Uranyl Reactivity

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

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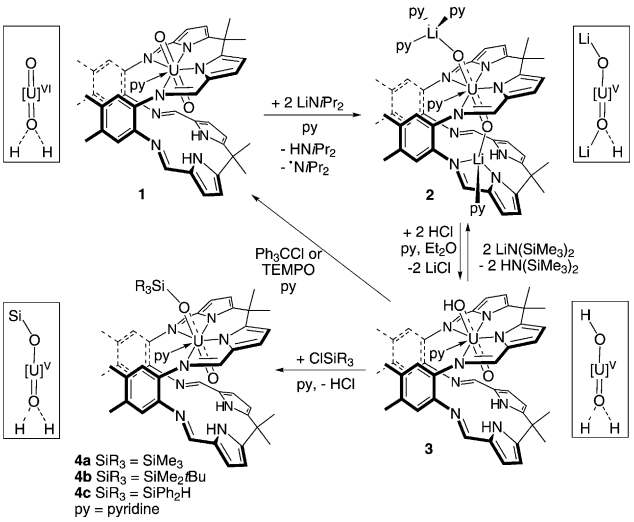
The chemical reactivity of the oxo group of the uranyl dication, $[UO_2]^{2+}$, the most prevalent aqueous and environmental form of uranium and by far the most chemically inert, has been transformed in recent years.[1,2] For example, new routes to the singly reduced, pentavalent uranyl have been developed 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_3SiI results in U^{V} and U^{IV} oxo-silylated complexes.[13] Furthermore, complete deoxygenation of $[UO_2]^{2+}$ can be realized by reaction with trimethylsilyl halides, forming U^{IV} halides and $(Me_3Si)_2O$, presumably through 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 $[UO_2H]^{2+}$ 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.



Scheme 1. Synthesis of protonated and silylated pentavalent uranyl Pacman complexes **3** and **4**.

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 and IR spectroscopic, and microanalytical data of **3** and its deuterated analogue **[D_2]-3**, in which 2 D′s are incorporated (formed from the reaction between **2** and two molar equivalents of DCl) fully support its formulation. The IR spectrum of **3** confirms the retention of the U^{V} oxidation state with a UO_2 stretch observed at 765 cm^{-1} (cf. $\nu_3 = 908$ 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 deuteration was not observed, and likely indicates that a H/D exchange process operates between the OH and NH protons.

The ^{1}H NMR spectrum of **3** reveals the presence of paramagnetically shifted resonances between $\delta = +90$ and -10 ppm, the number and integrals of which are consistent with the retention of a wedged, Pacman structure in solution of C_s symmetry (Figure S2). The most strongly paramagnetically contact-shifted resonance at $\delta = 86.4$ ppm integrates as a

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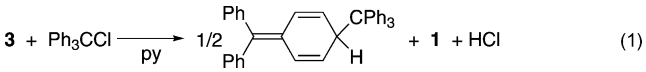
single proton and is assigned to the UOH group. The ^{2}H NMR spectrum of **[D$_2$]-3** shows deuterium incorporation at this resonance, and also at $\delta = 7.3$ ppm. This latter resonance is therefore assigned as pyrrolic N–D (Figure S3) and is obscured by pyridine solvent in the related ^{1}H NMR 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 confirm the pentavalent oxidation state of **3**, the stoichiometric reaction between **3** and trityl chloride was carried out [Eq. (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.[16] Furthermore, reaction between **3** and TEMPO ((2,2,6,6-tetramethylpiperidine-1-yl)oxyl) cleanly regenerated **1** through H-abstraction, while reaction of **3** with two molar equivalents of LiN(SiMe$_3$)$_2$ reformed **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)$_3$OUO(py)Li$_2$(py)$_2$(L)] reported by us previously.[3]



(1)

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.[17,18] Indeed, the spectroscopic data for **3** and its derivatives may provide insight into the speciation of complex aqueous uranyl oxo–hydroxo mixtures.[19]

Reactions between **3** and the chlorosilanes Me$_3$SiCl, *t*BuMe$_2$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 monolithiated **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 $\delta = +60$ and -10 ppm, the number and integrals of which are consistent with a wedged, Pacman structure in solution (Figure S5). Significantly, the resonance at $\delta = 86.4$ ppm, assigned as the OH proton in **3**, is absent in **4a**. Furthermore, a single resonance for the SiMe$_3$ protons is seen at $\delta = 15.0$ ppm and the NH resonance has shifted from $\delta = 7.3$ in **3** to 58.1 ppm in **4a**. In the *t*BuMe$_2$Si-functionalized analogue **4b**, the SiMe$_2$ and NH protons resonate at $\delta = 14.8$ and 56.6 ppm, respectively, while the SiH and NH protons in **4c** appear at $\delta = 37.2$ and 54.1 ppm (Figure S6, S7). To confirm the assignment of the NH protons in **4a**, the reaction between **[D$_2$]-3** and Me$_3$SiCl was carried out to form **[D$_2$]-4a**, which displayed a resonance at $\delta = 58$ ppm in the ^{2}H NMR spectrum (Figure S8). In the IR spectra of **4a–c** (Figure S9, S10), U=O stretches 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.

