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Oxo–Group-14-Element Bond Formation in Binuclear Uranium(V) Pacman Complexes**

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Synopsis:
Keeping it in the carbon family: Simple and versatile metalation and exchange reactions lead to a new family of binuclear uranium(V) oxo complexes that are functionalised by the Group 14 elements C, Si, and Sn. These Pacman-shaped compounds display distinct U-O single and multiple bonding patterns and exhibit unique stability against oxidation.

Keywords:
Oxido ligands; uranium; macrocyclic ligands; structure elucidation; Schiff bases; synthesis design; metalation

Abstract

Simple and versatile routes to the functionalization of uranyl-derived U(V) oxo groups are presented. The oxo-lithiated, binuclear uranium(V) oxo complexes [{$(py)_3$LiOUO}$_2$(L)] and [{$(py)_3$LiOUO}(OUO$SiMe_3$)(L)] are prepared by the direct combination of the uranyl(VI) silylamide 'ate' complex [Li$(py)_2$][(OUO)(N")$_3$] (N" = N$(SiMe_3)_2$) with the polypyrrolic macrocycle H_4L or the mononuclear uranyl(VI) Pacman complex [UO_2(py)(H_2L)], respectively. These oxo-metalated complexes display distinct U-O single and multiple bonding patterns and an axial/equatorial arrangement of oxo ligands. Their ready availability allows the direct functionalisation of the uranyl oxo group leading to the binuclear uranium(V) oxo-stannylated complexes [{(R_3Sn)OUO}$_2$(L)] (R = ^{n}Bu, Ph) which represent rare examples of mixed uranium/tin complexes. Also, uranium oxo-group exchange occurs in reactions with [TiCl(O^{i}Pr)$_3$] to form U-O-C bonds [{$(py)_3$LiOUO}(OUO^{i}Pr)(L)] and [(^{i}PrOUO)$_2$(L)]. Overall, these represent the first family of uranium(V) complexes that are oxo-functionalised by Group 14 elements.

Introduction

The synthesis of stable complexes of uranium(V) has been one of the most exciting discoveries in synthetic actinide chemistry in recent years,[1] a feat accomplished in spite of the high propensity of these compounds to decompose by disproportionation and oxidation pathways.[2] Of particular importance within this emerging field are uranyl(V) complexes that result from the single electron reduction of the uranyl(VI) dication, the most common form of uranium in the environment.[3] The uranyl dication (Figure 1, i) comprises a uranium centre with two strongly-bound, mutually *trans* oxo groups, and is traditionally considered highly inert to towards -yl group substitution or functionalisation.[4] Recent studies have shown that reduction of $[UO_2]^{2+}$ to $[UO_2]^{+}$ greatly increases the oxo-group reactivity, allowing cation-cation interactions (CCIs) to occur in which the more Lewis basic oxo-group of the uranyl(V) cation coordinates to other metal centres (Figure 1, ii)[5, 6-9] or another uranyl (Figure 1, iii).[10] Also of synthetic interest is uranyl oxo-group functionalisation, in which the single electron reduction of the uranyl dication occurs alongside covalent bond formation to the oxo group (Figure 1, iv); to date, only bonds to protons[11] and silyl groups[6, 12] have been observed. A final class of compounds in oxo uranium chemistry feature terminal mono-oxo ligands (Figure 1, v) and have been isolated for both uranium(V)[13, 14] and uranium(VI),[14, 15] and commonly incorporate bulky ligands to prevent further reaction of the highly nucleophilic oxo group.[16]

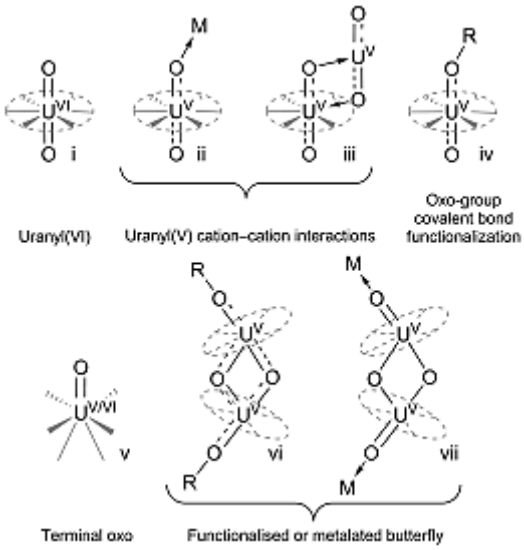
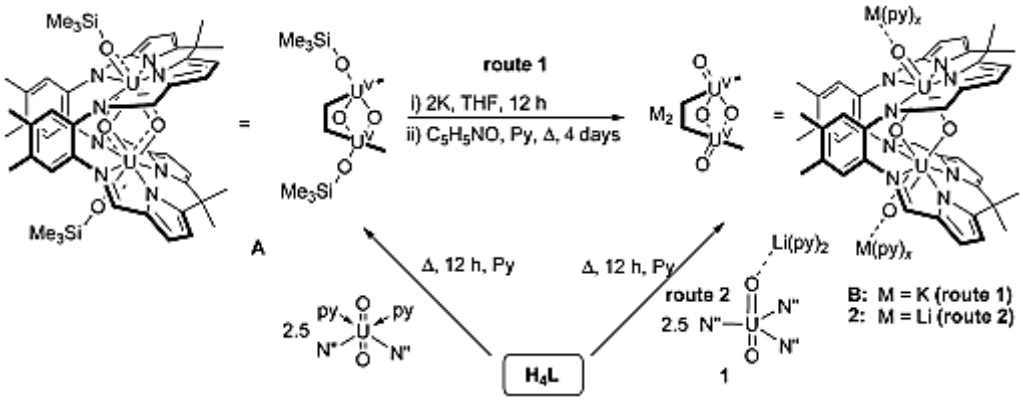


