Oxo Group Protonation and Silylation of Pentavalent Uranyl Pacman Complexes**

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Abstract

New bonds for the uranyl - The controlled conversion of one uranyl oxo group to either a covalently-bonded UO-H or UO-Si group is described for pentavalent uranyl ([UO$_2^+$]) Pacman complexes. The unusual oxo-hydroxyl motif is achieved by a protonation reaction and retains the normally unstable U(V) uranyl oxidation state. This product is readily silylated by treatment with a chlorosilane resulting in UO-Si bond formation.

Main text

The chemical reactivity of the oxo-group of the uranyl dication, [UO$_2$$^+$], the most prevalent aqueous and environmental form of uranium and by far the most chemically inert, has been transformed in recent years.$^{[1, 2]}$ For example, new routes to the singly-reduced, pentavalent uranyl have been developed and have facilitated fascinating new Lewis acid-base interactions between the oxo-groups and alkali metals,$^{[3, 4]}$ boranes,$^{[5-7]}$ transition metals,$^{[8]}$ rare earth metals,$^{[9]}$ and other uranyl cations.$^{[10]}$ In some cases it is evident that oxo-group functionalization can modify the U$^{VI}$/U$^{V}$ reduction potential such that reduction is facilitated.$^{[3, 6, 7]}$

While the above cation-cation interactions (CCIs) in [UO$_2$]$^+$ compounds are becoming increasingly understood, reactions of [UO$_2$$^{2+}$] that result in covalent bond formation at one or both oxo groups are extremely rare and at present limited to reductive silylation that forms a UO-Si bond. We showed recently that uranyl Pacman complexes, in which the uranyl oxo groups are in different spatial environments, underwent reduction and oxo-group silylation reactions on treatment with potassium bases and transition metal halides.$^{[11, 12]}$ Subsequently, perfluoroaryl borane-functionalized uranyl complexes have been shown to undergo reductive silylation reactions with tertiary silanes,$^{[6]}$ while the direct reaction of uranyl complexes with Me$_3$SiI results in U$^V$ and U$^{IV}$ oxo-silylated complexes.$^{[13]}$ Furthermore, complete de-oxygenation of [UO$_2$]$^{2+}$ can be realized by reaction with trimethylsilyl halides, forming U$^{IV}$ halides and (Me$_3$Si)$_2$O, presumably via a reduced, oxo-silylated intermediate.$^{[14]}$ These reactions can be contrasted to those of the photochemically-generated *[UO$_2$]$^{2+}$ ion which, in aqueous solution, can abstract an H-atom from alkanes and arenes to form carbon radicals and transient [UO$_2$H]$^{2+}$ which contains a new O-H bond.$^{[15]}$

We recently reported the synthesis of a variety of lithium-functionalized, pentavalent uranyl Pacman complexes that result from either direct reduction of the hexavalent, uranyl Pacman complex 1 (Scheme 1) or by a C-H activation process.$^{[3]}$ The ready availability of the thermally-stable, doubly-lithiated pentavalent uranyl complex 2 has now allowed us to probe reactions at the uranyl oxo
groups. Here we describe protonation and silylation reactions of 2 that lead to new, covalently-functionalized uranyl complexes.

The reaction between 2 and two equivalents of HCl in pyridine/diethyl ether resulted in the clean formation of the protonated pentavalent uranyl complex 3 as a poorly soluble yellow-brown solid (Scheme 1). We have, as yet, been unable to crystallize 3 and unequivocally determine its structure in the solid state, but the NMR, IR, and microanalytical data of 3 and its deuteriated analogue d2-3 (formed from the reaction between 2 and DCl) fully support its formulation. The IR spectrum of 3 confirms the retention of the U(V) oxidation state with a UO2 stretch observed at 765 cm\(^{-1}\) (cf. \(v_3 = 908\) for 1 and 709 cm\(^{-1}\) for 2).\(^2\) The OH and two NH groups have overlapping absorptions in the range 3378 - 3108 cm\(^{-1}\) (Supporting Information, Figure S1) while the NH stretch in 1 is at 3368 cm\(^{-1}\), and in 2 is at 3310 cm\(^{-1}\). The OH/NH absorptions shift on deuteriation to 2478 - 2269 cm\(^{-1}\), in accordance with reduced mass calculated values between 2465 and 2259 cm\(^{-1}\). Complete deuteriation was not observed, and likely indicates that a H/D exchange process operates between the OH and NH protons.

