeOD 4:1 CDCl\textsubscript{3}) sample of 6,6’-di-tert-butyldimethylsilylmethyl-2,2’-bipyridine (5.07 mg, 12.5 mmol) was transferred to the salt via syringe, resulting in a colour change from pink to yellow/green. The subsequent solution was transferred to a Young’s tap NMR tube and transported to the NMR machine in double containment for study. \(^1\text{H}\) NMR (MeOD 4:1 CDCl\textsubscript{3}, 400 MHz) \(\delta\) (ppm): 0.01 (s, 12H, Si(CH\textsubscript{3})\textsubscript{2}), 0.95 (s, 18H, SiC(CH\textsubscript{3})\textsubscript{3}), 2.50 (s, 4H, CH\textsubscript{2}), 7.14 (br, 2H, H\textsubscript{2}), 7.77 (br, 2H, H\textsubscript{3}), 7.98 (d, \(^3\)J\textsubscript{HH} = 8.0 Hz, 2H, H\textsubscript{4}); \(^{13}\)C-\(^1\text{H}\) NMR (MeOD 4:1 CDCl\textsubscript{3}, 101 MHz) \(\delta\)
(ppm): -5.9 (Si(CH₃)₂), 17.4 (SiC(CH₃)₃), 26.8 (CH₂), 118.2 (C₄), 124.1 (C₂), 138.4 (C₃), 150.3 (C₅), 162.2 (C₁).

**Reaction of Am(NO₃)₃ with 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine**

A solution containing Am(III) (1 mg, 4.1 mmol) in 0.5 M HNO₃ was heated to dryness by Dr A. Geist. A 600 μL (MeOD 5:1 CDCl₃) sample of 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine (6.26 mg, 12.6 mmol) was transferred to the salt via syringe, resulting in a colour change from pink to yellow/green. The subsequent solution was transferred to a Young’s tap NMR tube and transported to the NMR machine in double containment for study. ¹H NMR (MeOD 5:1 CDCl₃, 400 MHz) δ (ppm): 1.07 (d, ³JHH = 7.0 Hz, 36H, SiC(CH₃)₂), 1.15 (sept., ³JHH = 7.0 Hz, 6H, SiCH), 2.56 (s, 4H, CH₂), 7.21 (br, 2H, H₂), 7.75 (br, 2H, H₃), 8.06 (d, ³JHH = 8.0 Hz, 2H, H₄); ¹³C-{¹H} NMR (MeOD 5:1 CDCl₃, 101 MHz) δ (ppm): 12.5 (SiCH), 19.4 (SiC(CH₃)₂), 23.5 (CH₂), 117.3 (C₄), 123.7 (C₂), 161.0 (C₁).

**Reaction of Am(NO₃)₃ with 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine**

A solution containing Am(III) (1 mg, 4.1 mmol) in 0.5 M HNO₃ was heated to dryness by Dr A. Geist. A 600 μL (MeOD 2:1 CDCl₃) sample of 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine (8.33 mg, 12.6 mmol) was transferred to the salt via syringe, resulting in a colour change from pink to yellow/green. The subsequent solution was transferred to a Young’s tap NMR tube and transported to the NMR machine in double containment for study. ¹H NMR (MeOD 2:1 CDCl₃, 400 MHz) δ (ppm): 1.11 (s, 18H, SiC(CH₃)₃), 3.09 (s, 4H, CH₂), 6.92 (br, 2H, H₂), 7.22-7.40 (br, 14H, H₄, o-ph and p-ph), 7.46-7.60 (br, 14H, H₃ and m-ph); ¹³C-{¹H} NMR (MeOD 2:1 CDCl₃, 101 MHz) δ (ppm): 18.5 (SiC(CH₃)₃), 27.5 (CH₂), 118.0 (C₃), 125.0 (C₂), 127.6 (o-ph), 129.5 (p-ph), 133.0 (i-ph), 136.2 (m-ph), 139.1 (C₄), 159.50 (C₁), 161.2 (C₅).