Figure 1. Bonding motifs in high oxidation state uranium oxo chemistry

Since 2004, we have been studying the reactivity of mononuclear uranyl complexes of the binucleating Schiff base polypyrrolic macrocycle L, in which the ligand adopts a unique wedge-shaped "Pacman" geometry upon uranyl complexation.[17] This ligand arrangement facilitates both uranyl reduction and functionalisation chemistry by the formation of heterobimetallic complexes,[6-8] and prompted us to explore the chemistry of binuclear analogues.[18] We reported recently the binuclear uranium(V) dioxo complex $[(Me_3SiOUO)_2(L)]$ **A** and its desilylation chemistry to form the doubly-anionic, binuclear uranium(V) complex $[K(py)_4]_2[(OUO)_2(L)]$ **B** (Scheme 1).[19, 20] Both complexes are unique in that they are derived from two *trans*-uranyl dications, but feature both bridging oxo ligands in axial and equatorial positions arranged in a U_2O_4 core and terminally functionalised *exo*-oxo groups. The resulting $[OU(\mu\text{-}O)_2UO]$ "butterfly" bonding represents a new motif in high oxidation state uranium chemistry (Figure 1, vi + vii) having been previously predicted by Schreckenbach and co-workers using computational methods.[21] The motif bridges the gap between classical *trans* uranyl(V) complexes and rarer U^V/U^V bis-μ-O complexes such as $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}O)_2]$ (Ad = adamantyl).[22] While **A** and **B** exhibit a similar arrangement of uranium and oxygen atoms they differ in the precise nature of their uranium-oxygen bonding, with **A** displaying delocalised U-O bonds (2.03 -- 2.10 Å) and **B** exhibiting two short bonds to the *exo*- oxygen atoms (1.85 and 1.87 Å) and four longer bonds between the metal centres (2.09 -- 2.17 Å). This contrasting bonding between the two structurally comparable complexes is mirrored in their reactivity, with the silylated complex **A** being highly inert towards oxidation or hydrolysis, even at elevated temperatures, whereas the desilylated analogue **B** undergoes rapid decomposition in the presence of oxygen and water. In light of this, we proposed that oxo-group silylation of uranium(V) oxo groups protects the highly reactive uranium(V) centres from decomposition, leading us to speculate whether oxo-group functionalisation by other elements can be used to achieve the same effect. Herein, we describe the first synthesis of binuclear uranium(V) dioxo complexes that

are functionalised at an oxo-group by tin and carbon groups. We proceed to show how these alternatively-functionalised analogues of **A** display similarly remarkable stability against oxidation and how the uranium bonding in each complex may be varied between fully delocalised or discrete U-O multiple bonding through the choice of oxo-group substituents. Furthermore, we describe the direct and more convenient synthesis of the dilithiated analogue of **B** as well as a new mixed lithium/silyl complex which shows both metalated and covalently functionalised oxo groups in the same molecule.

Results and Discussion



Scheme 1. Synthesis of the binuclear uranium(V) oxo complexes $[M(py)_x]_2[(OUO)_2(L)]$ from either redox-induced desilylation of the doubly silylated complex $[(Me_3OUO)_2(L)]$ **A** (route 1, M = K, **B**) or from the free macrocycle H_4L and $[Li(py)_2][(OUO)\{N(SiMe_3)_3\}_3]$ **1** (route 2, M = Li, **2**).

Binuclear, oxo-lithiated uranium(V) complex 2

We recently reported the synthesis of $K_2[(OUO)_2(L)]$ **B** through a multi-step process, first requiring the synthesis of doubly silylated **A** by reaction between H_4L and 2.5 equivalents of uranyl silylamide followed by desilylation by reduction with potassium metal and subsequent re-oxidation with pyridine-*N*-oxide (Scheme 1, route 1). The laborious nature of this synthesis encouraged us to seek an alternative method. We have shown that the reaction between $[UO_2(py)(H_2L)]$ and 2 equivalents of LiN" (N" = $N(SiMe_3)_2$) led to single electron reduction and concomitant oxo-group lithiation of the uranyl centre to form the uranyl(V) complex $[(py)_3LiOUO(py)Li(py)(HL)]$.[7] This led us to speculate that the addition of LiN" to the reaction mixture used to synthesise **A** could yield oxo-lithiated, rather than oxo- silylated complexes. Initially, the reaction of a 1:1 mixture of LiN" and $[UO_2(N")_2(py)_2]$ in toluene was carried out and was found to form the new "-ate" complex $[(py)_2LiOUO(N"_3)]$ **1** in 58 % yield. Crystallographic analysis of **1** reveals it to be isostructural to the known Na analogue $[(THF)_2NaOUO(N")_3]$,[23] featuring a trigonal bipyramidal $[UO2(N")_3]^-$ anion

comprising a linear $[UO_2]^{2+}$ dication with three $N(SiMe_3)_2$ ligands in the equatorial plane (see supplementary information, SI).

