Uranyl Complexes

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Controlled Deprotection and Reorganization of Uranyl Oxo Groups in a Binuclear Macrocyclic Environment**

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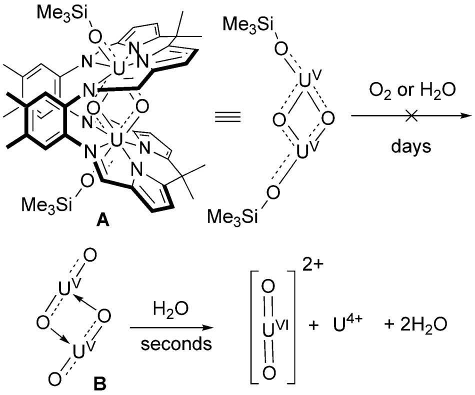
The two, strongly covalently bound, mutually *trans* oxo ligands of uranyl compounds are highly inert towards yl group reactions or exchange,[1] even upon single-electron reduction to $[UO_2]^+$. However, these latter f^1 compounds show enhanced Lewis basicity, resulting in recent studies on oxo coordination to alkali metals,[2,3] lanthanides,[4] actinides,[5] and other uranyl cations[3,6,7] through so-called cation–cation interactions (CCIs), as well as coordination to Lewis acidic boranes.[8] Although kinetically inert under anaerobic conditions, the vast majority of uranyl(V) complexes decompose upon exposure to air, either by oxidation or, more frequently, proton-coupled disproportionation reactions.[9,10]

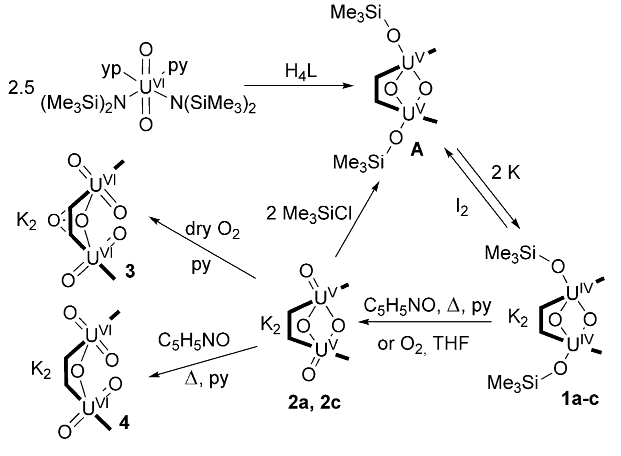
In 2008 we reported a new reaction for the uranyl dication in which concurrent single-electron reduction and oxo-group silylation occurred, providing the first example of covalent bond formation for the uranyl oxo group.[11] In this case, a single uranyl cation was complexed by the Schiff base polypyrrolic macrocycle L in a Pacman-shaped cleft structure, a design that facilitates this chemistry. Since this discovery, the reductive silylation of uranyl β-ketoiminate complexes[12] and their perfluoroborane adducts has been reported, but overall oxo functionalization reactions remain rare.[8,13] These oxo-silylated complexes are stable indefinitely under anaerobic conditions, although little is known of their stability in air.

We reported recently the synthesis of the binuclear uranium(V) dioxo complex **A** of L (Scheme 1).[14] This complex is unique in that it is derived from two *trans*-uranyl dications, but features one mutually *trans* and one mutually *cis* oxo ligand within a multiply bonded U_2O_2 core, as well as two silylated *exo*-oxo groups; **A** can be considered as an oxo-rearranged, silylated analogue of the dimeric CCI complex **B**. The ready availability of **A** and its surprising inertness towards disproportionation, hydrolysis, and oxidation led us to investigate the origin of its unique stability. Herein, we describe for the first time a method that allows the removal of the silyl groups, reinstating oxo yl character, and show that this deprotection step is key to the rearrangement of the *cis*/*trans*-oxo motif back to the traditional linear uranyl geometry. We also show that the $U^{VI/V}$ redox couple can be exploited to carry out the two-electron reduction of dioxygen to peroxide.



Scheme 1. Aerobic and aqueous stability of the uranium siloxydioxo complex $[(Me_3SiOUO)_2(L)]$ **A** and the contrasting spontaneous disproportionation of structurally related CCI complexes **B**.