\[\text{Scheme 1. Synthesis of protonated and silylated pentavalent uranyl Pacman complexes 3 and 4}\]

The \(^1\)H NMR spectrum of 3 reveals the presence of paramagnetically-shifted resonances between +90 and –10 ppm, the number and integrals of which are consistent with the retention of a wedged, Pacman structure in solution of Cs symmetry (Figure S2). The most strongly paramagnetically
contact-shifted resonance at 86.4 ppm integrates as a single proton and is assigned to the UOH group. The $^2$H NMR spectrum of $d_5$-3 shows deuterium incorporation at this resonance, and also at 7.3 ppm. This latter resonance is therefore assigned as ND (Figure S3) and is obscured by pyridine solvent in the related $^1$H NMR spectrum. Complex 3 is remarkably stable, showing no signs of disproportionation or decomposition in solution at room or elevated temperatures by $^1$H NMR spectroscopy.

To further confirm the pentavalent oxidation state of 3, the stoichiometric reaction between 3 and trityl chloride was carried out (Equation 1 and Figure S4). The $^1$H NMR spectrum of the reaction mixture showed a 2:1 ratio of the single-electron oxidized product 1 and Gomberg’s dimer, the latter formed as a result of single electron reduction.\cite{16} Furthermore, reaction between 3 and TEMPO cleanly regenerated 1 through H-abstraction, while reaction of 3 with two molar equivalents of LiN(SiMe$_3$)$_2$ re-formed 2. It is also clear that 3 is not a monolithiated species as no paramagnetic Li environments are seen in the $^7$Li NMR spectrum and its reaction with two equivalents of LiN(SiMe$_3$)$_2$ generates 2 and not the triply-lithiated compound [Li(py)$_3$OOUO(py)Li$_2$(py)$_2$(L)] reported by us previously.\cite{13}

\begin{equation}
\text{3 + Ph$_3$Cl} \rightarrow 1/2 \text{Ph}_3\text{C}=\text{Cl} + 1 + \text{HCl}
\end{equation}

H-atom functionalization of the uranyl oxo group is important to aqueous uranyl chemistry. At high pH, equatorial hydroxide ligands are formed at [UO$_2$]$^{2+}$ from the five equatorially-bound water ligands. The deprotonation of one equatorial OH group and proton-shuttling to an axial oxo has been suggested as key to the exchange of axial and equatorial O-ligands and suggests the existence of interesting T-shaped UO$_3$ and cis-uranyl cations, which are as yet unobserved uranium geometries.\cite{17,18} Indeed, the spectroscopic data for 3 and its derivatives may provide insight into the speciation of complex aqueous uranyl oxo-hydroxo mixtures.\cite{19}

Reactions between 3 and the chlorosilanes Me$_3$SiCl, Bu'Me$_3$SiCl, or Ph$_2$HSiCl in pyridine resulted in the clean formation of the oxo-silylated products 4a, 4b, and 4c, respectively (Scheme 1) and the loss of HCl to the pyridine solvent. To our knowledge, this is the first time that metathesis of a functional group that is covalently bound to the uranyl oxo has been seen. While the direct salt elimination reaction between 2 and a molar equivalent of Me$_3$SiCl resulted in the possible formation of mono-lithiated 4a (by $^1$H NMR spectroscopy), pure samples could not be isolated due to the presence of other, as yet unidentified paramagnetic complexes. As with 3, the $^1$H NMR spectrum of 4a shows the
presence of paramagnetically-shifted resonances between +60 and –10 ppm, the number and integrals of which are consistent with a wedged, Pacman structure in solution (Figure S5). Significantly, the resonance at 86.4 ppm, assigned as the OH proton in 3, is absent in 4a. Furthermore, a single resonance for the SiMe₃ protons is seen at 15.0 ppm and the NH resonance has shifted from 7.3 in 3 to 58.1 ppm in 4a. In the 'BuSiMe₂-functionalized analogue 4b, the SiMe₂ and NH protons resonate at 14.8 and 56.6 ppm, respectively, while the SiH and NH protons in 4c appear at 37.2 and 54.1 ppm (Figures S6, S7). To confirm the assignment of the NH protons in 4a, the reaction between d₂-3 and Me₃SiCl was carried out and formed d₂-4a which displayed a resonance at 58 ppm in the ²H NMR spectrum (Figure S8). In the IR spectra of 4a-c (Figures S9, S10), U=O stretches in 4a-c are found between 860-823 cm⁻¹ and ca. 700 cm⁻¹, respectively,[2] whilst the NH stretches are seen at ca. 3290 cm⁻¹. In order to confirm the gross structure and O-Si bond formation, crystals of 4a and 4b were grown and their solid state structures determined by X-ray crystallography (Figure 1). The X-ray data for 4b showed problems consistent with multiple twinning. As such, only the connectivity was established (Figure S11), but it is clear from these data that 4a and 4b have the same core structure.