With this material in hand, the reaction between 2.5 equivalents of **1** and H_4L in boiling pyridine over 12 h was carried out and results in the formation of the oxo-lithiated, binuclear, uranium(V) complex $[\{(py)_3LiOUO\}_2(L)]$ **2** and HN" as the only soluble products, as well as some intractable brown solids; pure **2** was isolated in 21 % yield by filtration and recrystallisation from pyridine. The ^1H NMR spectrum of **2** is almost identical to that of the potassium analogue $K_2[(OUO)_2(L)]$ **B**, with seven resonances between δ=12 and −12 ppm indicative of the formation of a bimetallic uranium(V) Pacman complex with C_{2v} symmetry. In addition, the vis/NIR spectrum of **2** shows striking similarity to **B**, with broad absorptions at 913, 1152, 1190, 1320 and 1684 nm that match those in the spectrum of **B** (897, 1142, 1191, 1300 and 1684 nm, Figure 4 and SI). The solid state structure of **2** reveals the presence of the $[(OUO)_2(L)]^{2-}$ dianion, with the wedge-shaped, binucleating Pacman macrocycle holding the two uranium centres proximate (U1···U2 3.3793(4) Å) (Figure 2). Each uranium atom has a Li-bound *exo*-oxo group, with the U-O bond lengths of 1.877(4) (U1-O1) and 1.883(4) Å (U2-O4) similar to those in **B** (1.851(6) and 1.871(5) Å). The two *endo*- oxo atoms bridge the uranium centres in mutually axial and equatorial positions forming the diamond-shaped, $U^V{}_2O_2$ core observed in both **A** and **B** as well as in the complex $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}O)_2]$.[22] These four *endo* U-O bonds are lengthened and correspond to uranium-oxygen single bonds. In contrast to **B** which exists as a crystallographic dimer, the smaller size and electronegativity of the lithium cation means that **2** does not aggregate in the solid state, with much shorter O-Li bonds (1.87(1) and 1.93(1) Å) as compared to the O-K bonds in **B** (2.658(6) - 2.764(6) Å). These O-Li bond distances are similar to those seen in other lithiated uranyl(V) complexes.[7]

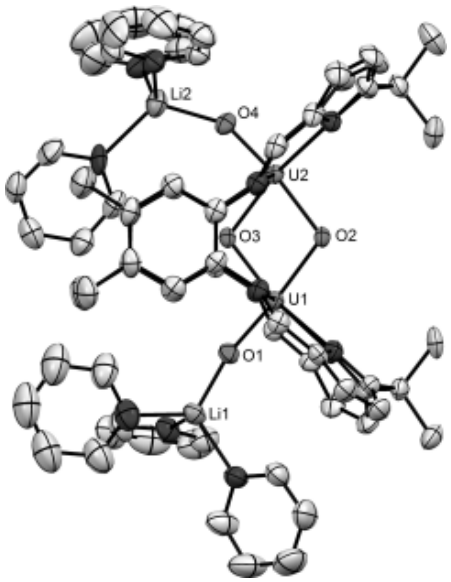
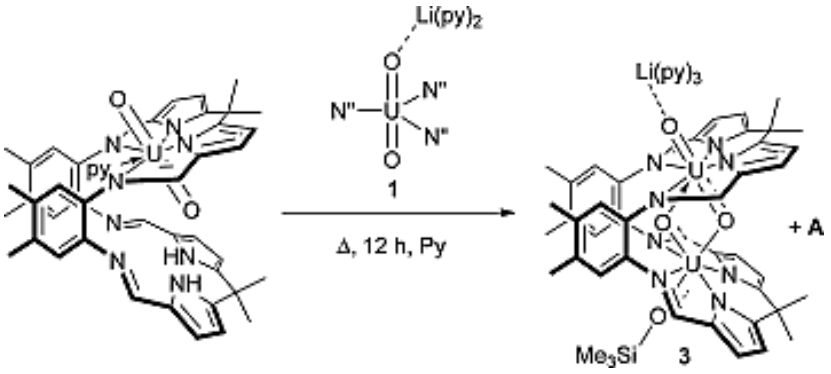


Figure 2. Crystal structure of $[\{(py)_3LiOUO\}_2(L)]$ **2**. For clarity, all hydrogen atoms and solvent of crystallization are omitted (displacement ellipsoids are drawn at 50 % probability).

This new synthesis provides a more convenient route to salts of the $[(OUO)_2(L)]^{2-}$ dianion. Although the mechanism of formation of **2** from H_4L and **1** has yet to be elucidated, it is possible that it proceeds by a similar route to the formation of **A**, resulting in a pyridine-insoluble by-product being formed in both cases and which is proposed to be an aggregate of a $[(OUO)_2(L)]^{2-}$ units linked through coordination of the *exo* oxo groups to uranyl(VI) dications.[19]

Mono-lithiated, mono-silylated butterfly complex 3

The reaction between $[UO_2(py)(H_2L)]$ and one equivalent of **1** in boiling pyridine yields the asymmetric, mono-lithiated, mono-silylated, complex $[\{(py_3)Li\ OUO\}(OUOSiMe_3)(L)]$ **3**, half an equivalent of doubly silylated **A** and HN" as the only products by ^{1}H NMR spectroscopy (Scheme 2). A toluene wash successfully separates **3** from **A** and HN" allowing its isolation in 25 % yield.