**Reaction of Cm(ClO₄)₃ with 6,6'-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine**

20 μL of Cm(III) (6.67 μM) in 32 mM HClO₄ was added to a cuvette and made up to 1 mL by addition of a MeOH 2:1 CDCl₃ mixture to produce a 100 nM solution of Cm(ClO₄). Solutions of 1 mM and 10 mM 6,6'-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine in MeOH 2:1 CDCl₃ were added in aliquots to the Cm(III) perchlorate solution and the emission spectrum was recorded at each step. The total volume of ligand in the sample at each step was: 50 and 100 μL of a 1 mM solution; 35, 85, 135, 235, 455 and 665 μL of a 10 mM solution.
Reaction of Cm(ClO$_4$)$_3$ with 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine

20 μL of Cm(III) (6.67 μM) in 32 mM HClO$_4$ was added to a cuvette and made up to 1 mL by addition of a MeOH 2:1 CDCl$_3$ mixture to produce a 100 nM solution of Cm(ClO$_4$)$_3$. Solutions of 0.1 mM, 1 mM, 10 mM and 100 mM 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine in MeOH 2:1 CDCl$_3$ were added in aliquots to the Cm(III) perchlorate solution and the emission spectrum was recorded at each step. The total volume of ligand in the sample at each step was; 10, 20, 40, 100 and 200 μL of a 0.1 mM solution; 40, 60, 100, 170 and 270 μL of a 1 mM solution; 37, 57, 77, 127, 177, 277, 377, 477, 677, 877 and 1377 μL of a 10 mM solution; 188, 238, 338, 438 and 638 μL of a 100 mM solution.

Reaction of Cm(ClO$_4$)$_3$ with 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine

20 μL of Cm(III) (6.67 μM) in 32 mM HClO$_4$ was added to a cuvette and made up to 1 mL by addition of a MeOH 2:1 CDCl$_3$ mixture to produce a 100 nM solution of Cm(ClO$_4$)$_3$. A solution of 10 mM 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine in MeOH 2:1 CDCl$_3$ was added in aliquots to the Cm(III) perchlorate solution and the emission spectrum recorded at each step. The total volume of ligand in the sample at each step was; 10, 50, 100, 200, 300, 500 and 700 μL of a 10 mM solution.

Reaction of NpO$_2$Cl with 6,6'-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine

A solution containing Np(V) (1.42 mg, 6.0 mmol) in 0.01 M HCl was heated to dryness, dissolved in 150 μL D$_2$O and heated to dryness again. A 600 μL (MeOD 5:1 CDCl$_3$) sample of 6,6'-di-tert-butyldimethylsilylmethyl-2,2'-bipyridine (5.07 mg, 12.6 mmol) was transferred to the salt via syringe. The subsequent green solution was transferred to a NMR tube and transported to the NMR machine in double containment for study. UV/ vis (MeOH 2:1 DCM): $\lambda_{max}$ nm = 977, 1032, 1096, 1104. $^1$H NMR (MeOD 5:1 CDCl$_3$, 400 MHz) $\delta$ (ppm): 0.09 (s, 12H, Si(CH$_3$)$_2$), 0.96 (s, 18H, SiC(CH$_3$)$_3$), 2.51 (s, 4H, CH$_2$), 7.15 (br, 2H, H$_2$), 7.78 (br, 2H, H$_3$), 7.97 (br, 2H, H$_4$); $^{13}$C-{$^1$H} NMR (MeOD 5:1 CDCl$_3$, 101 MHz) $\delta$ (ppm): -5.1 (Si(CH$_3$)$_2$), 18.2 (SiC(CH$_3$)$_3$), 27.6 (CH$_2$), 118.9 (C$_4$), 124.7 (C$_2$), 140.7 (C$_3$), 162.8 (C$_1$).