The reaction between **A** and two equivalents of potassium graphite or potassium metal in THF cleanly generates the U^{IV}/U^{IV} salt $K_2[(Me_3SiOUO)_2(L)]$ (**1a**) in solution (Scheme 2). The complex retains its C_{2v} symmetry upon reduction, with seven ligand resonances displayed between +35 and −35 ppm in the ^{1}H NMR spectrum. The additional resonance at 39.6 ppm, integrating to 18 protons, demonstrates that both of the $SiMe_3$ groups are retained upon reduction of the uranium centers. Although highly soluble, **1** can be isolated as a solid by treating a solution of the THF



Scheme 2. Synthesis of complexes **1**–**4**: **a** = THF solvate, **b** = THF/[18]crown-6 solvate, **c** = pyridine solvate. **3** and **4** are solvated by pyridine. The bonding of potassium and the resulting nuclearities of the complexes are not shown.

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solvate **1a** with two equivalents of [18]crown-6, precipitating $[K(thf)_2([18]crown\text{-}6)]_2[(Me_3SiOUO)_2(L)]$ (**1b**) in 60 % yield.

While the growth of single crystals suitable for X-ray diffraction was not possible owing to the poor solubility of this material in THF, its composition is supported by ^{1}H NMR, IR, and UV/Vis spectroscopy and elemental analysis (see the Supporting Information). As expected, reoxidation of either **1a** or **1b** with single equivalents of iodine leads to the clean reformation of **A** with elimination of potassium iodide. To our surprise however, carrying out the analogous two-electron oxidation with pyridine-*N*-oxide results in the formation of the doubly desilylated, binuclear U^V compound $K_2[(OUO)_2(L)]$ (**2**) and half an equivalent of $(Me_3Si)_2O$ as the only products observable by ^{1}H NMR spectroscopy (Scheme 2). The ^{1}H NMR spectrum of **2** is similar to **A**, albeit with the notable absence of a $SiMe_3$ resonance at 15 ppm. Isolation of the pyridine solvate **2c** in the bulk is achieved using a one-pot strategy in which **A** is reduced to the U^{IV}/U^{IV} salt **1c** and then oxidized by the addition of one equivalent of pyridine-*N*-oxide; boiling the resulting mixture for 6 days results in the precipitation of crystalline **2c** in 69 % yield.

Analysis of the crystal structure of **2c** (Figure 1) confirmed the absence of the silyl substituents and the presence of U^V oxidation states in which the average U–O bond length of 2.03 Å is comparable to that seen in the silylated analogue **A** (2.09 Å). In contrast to **A**, which exhibits six almost identical U–O bond distances of between 2.03 to 2.10 Å, those in **2c** show significant variation between the four U–O_{endo} bonds (2.090(6), 2.101(5), 2.105(6), and 2.168(5) Å) and the two U–O_{exo} bonds (1.871(5) and 1.851(6) Å), with the latter being much more indicative of yl-type U–O multiple bonding. The U1⋯U2 separation of 3.3795(5) Å is short but elongated slightly compared to that of 3.3557(5) Å seen in **A**. The contrast in bonding in **2c** to its silylated analogue **A** is further represented in their UV/Vis-NIR spectra, which are very different despite their common oxidation states (see the Supporting Information). The alternative, unsolvated analogue **2a** was synthesized by direct exposure of a THF solution of **1a** to air, resulting in the immediate precipitation of crystals of **2a** along with other intractable materials. In contrast to **2c**, in which pyridine solvation of the external potassium cations truncates the structure as a crystallographic dimer, **2a** has a polymeric structure in which each potassium bridges two Pacman molecules in a K_2O_2 diamond motif (see the Supporting Information). These desilylated compounds are best classified as displaying bimetallic *endo*-oxo-bridged U^V motifs with terminal *exo*-oxo groups. Although the former presents a very common bonding motif in uranium chemistry, U^V complexes exhibiting terminal oxo groups are still rare,[15] with $[U(O)\{N(SiMe_3)_2\}_3]$ having a similar U=O bond length (1.817(1) Å) to those in **2c**.[16] Furthermore, the terminal U^V oxo complexes $[\{(RArO)_3tacn\}U(O)]$ (R = *t*Bu or 1-adamantyl, tacn = 1,4,7-triazacyclononane)[17] can be oxidized to their U^{VI} analogues.[18]