Scheme 2. Reaction between the mono-uranyl(V) complex $[(UO_2)(py)(H_2L)]$ and **1** to form the mono-silylated, mono-lithiated, binuclear uranium(V) oxo complex **3**

The ^{1}H NMR spectrum of **3** shows fourteen resonances between 14 and −12 ppm for L, double the number observed for the complexes **A**, **2** and **B**, indicating inequivalent occupation of the two N_4-donor pockets of the Pacman macrocycle. No resonances consistent with N-H protons are seen and the resonance at δ = 12.2 ppm, integrating to nine protons, is symptomatic of silylation of a single oxo-group. This, coupled with the presence of a single, paramagnetically shifted resonance at δ=33.2 ppm in the ^{7}Li{^{1}H} NMR spectrum, supports dissimilar functionalisation of the uranium(V) oxo groups.

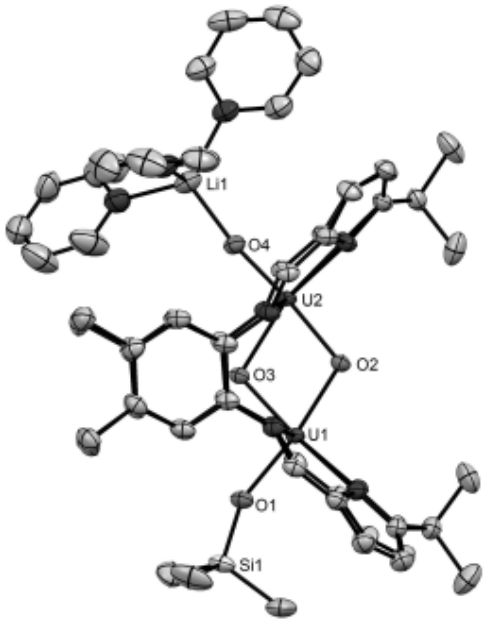


Figure 3. Crystal structure of [{(py_3)LiOUO}(OUOSiMe_3)(L)] **3**. For clarity, all hydrogen atoms and solvent of crystallization are omitted (displacement ellipsoids are drawn at 50 % probability).

The growth of single crystals of **3** (Figure 3) allowed the solid state structure of the complex to be determined and shows that the wedge-shaped, Pacman macrocycle accommodates two uranium centres, each with an *exo*-bound oxygen atom, bridged by axial and equatorial oxo groups, all features of which are present in complexes **A**, **B** and **2** (Figure 3). The average U-O bond length in the complex is 2.06 Å, consistent with two uranium(V) oxidation states and close to that displayed in complexes **A** (2.07 Å), **B** (2.03 Å) and **2** (2.03 Å). In contrast to these complexes however, significant asymmetry is present across all six of the U-O bonds in **3**. The U1-O1 bond length is comparable to those in **A** (2.056(2) *vs.* 2.034(5) and 2.085(4) Å), while the opposing, lithium-bound *exo* oxo group displays a much a shorter U-O bond length of 1.857(3) Å, analogous to the terminal oxo-uranium bonds exhibited in the doubly lithiated complex **2** (1.87(1) and 1.93(1) Å). The four U-O bonds between each of two uranium centres and the two *endo* bridging oxygen atoms exhibit much greater variability in bond length than in any of the symmetric complexes, with the U1-O3 and U2-O2 bond lengths of 2.024(3) and 2.077(2) Å respectively similar to those in **A** (2.095(3) – 2.099(3) Å) whereas the other two U-O bonds in the molecule, U1-O2 and U2-O3, have bond lengths of 2.113(2) and 2.238(2) Å respectively. These letter bonds are too long for uranium-oxygen multiple bonding and closer in length to the predominantly ionic bonding seen between discrete uranyl cations $[UO_2]^{n+}$ (n = 1,2) and their equatorially-bound ligands such as in polyoxo uranyl(VI) clusters.[24] In light of these assessments, the bonding in **3** may be considered as one axial and lithiated U^VO_2 motif (O4-U2-O2), and one with an equatorial oxo group and silylated oxo (O1-U1-O3), with each of these multiply-bonded $[UO_2]^+$ cations linked by weaker bonds (U1-O2 and U2-O3) of lower bond order. This alternate bonding motif is reflected in the Vis/NIR spectrum of **3**,

which does not feature the absorptions characteristic of either the fully silylated complex **A** or the Group 1 metal salts of the $[(OUO)_2L]^{2-}$ anion **B** and **2**, with features instead at 954, 1063, 1225 and 1430 nm and intermediate to those of **A** and **2** (Figure 4).