Reaction of NpO$_2$Cl with 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine

A solution containing Np(V) (1.42 mg, 6.0 mmol) in 0.01 M HCl was heated to dryness, dissolved in 150 μL D$_2$O and heated to dryness again. A 600 μL (MeOD 2:1 CDCl$_3$)
sample of 6,6'-di-tri-iso-propylsilylmethyl-2,2'-bipyridine (5.95 mg, 12.0 mmol) was transferred to the salt via syringe. The subsequent green solution was transferred to a NMR tube and transported to the NMR machine in double containment for study. UV/vis (MeOH 2:1 DCM): $\lambda_{\text{max}}$/ nm = 977. $^1$H NMR (MeOD 2:1 CDCl$_3$, 400 MHz) $\delta$ (ppm): 1.06 (d, $^3$J$_{HH}$ = 6.5 Hz, 36H, SiC(CH$_3$)$_2$), 1.15 (sept, $^3$J$_{HH}$ = 6.5 Hz, 6H, SiCH), 2.53 (s, 4H, CH$_2$), 7.12 (d, $^3$J$_{HH}$ = 7.5 Hz, 2H, H$_2$), 7.61 (dd, $^3$J$_{HH}$ = 7.5 Hz, $^3$J$_{HH}$ = 7.0 Hz, 2H, H$_3$), 8.04 (d, $^3$J$_{HH}$ = 7.0 Hz, 2H, H$_4$); $^{13}$C-$^1$H NMR (MeOD 2:1 CDCl$_3$, 101 MHz) $\delta$ (ppm): 19.8 (SiC(CH$_3$)$_3$), 28.8 (CH$_2$), 118.7 (C$_3$), 127.3 (C$_2$), 128.8 (o-ph), 130.5 (p-ph), 135.4 (i-ph), 137.7 (m-ph), 151.8 (C$_4$), 159.3 (C$_1$), 160.8 (C$_5$).

**Reaction of NpO$_2$Cl with 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine**

A solution containing Np(V) (1.42 mg, 6.0 mmol) in 0.01 M HCl was heated to dryness, dissolved in 150 μL D$_2$O and heated to dryness again. A 600 μL (MeOD 2:1 CDCl$_3$) sample of 6,6'-di-tert-butyldiphenylsilylmethyl-2,2'-bipyridine (7.92 mg, 12.0 mmol) was transferred to the salt via syringe. The subsequent green solution was transferred to a NMR tube and transported to the NMR machine in double containment for study. UV/vis (MeOH 2:1 DCM): $\lambda_{\text{max}}$/ nm = 977, 1032, 1102. $^1$H NMR (MeOD 2:1 CDCl$_3$, 400 MHz) $\delta$ (ppm): 1.08 (s, 18H, SiC(CH$_3$)$_3$), 3.04 (s, 4H, CH$_2$), 6.70 (br, 2H, H$_2$), 7.11-7.80 (br, 28H, H$_3$, H$_4$, o-ph, m-ph and p-ph); $^{13}$C-$^1$H NMR (MeOD 2:1 CDCl$_3$, 101 MHz) $\delta$ (ppm): 19.8 (SiC(CH$_3$)$_3$), 28.8 (CH$_2$), 118.7 (C$_3$), 127.3 (C$_2$), 128.8 (o-ph), 130.5 (p-ph), 135.4 (i-ph), 137.7 (m-ph), 151.8 (C$_4$), 159.3 (C$_1$), 160.8 (C$_5$).

**Transuranic Complexations of TPIP**

**Synthesis of Np(VI)O$_2$(TPIP)$_2$(HTPIP)$_{1/2}$C$_6$H$_4$**

Np(VI)O$_2$(O$_4$Cl)$_2$ in perchloric acid (330 μL; 0.007 mmol $^{237}$Np) was heated until dry and dissolved in deionised water (1 mL). NaTPIP (6 mg, 0.014 mmol) was immediately added and the solution stirred for 20 min. to yield a pale green solution. The solution was filtered and the pale green solid solubilised with DCM (1 mL). Immediate layering of the solution with hexane led to the isolation of crystals. UV/vis (DCM): $\lambda_{\text{max}}$/ nm = 225 (sh), 257, 307 (sh), 595, 1235.