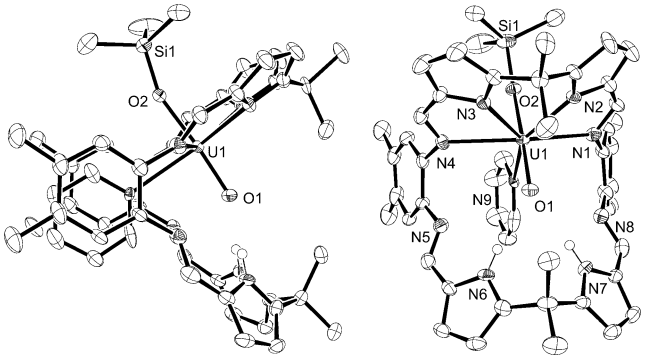


Figure 1. X-ray crystal structure of the trimethylsilylated pentavalent uranyl complex **4a**. For clarity, all hydrogen atoms except those involved in hydrogen bonding and solvent of crystallization are omitted (displacement ellipsoids drawn at 50% probability). Selected distances [Å] and angles [°]: 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 N$_4$-donor set of the macrocycle and a molecule of pyridine, sandwiched between the two macrocyclic aryl hinges. The vacant, lower macrocyclic N$_4$-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 U^{VI} 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) are similar to those seen in related uranyl siloxides and pentavalent uranyl complexes (1.97 to 2.04 Å);[2,6,11,13] in contrast, U^{IV} and U^{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 occur-

rence 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** 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 Et_2O (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. Elemental analysis (%) for $C_{47}H_{46}N_9O_2Li_2U$, found: C 56.19, H 4.93, N 12.56; calcd: C 55.95, H 4.80, N 12.49. IR (Nujol mull): $\tilde{\nu}$ = 3376, 3189, 1623, 1600, 1583, 1288, 1265, 1218, 1103, 1045, 1020, 892, 782, 765 (UO stretch), 725, 709 cm^{-1}; ^1H NMR ([D_5]pyridine): δ_H = 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 ppm (s, 2H).

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), Me_3SiCl (9.4 μL, 0.074 mmol), Yield 63 mg, 78%. Elemental analysis (%) for $C_{50}H_{56}N_9O_2SiU$, found: C 53.28, H 4.79, N 11.93; calcd: C 55.55, H 5.22, N 11.66; IR (Nujol mull): $\tilde{\nu}$ = 3286 (NH), 1621, 1602, 1583, 1284, 1263, 1216, 1186, 1045, 1033, 1016, 894, 860 (UO stretch), 802, 781, 767, 744, 703 cm^{-1} (UO stretch); ^1H NMR ([D_5]pyridine): δ_H = 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, 2×2H), 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 ppm (s, 3H).

4b: **3** (100 mg, 0.09 mmol), Bu*t*Me_2SiCl (14.9 mg, 0.09 mmol), Yield 70 mg, 63%. Elemental analysis (%) for $C_{53}H_{62}N_9O_2SiU$, found: C 56.06, H 5.69, N, 9.90; calcd; C 56.67, H 5.56, N 11.22; IR (Nujol mull): $\tilde{\nu}$ = 3290 (NH), 1622, 1583, 1282, 1263, 1217, 1182, 1047, 1020, 893, 831 (UO stretch), 769, 725, 694 cm^{-1} (UO stretch); ^1H NMR ([D_5]pyridine): δ_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, 2×2H), 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 ppm (s, 3H).

4c: **3** (75 mg, 0.074 mmol), Ph_2HSiCl (14.6 μL, 0.074 mmol), 60 mg, Yield 67%. IR (Nujol mull): $\tilde{\nu}$ = 3291, 2142 (Si-H), 1619, 1600, 1583, 1282, 1261, 1218, 1184, 1118 (Si-Ph), 1047, 1022, 894, 823 (UO stretch), 771, 734, 700 cm^{-1} (UO stretch); ^1H NMR ([D_5]pyridine): δ_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 ppm (s, 3H).

Reaction between **3** and Ph_3CCl: 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 ^1H NMR spectroscopy from which it was evident that Gomberg's dimer $Ph_2C{=}(C_6H_5)CPh_3$ and $[UO_2(py)(H_2L)]$ (**1**) had formed in a 0.5:1.0 ratio.

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