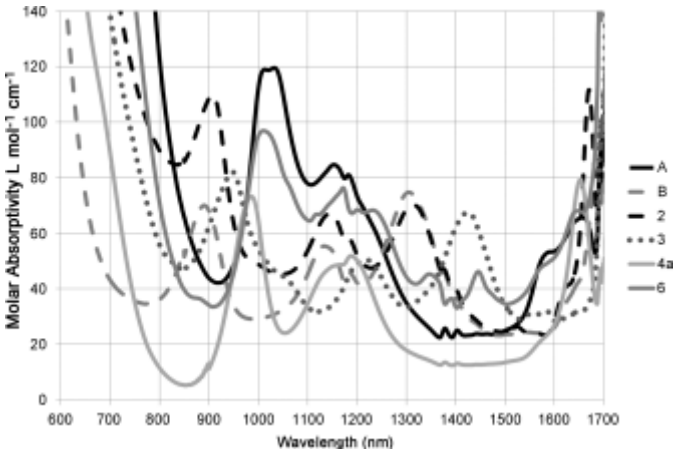
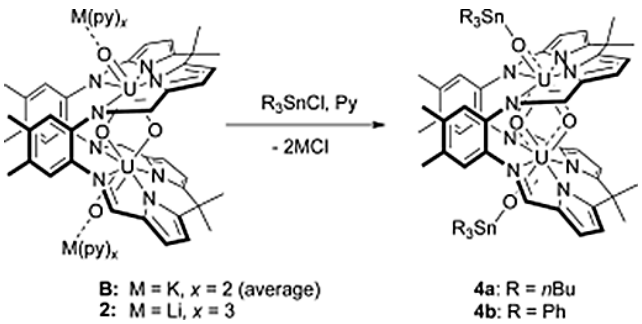


Figure 4. Visible/NIR spectra of binuclear uranium oxo complexes in THF. Covalently-functionalised $[(ROUO)_2(L)]$ (bold lines): **A** (11.2 M), **4a** (5.6 M) and **6** (6.6 M), Group 1 salts $[M]_2[(OUO)_2(L)]$ (dashed lines): **B** (5.6 M) and **2** (6.1 M), mixed lithium/silyl complex **3** (dotted line, 7.2 M).

Binuclear uranium(V) complexes with O-Sn bonds

The availability of the alkali metal salts **B**, **2**, and **3** has allowed us to investigate the formation and stabilities of alternatively functionalised uranium oxo groups. In the first instance, complexes **B**, **2** and **3** can be converted straightforwardly to the doubly-silylated complex **A** by treatment with trimethylsilyl chloride, demonstrating the ability of these Group 1 uranium oxo complexes to undergo salt elimination reactions with Group 14 halides. In light of this, the reaction between either **B** or **2** with two equivalents of $^nBu_3SnCl$ was carried out in pyridine solvent and found to yield the expected doubly stannylated complex $[\{(^nBu_3Sn)OUO\}_2(L)]$ **4a** in 70 % yield after work-up in hexane.



Scheme 3. Oxo-group stannylation of the $[(OUO)_2(L)]^{2-}$ salts **B** and **2** with R_3SnCl to form $[\{(R_3Sn)OUO\}_2(L)]$ **4a** (R = ^nBu) and **4b** R = Ph).

The ^{1}H NMR spectrum of **4a** exhibits eleven paramagnetically shifted resonances between 13 and −12 ppm, seven of which are attributed to the symmetrically occupied, folded Pacman macrocycle, being situated in almost identical positions to **A**, **B** and **2**. The remaining four resonances are assigned to the three methylene and one methyl group of each of the six identical n-butyl chains and are subject to a greater paramagnetic shift the closer they are sited to the uranium centre. The Ph_3Sn complex **4b** displays a similar ^{1}H NMR spectrum to **4a** and is isostructural with both **A** and **4a** in the solid state (Figure 5. See SI for the structure of **4a**). The U-O bond lengths in **4b** range between 1.987(8)–2.13(1) Å and close to those of **A**, with shorter U-O bonds to the *exo*-stannylated oxygen atoms O1 (1.987(8) Å) and O4 (2.00(1) Å), and longer U-O bonds to the *endo*-bridging oxygen atoms O2 and O3 (2.057(8)–2.13(1) Å). The smaller variation of the uranium-oxygen bond lengths in comparison to the partially- or fully-metalated compounds **B**, **2**, and **3** is indicative of more delocalised uranium-oxygen bonding as a result of significant π-bonding interactions across the $OU(O)_2UO$ network. Both **4a** and **4b** are inert towards oxidation in solution, remaining unchanged for days under an oxygen atmosphere in boiling benzene (see SI). This lack of oxidation chemistry contrasts to that shown by the unfunctionalised complex **B** (and **2**) which readily undergoes reactions with oxygen to form binuclear uranyl(VI) Pacman complexes.[20] The stability of **4a** and **4b** towards oxidation suggests that R_3Sn groups may act similarly to R_3Si groups as protecting groups for U(V) oxo groups. To the best of our knowledge, no stannylated uranyl complex has been characterised. In addition, complexes **4a** and **4b** provide only the second and third structurally characterised examples of heterobimetallic uranium-tin complexes, the first being the complex $[(C_5H_5)_3USnPh_3]$ that contains the first uranium-metal bond.[25]