**Synthesis of Np(VI)O$_2$(TPIP)$_2$(HTPIP)$_{1/2}$C$_6$H$_6$**

Np(VI)O$_2$(O$_4$Cl)$_2$ in perchloric acid (330 μL; 0.007 mmol $^{237}$Np) was heated until dry and dissolved in deionised water (1 mL). NaTPIP (6 mg, 0.014 mmol) was immediately added.
and the solution stirred for 20 min. to yield a pale green solution. The solution was filtered and the pale green solid solubilised with benzene (1 mL). Immediate layering of the solution with hexane led to the isolation of crystals. UV/vis (DCM): $\lambda_{\text{max}}$/ nm = 284, 313, 1215. $^{31}$P-$^1$H NMR (CD$_2$Cl$_2$, 162 MHz) $\delta$ (ppm): -29.9 (br, Np-TPIP), 20.5 (br, Np-HTPIP), 22.9 (HTPIP); $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) $\delta$ (ppm): 6.21 br, 6.55 (br), 6.83-7.2 (overlapping resonances), 7.76 (m), 8.14 (m), 8.21 (m), 8.27 (m).

**Synthesis of [Np(VI)O$_2$(TPIP)$_2$]$_2$**.
Np(VI)O$_2$(O$_4$Cl)$_2$ in perchloric acid (330 μL; 0.007 mmol $^{237}$Np) was heated until dry and dissolved in deionised water (1 mL). NaTPIP (6 mg, 0.014 mmol) was immediately added and the solution stirred for 20 min. to yield a pale green solution. The solution was filtered and the pale green solid solubilised with DCM (1 mL). The solution was left to stand overnight and then layered with hexane, leading to the isolation of crystals. UV/vis (DCM): $\lambda_{\text{max}}$/ nm = 225 (sh), 257, 307 (sh), 595, 1235. $^{31}$P-$^1$H NMR (CD$_2$Cl$_2$, 162 MHz) $\delta$ (ppm): -30.0 (br, Np-TPIP), 20.6 (br, Np-TPIP), 23.0 (HTPIP); $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) $\delta$ (ppm): 6.85 (br, Np-TPIP), 7.09-7.80 (overlapping resonances, Np-TPIP + HTPIP), 8.01 (m, HTPIP).

**Synthesis of Np(VI)O$_2$(TPIP)$_2$(Ph$_3$PO)**.
Np(V)O$_2$(Cl) in hydrochloric acid (200 μL; 0.006 mmol $^{237}$Np) was heated until dry and dissolved in MeOD 1:1 CDCl$_3$ (1 mL). NaTPIP (5 mg, 0.011 mmol) and Ph$_3$PO (1 mg, 0.004 mmol) were added and the green solution transferred to an NMR tube. Standing for three months led to the isolation of crystals. UV/vis (DCM): $\lambda_{\text{max}}$/ nm = 243, 266, 273, 290 (sh), 585, 1232. $^{31}$P-$^1$H NMR (CDCl$_3$, 162 MHz) $\delta$ (ppm): -28.5 (br, Np-TPIP), 20.6 (br, Np-TPIP), 29.2 (Ph$_3$PO); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): 6.80-8.10 (overlapping resonances, Np-TPIP + Np-Ph$_3$PO + Ph$_3$PO), 7.39 (t, $^3$J$_{HH}$ = 7.0 Hz, Np-TPIP), 7.48 (t, 7.0 Hz, Np-TPIP), 7.58 (br, Np-TPIP).

**Reaction of Np(V)O$_2$ with one equivalent of NaTPIP**
Np(V)O$_2$(Cl) in hydrochloric acid (200 μL; 0.006 mmol $^{237}$Np) was heated until dry and dissolved in MeOD (0.5 mL). NaTPIP (3 mg, 0.007 mmol) was added and the green solution transferred to an NMR tube. UV/vis (DCM): $\lambda_{\text{max}}$/ nm = 250, 275, 423, 459, 475, 517, 590, 618, 687, 746, 910, 977, 1030, 1101, 1117, 1237. $^{31}$P-$^1$H NMR (d$_4$-MeOD, 162 MHz) $\delta$ (ppm): -1.2 (br, Na(TPIP)$_3$); $^1$H NMR (d$_4$-MeOD, 400 MHz) $\delta$ (ppm): 7.46 (t, $^3$J$_{HH}$ = 7.5 Hz, ph-H), 7.63 (br, ph-H), 7.70 (br, ph-H), 7.75 (br, ph-H), 8.00 (m, ph-H).
Reaction of Np(V)O$_2$ with two equivalents of NaTPIP