**Figure 1.** X-ray crystal structure of the trimethylsilylated pentavalent uranyl complex 4a. For clarity, all hydrogen atoms except those involved in hydrogen bonding and solvent of crystallization are omitted (displacement ellipsoids drawn at 50% probability). Selected bond lengths (Å) and angles (°): U1-O1 1.854(4); U1-O2 2.034(4); Si1-O2 1.667(5), N6⋯O1 3.043(6); N7⋯O1 3.037(6); O1⋯U1⋯O2 176.00(19); U1-O2-Si1 160.2(3)

In the structure of 4a the uranium adopts a distorted pentagonal bipyramidal geometry in which the oxygen ligands are linear and co-axial and the five equatorial sites are made up from the N₄-donor set of the macrocycle and a molecule of pyridine, sandwiched between the two macrocyclic aryl hinges.
The vacant, lower macrocyclic N₄-donor compartment is oriented such that hydrogen bonds are evident between the pyrrole NH groups and the endogenous uranyl oxo group; the N⋯O separations are slightly shorter in 4a than in the analogous U⁶⁺ complex 1 (N⋯O 3.078(3)/3.103(3) Å). It is clear from the structure that silylation has occurred and that the pentavalent uranium oxidation state is retained. The silylated oxo-uranium bond distance U₁-O₂ 2.034(4) Å and the endogenous U₁-O₁ distance 1.854(4) Å are similar to those seen in related uranyl siloxides and are consistent with the pentavalent oxidation state (1.97 to 2.04 Å);[2,6,11,13] in contrast, U(IV) and (III) siloxide bonds are significantly longer (2.06 to 2.20 Å).[20]

In summary, we have shown that it is possible to carry out new OH and OSi bond-forming reactions and interconversions from a pentavalent uranyl complex without the occurrence of deleterious redox processes such as disproportionation. Work is also in progress to identify whether modification of the fifth equatorial solvent site in 3 will enable us to identify possible adducts of 3 and 4 that can help better define uranyl oxo-ion exchange processes.

**Experimental Section**

**Synthetic procedures and characterizing data**

3: To a solution of 2 (250 mg, 0.21 mmol) in pyridine was added 1.9 equivalents of HCl in Et₂O (2.0 mL, 0.4 mmol). The resulting suspension was stirred for 2 h, after which the precipitate was isolated and dried under vacuum, to afford 152 mg, 71% of 3 as a brown-yellow solid. Analysis. Found: C, 56.19; H, 4.93; N, 12.56 %. C₄₇H₄₆N₉O₂Li₂U requires C, 55.95; H, 4.80; N, 12.49 %. IR (Nujol mull, cm⁻¹): 3376, 3189, 1623, 1600, 1583, 1288, 1265, 1218, 1103, 1045, 1020, 892, 782, 765 (UO stretch), 725, 709; ¹H NMR (pyridine-d₅): δH 86.39 (s, 1H), 32.47 (s, 3H), 13.94 (s, 2H), 10.73 (s, 3H + 2H), 5.66 (s, 2H), 3.30 (s, 3H), 2.05 (s, 2H), 1.74 (s, 2H), 0.49 (s, 6H), -1.89 (s, 2H), -2.39 (s, 6H), -2.56 (s, 2H), -3.67 (s, 2H), 7.01 (s, 3H), -8.75 (s, 2H) ppm.

4a-c: To a solution of 3 in pyridine was added neat silyl chloride. The mixture was stirred for 2 h after which the suspension was filtered and the volatiles evaporated from the filtrate to afford silylated 4a-c as brown-yellow solids.