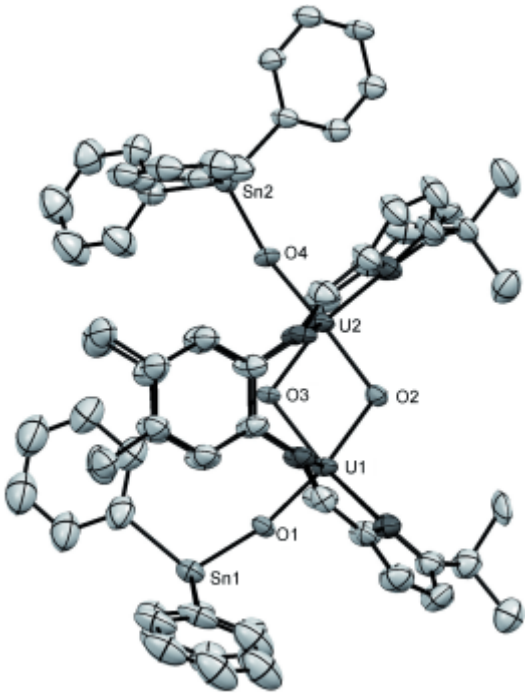
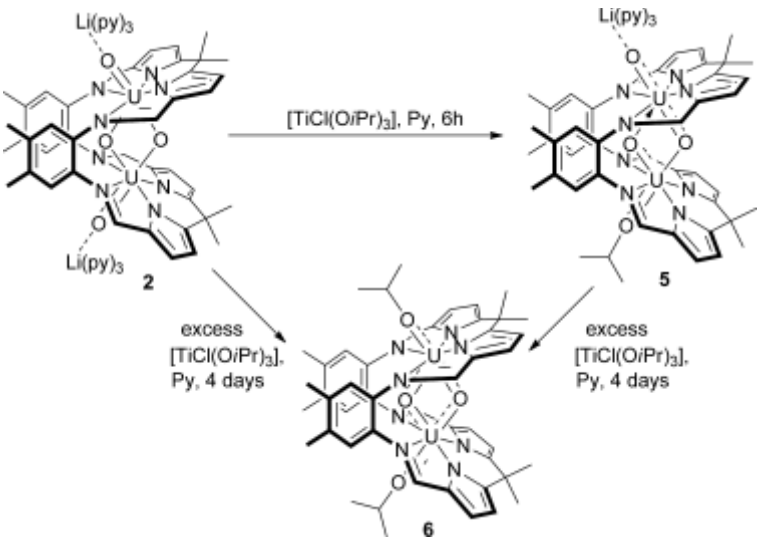


Figure 5. Crystal structure of $[\{(Ph_3Sn)OUO\}_2(L)]$ **4b**. For clarity, all hydrogen atoms and solvent of crystallization are omitted (displacement ellipsoids are drawn at 50 % probability).

Titanium-mediated oxo group exchange

The ease at which the salts of the $[(OUO)_2(L)]^{2-}$ anion can be functionalised with silyl and stannyl groups prompted us to investigate their reactivity with transition metal halides as a number of complexes have been synthesised recently that feature oxo-group coordination of uranyl cations to transition metals.[6, 8, 26] The commercially available $Ti(O^iPr)_3Cl$ selected due to the oxophilicity of titanium and single exchangeable halide ligand. To our surprise, the reaction between doubly lithiated **2** and two equivalents of $Ti(O^iPr)_3Cl$ does not generate the expected titanium-functionalised U^V-O-$Ti(O^iPr)_3$ complex but instead forms the mixed lithium/isopropyl binuclear uranium complex $[\{(py)_3LiOUO\}(OUO^iPr)(L)]$ **5** as the only product visible by ^1H NMR spectroscopy after 6 h (Scheme 4). Complex **5** displays sixteen resonances in its ^1H NMR spectrum, fourteen of which are attributable to the Pacman ligand and occur at very similar chemical shifts to those observed for asymmetrically functionalised $[\{(py)_3LiOUO\}(OUOSiMe_3)(L)]$ **3**. The remaining two, highly paramagnetically shifted resonances at 16.0 (6H) and 42.8 ppm (1H) are mutually coupled, as evidenced in a ^1H-^1H COSY NMR spectrum, and support the presence of a single isopropoxide group proximate to U(V).



Scheme 4. Synthesis of the binuclear uranium(V) isopropoxide complexes $[\{(py)_3LiOUO\}(OUO^iPr)(L)]$ **5** and $[(^iPrOUO)_2(L)]$ **6**.

This characterisation is further supported by the solid state structure of **5** (Figure 6) which shows a similar $OU(O)_2O$ core as seen in the starting material, incorporated within the Pacman macrocycle and with the *exo*-bound oxygen atoms bound to either an isopropyl group (O1) or a lithium cation (O4). The U1-O1 distance of 2.034(2) Å is consistent with a uranium(V) centre bound to a covalently functionalised oxo group, and is comparable to those in **A** (2.034(5) and 2.040(4) Å), **3** (2.056(2) Å), and **4b** (1.987(8) and 2.00(1) Å). Similar U-O bond distances are present in $[U_2(O^iPr)_{10}]$ (e.g. 2.03(1) Å), the only other structurally characterised