Np(V)O$_2$(Cl) in hydrochloric acid (200 μL; 0.006 mmol $^{237}$Np) was heated until dry and dissolved in MeOD (0.5 mL). NaTPIP (5 mg, 0.011 mmol) was added and the green solution transferred to an NMR tube. UV/vis (DCM): $\lambda_{\text{max}}$/ nm = 249, 272, 425, 475, 518, 592, 618, 688, 760, 909, 978, 987, 1024, 1101, 1120, 1240. $^{31}$P-{1}H NMR (d$_4$-MeOD, 162 MHz) δ (ppm): -161.4 (br, Np-TPIP), -21.7 (br, Np-TPIP); $^1$H NMR (d$_4$-MeOD, 400 MHz) δ (ppm): 7.38 (br, $ph$-H), 7.64 (br, $ph$-H).

Reaction of Np(V)O$_2$ with two equivalents of NaTPIP and Ph$_3$PO

Np(V)O$_2$(Cl) in hydrochloric acid (200 μL; 0.006 mmol $^{237}$Np) was heated until dry and dissolved in MeOD (0.5 mL). NaTPIP (5 mg, 0.011 mmol) and Ph$_3$PO (1 mg, 0.004 mmol) were added. Layering of the green solution with diethyl ether led to the isolation of crystals. UV/vis (DCM): $\lambda_{\text{max}}$/ nm = 244, 273, 423, 475, 516, 591, 619, 687, 752, 911, 977, 986, 1028, 1101, 1118, 1235. $^{31}$P-{1}H NMR (d$_4$-MeOD, 162 MHz) δ (ppm): -161.4 (br, Np-TPIP), -21.7 (br, Np-TPIP), 31.6 (Ph$_3$PO); $^1$H NMR (d$_4$-MeOD, 400 MHz) δ (ppm): 7.31 (br, $ph$-H), 7.56 (br, $ph$-H) 7.64 (br, $ph$-H).

Titration of UO$_2$(TPIP)$_2$(Ph$_3$PO) into Np(VI)O$_2$(TPIP)$_2$(Ph$_3$PO)

A solution of Np(VI)O$_2$(TPIP)$_2$(Ph$_3$PO) (1.5 mL, ~2 mM) was transferred to a screw-cap cuvette. Aliquots of UO$_2$(TPIP)$_2$(Ph$_3$PO) in DCM (150 μL, 0.2 mM) were added to the cuvette and the UV/vis and emission spectrum recorded at each point. Aliquots were added until there was 1950 μL of UO$_2$(TPIP)$_2$(Ph$_3$PO) (2.6 mM) in the sample. $^{31}$P-{1}H NMR (CD$_2$Cl$_2$, 162 MHz) δ (ppm): 15.6 (br), 16.2 (br), 19.5 (br), 21.2-25.9 (overlapping resonances, U-TPIP), 27.4 (s, Ph$_3$PO), 34.2 (br), 40.6 (br, U-Ph$_3$PO); $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) δ (ppm): 6.51-8.40 (overlapping resonances).

Reaction of Am(NO$_3$)$_3$ with NaTPIP

A solution containing Am(III) (1 mg, 4.1 mmol) in 0.5 M HNO$_3$ was heated to dryness by Dr A. Geist. A 600 μL sample of NaTPIP (5.54 mg, 12.6 mmol) in MeOD was transferred to the salt via syringe, resulting in a colour change from pink to yellow/ green. The subsequent solution was transferred to a Young’s tap NMR tube and transported to the NMR machine in double containment for study. $^1$H NMR (MeOD, 400 MHz) δ (ppm): 7.15 (m, 2H, $o$-ph), 7.28 (t, $^3$J$_{HH}$ = 7.5 Hz, 2H, $p$-ph), 7.62 (dd, $^3$J$_{HH}$ = 7.5 Hz, $^3$J$_{HH}$ = 7.0 Hz, 2H, $m$-ph); $^{13}$C-{1}H NMR (MeOD, 400 MHz) δ (ppm): 128.9 (d, $^3$J$_{PC}$ = 13.84 Hz,
Reaction of Ln(NO$_3$)$_3$ with NaTPIP