4a: 3 (75 mg, 0.074 mmol), Me₃SiCl (9.4 μL, 0.074 mmol), Yield 63 mg, 78 %. Analysis. Found: C, 53.28; H, 4.79; N, 11.93 %. C₅₀H₅₆N₉O₃SiU requires C, 55.55; H, 5.22; N, 11.66 %. (MEDAC Ltd, duplicate); IR (Nujol, cm⁻¹): 3286 (NH), 1621, 1602, 1583, 1284, 1263, 1216, 1186, 1045, 1033, 1016, 894, 860 (UO stretch), 802, 781, 767, 744, 703 (UO stretch); ¹H NMR (pyridine-d₅): δH 58.10 (s, 2H), 15.02 (s, 9H), 14.58 (s, 3H), 11.13 (s, 2H), 10.04 (s, 2H), 8.63 (s, 2H), 6.65 (s, 3H), 3.60 (s,
2x2H), 3.19 (s, 2H), 2.48 (s, 2H), 1.87 (s, 2H), 0.14 (s, 6H), -0.46 (s, 6H), -2.95 (s, 3H), -8.40 (s, 3H) ppm.

4b: 3 (100 mg, 0.09 mmol), \textsuperscript{1}BuMe\textsubscript{2}SiCl (14.9 mg, 0.09 mmol), Yield 70 mg, 63 %. Analysis. Found: C, 56.06; H, 5.69; N, 9.90 %. \textsuperscript{13}C\textsubscript{53}H\textsubscript{62}N\textsubscript{9}O\textsubscript{2}SiU requires C, 56.67; H, 5.56; N, 11.22 % (MEDAC Ltd, duplicate); IR (Nujol, cm\textsuperscript{-1}): 3290 (NH), 1622, 1583, 1282, 1263, 1217, 1182, 1047, 1020, 893, 831 (UO stretch), 769, 725, 694 (UO stretch); \textsuperscript{1}H NMR (pyridine-\textit{d}\textsubscript{5}): \textsuperscript{1}H 56.56 (s, 2H), 14.79 (s, 6H), 13.33 (s, 3H), 11.00 (s, 2H), 10.09 (s, 2H), 9.23 (s, 9H), 9.01 (s, 2H), 6.26 (s, 3H), 3.60 (s, 2 x 2H), 2.98 (s, 2H), 1.28 (s, 2H), 1.09 (s, 2H), -0.16 (s, 6H), -0.38 (s, 6H), -2.80 (s, 3H), -8.59 (s, 3H) ppm.

4c: 3 (75 mg, 0.074 mmol), Ph\textsubscript{2}HSiCl (14.6 \mu L, 0.074 mmol), 60 mg, Yield 67 %. IR (Nujol, cm\textsuperscript{-1}): 3291, 2142 (Si-H), 1619, 1600, 1583, 1282, 1261, 1218, 1184, 1118 (Si-Ph), 1047, 1022, 894, 823 (UO stretch), 771, 734, 700 (UO stretch); \textsuperscript{1}H NMR (pyridine-\textit{d}\textsubscript{5}): \textsuperscript{1}H 54.13 (s, 2H, NH), 37.21 (s, 1H, SiH), 17.65 (m, 4H, PhSi), 12.79 (s, 3H), 10.70 (s, 2H), 9.87 (m, 4H, SiPh), 9.79 (s, 2H), 9.15 (m, 2H, SiPh), 8.67 (s, 2H), 6.04 (s, 3H), 4.35 (s, 2H), 3.91 (s, 2H), 3.51 (s, 4H), 1.49 (s, 2H), 0.10 (s, 6H), -0.25 (s, 6H), -2.44 (s, 3H), -8.28 (s, 3H) ppm.

**Reaction between 3 and Ph\textsubscript{3}CCl:** Pyridine was added to a mixture of 3 (25 mg, 0.02 mmol) and trityl chloride (6.1 mg, 0.02 mmol) in a Teflon-tapped NMR tube at room temperature. After a few minutes the solution was dark brown. The reaction mixture was analyzed by \textsuperscript{1}H NMR spectroscopy from which it was evident that Gomberg’s dimer Ph\textsubscript{2}C=(C\textsubscript{6}H\textsubscript{5})CPh\textsubscript{3} and UO\textsubscript{2}(py)(H\textsubscript{2}L) \textbf{1} had formed in a 0.5:1.0 ratio.
References