uranium(V) isopropoxide complex.[9, 27] The opposing exo oxo group, O4, remains bound to a lithium cation resulting in a much shorter U2-O4 multiple bond of 1.865(2) Å. As indicated by the comparable ^{1}H NMR spectra, **5** is isostructural with the mixed lithium/silyl complex **3**, with the complexes displaying similar bonding between the uranium(V) centres and their *endo* bridging oxygen ligands. As seen in **3**, **5** is composed of co-planar sets of two shorter and two longer bonds between the four atoms of the U_2O_2 diamond, with U1-O3 and U2-O2 bonds of 2.013(2) and 2.076(2) Å shorter than those of U1-O2 (2.111(2) Å) and U2-O3 (2.221(2) Å). The disparity between the four bonds defines O1-U1-O3 and O2-U2-O4 as discrete uranyl(V)-like cations with respective equatorial and axial arrangements of oxo ligands, a description that contrasts to the more symmetric arrangements of U-O bonds in **A**, **B**, **2**, and **4b**. The surprising tendency of only one of the *exo* oxo groups to react with Ti(O^{i}Pr)$_3$Cl over the reaction period led us to repeat the reaction with a single equivalent of Ti(O^{i}Pr)$_3$Cl, producing **5** as the only major product in pyridine solution. Despite the stability of **5** in pyridine and our ability to form small quantities of crystalline **5** from the crude reaction mixture, its isolation in the bulk was not achieved. Attempts to separate **5** from the lithium- and titanium-containing by-products by extraction into toluene resulted in ligand redistribution to form 0.5 equivalents of the doubly lithiated salt **2** and half an equivalent of the binuclear isopropoxide-uranium(V) complex [(^{i}PrOUO)$_2$(L)] **6**.

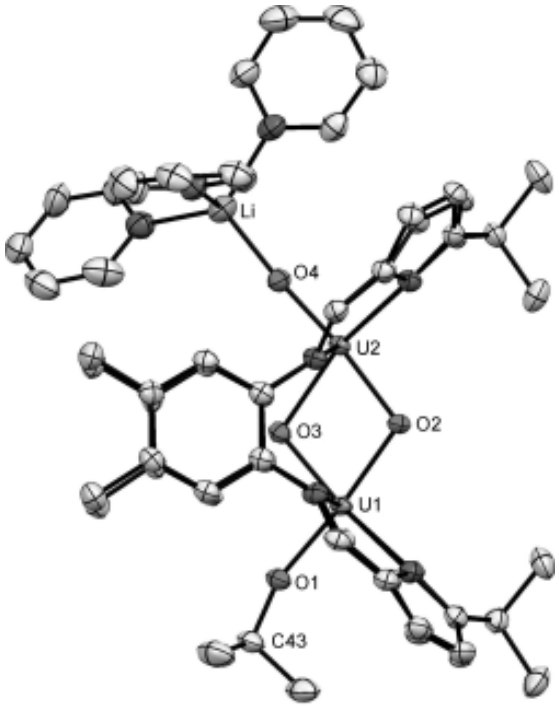


Figure 6. Crystal structure of [{(py)$_3$LiOUO}(OUO^{i}Pr)(L)] **5**. All hydrogen atoms and solvent of crystallization are omitted for clarity (displacement ellipsoids are drawn at 50 % probability).

The ^{1}H NMR spectrum of **6** exhibits seven resonances assigned to the Pacman ligand between 14 and −12 ppm and which are found in almost identical positions to those for **A**, **4a** and **4b**; the remaining resonances in the spectrum of **6** are the strongly paramagnetically shifted isopropyl resonances at 53.28 (2H) and 21.76 ppm (12H). Attempts to produce **6** in a more efficient manner by the reaction of **2** with two equivalents of Ti(*i*OPr)$_3$Cl in pyridine, were inhibited by the slow rate of reaction, with just 25 % completion to **6** after 4 days (see SI). The use of the alternative starting material **B** or non-coordinating solvents resulted in diminished solubility of the reactants, slowing the rate of reaction even further. Attempts to accelerate the conversion using elevated temperatures resulted in decomposition. Both the slow rate of reaction to form **6** and the aforementioned tendency of the intermediate complex **5** to rearrange to **2** and **6** suggested the presence of an equilibrium between the two complexes. As such, reactions using a five-equivalent excess of Ti(^{i}OPr)$_3$Cl result in the full conversion of the starting material to the desired product in four days. Removal of the excess Ti(*i*OPr)$_3$Cl by vacuum distillation followed by extraction and crystallisation from Et_2O allows pure **6** to be isolated in 85 % yield. The solid state structure of **6** displays isopropyl groups bound to each of the *exo*-bound oxo groups of the uranium(V) centres (Figure 7). The U1<C->O1 and U2<C->O4 bond lengths between the metal centres and the isopropoxide-functionalised oxo groups are 2.013(8) and 2.011(6) Å and are slightly shorter than the analogous bond in **5** (2.034(2) Å). In comparison with the other covalently-functionalised uranium(V) oxo compounds **A** and **4b**, the U-O bond lengths in **6** show less variation than those which are oxo-metalated, with the range of 2.011(6) - 2.117(6) Å suggestive of a delocalised metal-oxygen bonding environment.

The isolation of the isopropoxide complexes **5** and **6** is unexpected considering that salt elimination reactions between **2** or **B** and ^{i}PrCl did not result in formation of either **5** or **6**, instead yielding intractable mixtures. The formation of **5** and **6** from a titanium isopropoxide precursor suggests that a ligand exchange reaction between the uranium(V) and titanium(IV) metal centres occurs; this is perhaps due to the greater oxophilicity of the smaller Group IV metal than uranium, although the exact nature of the Ti- and Li- containing oxo by-product(s) could not be determined. To the best of our knowledge, the exchange of oxo-groups in **B** and **2** with titanium-bound isoproxide ligands is only the second example of the complete removal of a multiply-bound oxo ligand from a high-valent uranium complex, the first being the reductive abstraction of the oxo ligands in UO_2I_2 with Me_3SiX (X = Cl, Br, I) to form the U(IV) halides, UX_4 and $(Me_3Si)_2O$.[28] Complex **6** may be considered as an alkylated analogue of the doubly silylated or stannylated uranium(V) oxo complexes **A**, **4a**, and **4b**, and exhibits similar inertness towards oxidation in solution. Furthermore, the similarity between the Vis-NIR absorption spectra of **A**, **4a**, and **6** supports the assertion that they contain similar U-O bonding.