Methods 1-3

Ln(NO$_3$)$_3$ $+$ NaTPIP $\rightarrow$ Ln(NO$_3$)$_3$(TPIP) + Na(NO$_3$)$_3$ $+$ NaTPIP $\rightarrow$ Ln(NO$_3$)$_3$(TPIP)$_2$ + 2Na(NO$_3$)$_3$

Ln(NO$_3$)$_3$ (I: Nd(NO$_3$)$_3$; 2: Sm(NO$_3$)$_3$; 3: Eu(NO$_3$)$_3$; 2 mg, 0.004 mmol) was dissolved in d$_6$-DMSO (0.7 mL) and added to a NMR tube. Aliquots of NaTPIP (2 mg, 0.005 mmol) were added to each of the three NMR tubes and the spectrum recorded. The process was repeated up to a succession of four times.

Reaction of Am(NO$_3$)$_3$ with Na$^{15}$TPIP

A solution containing Am(III) (1 mg, 4.1 mmol) in 0.5 M HNO$_3$ was heated to dryness by Dr. A. Geist. A 600 μL sample of Na$^{15}$TPIP (10.06 mg, 12.6 mmol) in MeOD was transferred to the salt via syringe, resulting in a colour change from pink to yellow/green. The subsequent solution was transferred to a Young’s tap NMR tube and transported to the NMR machine in double containment for study. $^{19}$F NMR (MeOD, 374 MHz) δ (ppm): -164.29 (d, $^3$J$_{FF}$ = 62.0 Hz, 12F, o-ph), -160.12 (dd, $^3$J$_{FF}$ = 49.0 Hz, $^4$J$_{FF}$ = 13.5 Hz 12F, o’-ph), -152.35 (d, $^3$J$_{FF}$ = 105.5 Hz, 12F, p-ph), -136.4 (m, 12F, m'-ph), -134.5 (m, 12F, m''-ph); $^{13}$C{$_1^1$H} NMR (MeOD, 101 MHz) δ (ppm): 140.3 (tm, $^2$J$_{FC}$ = 267.5 Hz, phC), 145.89 (m, phC), 148.42 (dm, $^2$J$_{FC}$ = 252.0 Hz, phC); $^{31}$P NMR (MeOD, 162 MHz) δ (ppm): -9.3 – 32.8 (br, Am-OP), 35.6 (br).

Reaction of Cm(ClO$_4$)$_3$ with NaTPIP

20 μL of Cm(III) (6.67 μM) in 32 mM HClO$_4$ was added to a cuvette and made up to 1 mL by addition of MeOH to produce a 100 nM solution of Cm(ClO$_4$)$_3$. Solutions of 0.1 mM, 1 mM and 10 mM NaTPIP in MeOH 98:2 deionised H$_2$O were added in aliquots to the Cm(III) perchlorate solution and the emission spectrum was recorded at each step. The total volume of ligand in the sample at each step was; 30, 60 and 120 μL of a 0.1 mM solution; 22, 32, 42, 52, 62, 82, 102, 122, 142, 162, 182, 202,
222, 242, 282, 332 and 382 μL of a 1 mM solution; 48, 98, 198 and 798 μL of a 10 mM solution.

**Reaction of Cm(ClO₄)₃ with NaF TPIP**

20 μL of Cm(III) (6.67 μM) in 32 mM HClO₄ was added to a cuvette and made up to 1 mL by addition of MeOH to produce a 100 nM solution of Cm(ClO₄). Solutions of 0.1 mM, 1 mM and 10 mM NaF TPIP in MeOH 98:2 deionised H₂O were added in aliquots to the Cm(III) perchlorate solution and the emission spectrum was recorded at each step. The total volume of ligand in the sample at each step was; 30 and 60 μL of a 0.1 mM solution; 16, 26, 36, 46, 76, 96, 116, 136, 156, 196, 236 and 306 μL of a 1 mM solution; 41, 51, 61, 71, 81, 101, 121 and 151 μL of a 10 mM solution.

### 10.2 References