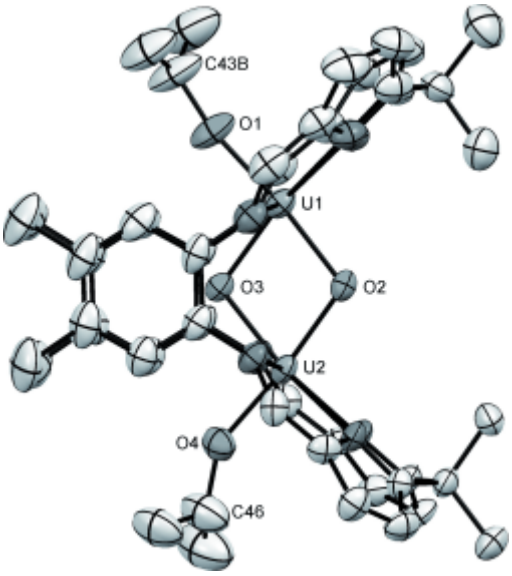


Figure 7. Solid state structure of [(^{i}PrOUO)$_2$(L)] **6**. The isopropoxide group starting at C43 is disordered over two sites, with only one model shown. For clarity, all hydrogen atoms and solvent of crystallization are omitted (displacement ellipsoids are drawn at 50 % probability).

	R1	R2	O1-R1	U1-O1	U1-O2	U1-O3	U2-O2	U2-O3	U2-O4	O4-R2
A	$SiMe_3$	$SiMe_3$	1.666(5)	2.034(5)	2.099(3)	2.098(3)	2.085(4)	2.095(3)	2.040(4)	1.665(4)
B	K	K	2.658(6)	1.851(6)	2.090(6)	2.168(5)	2.101(5)	2.105(6)	1.871(5)	2.747(6)
2	Li	Li	1.87(1)	1.877(4)	2.111(4)	2.110(4)	2.100(4)	2.115(4)	1.883(4)	1.93(1)
3	$SiMe_3$	Li	1.655(2)	2.056(2)	2.113(2)	2.024(3)	2.077(2)	2.238(2)	1.857(3)	1.929(8)
4b	$SnPh_3$	$SnPh_3$	1.996(8)	1.987(8)	2.057(8)	2.13(1)	2.11(1)	2.089(8)	2.00(1)	2.01(1)
5	$C(H)Me_2$	Li	1.438(4)	2.034(2)	2.111(2)	2.013(2)	2.076(2)	2.221(2)	1.865(2)	1.922(8)
6	$C(H)Me_2$	$C(H)Me_2$	1.48(3)	2.013(8)	2.105(6)	2.095(5)	2.081(5)	2.117(6)	2.011(6)	1.43(1)

Table 1. U-O and O-R bond distances (Å) in the complexes **A**, **B**, **2**, **3**, **4b**, **5** and **6**.

Conclusions

The complexes **4** and **6** add to the family of binuclear oxo uranium(V) complexes featuring the $(ROUO)_2$ motif, with alkyl, silyl, and stannyl derivatives all displaying an axial/equatorial arrangement of the oxo ligands and extending the covalent functionalization of uranium oxo groups to tin and carbon. Furthermore, the high stabilities of these compounds against oxidative decomposition provide further evidence that highly reactive uranium(V) centres can be 'protected' by functionalisation of their oxo ligands with Group 14 elements. The use of the new uranyl(VI) trimethylsilylamide '-ate' complex **1** as a reagent has facilitated the straightforward syntheses of the metalated, binuclear uranium(V) complexes **2** and **3**. Analysis of the solid

state structures of these latter compounds reveal that they are best described as containing terminal oxo ligands. The new synthetic routes discovered here build on our previous work that exploits metal silylamide compounds as single-electron reducing agents for the uranyl(VI) dication and facilitates the direct synthesis of complexes featuring the binuclear uranium(V) butterfly motifs from uranyl(VI) precursors. It is clear that the U-O bonding in these complexes is subtle and variant between localised and fully delocalised motifs. In some instances, for example **3** and **5**, the U_2O_4 bonding could be considered as derived from a classical *trans*-uranyl combined with a non-classical (and previously unseen) *cis*-uranyl. However, this assignment should be treated with some scepticism as computational work would need to be carried out to fully understand the bonding in these molecules and our previous work showed that oxidation reactions from U^V to U^{VI} regenerated binuclear *linear* uranyl motifs.[20] Even so, the successful synthesis and characterisation of complexes **2** to **6** demonstrate our ability to exploit macrocyclic Pacman ligands to create a diverse family of binuclear uranium(V) oxo complexes with the ability to tune the uranium-oxygen bonding and to elicit different reactivity by careful reagent choice.

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