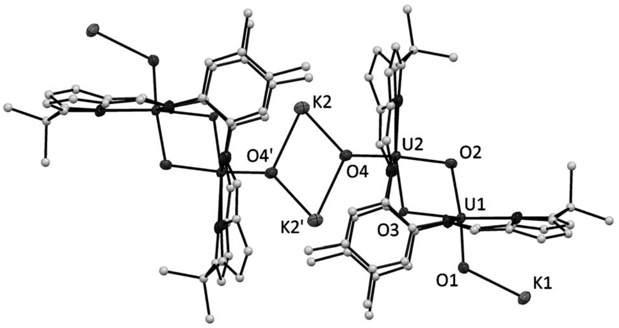

Figure 1. X-ray crystal structure of **2c**. For clarity, all of the hydrogen atoms and pyridine donors to potassium are omitted; where shown, ellipsoids are set at 50% probability.

The differences in structure and bonding between oxo-silylated **A** and oxo-unfunctionalized **2c** are mirrored by differences in their stability towards oxidation. While boiling solutions of **A** are stable indefinitely under an atmosphere of dry dioxygen, the exposure of a THF or pyridine solution of **2c** to dioxygen results in instantaneous oxidation and the sole formation of the binuclear U^{VI} peroxide $K_2[(\mu\text{-}\kappa^2\text{-}\kappa^2\text{-}O_2)(UO_2)_2(L)]$ (**3**), isolated in 55 % yield (Scheme 2). The ^{1}H NMR spectrum of **3** shows seven resonances indicating that the C_{2v} symmetry seen for **2**, and the silylated complexes **A** and **1**, is retained. In contrast however, all of these resonances are within the 0–10 ppm range, supporting the formation of a diamagnetic complex. The absence of f–f absorptions in the NIR spectrum supports the assignment of formal U^{VI} oxidation states, along with the presence of the asymmetric $[UO_2]^{2+}$ stretch in the IR spectrum at 924 cm^{-1}.

The solid-state structure of **3** (Figure 2) depicts a wedge-shaped, Pacman macrocycle, with symmetrical occupation of each of the N_4-donor pockets by uranyl dications. The $\{OU(\mu\text{-}O)_2UO\}$ *cis*/*trans* oxo-group bonding motif seen in **A** is replaced by two discrete, linear $[UO_2]^{2+}$ units in which the four U–O bond distances (1.781(6) to 1.788(6) Å) are characteristic of uranyl(VI). The accommodation of both $[UO_2]^{2+}$ dications by the macrocycle is facilitated by significant structural distortion away from the usual Pacman geometry, resulting in an inter-cleft bite angle of 90.1° for **3**

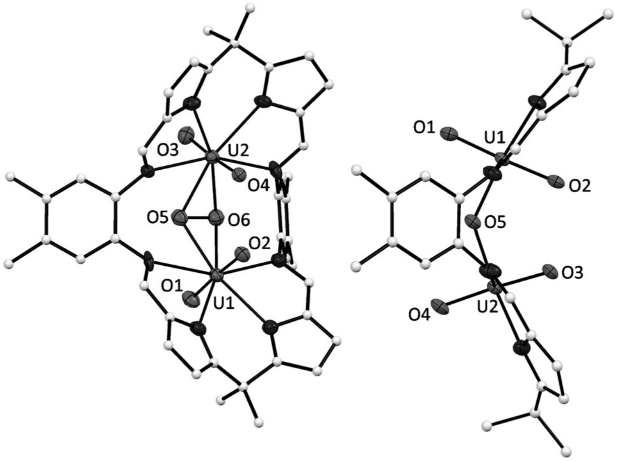

Figure 2. X-ray crystal structures of **3** (left) and **4** (right, side-on view). For clarity, all of the hydrogen atoms, K atoms, and solvent donors are omitted. Where shown, ellipsoids are set at 50% probability.

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compared to 61.3° and 65.1° for **A** and **2c**, respectively; this widening of the cleft presumably prevents clashing of the *endo*-oxo groups. In **3**, each uranium center has approximate hexagonal bipyramidal geometry, with the two axially bound oxo ligands sited perpendicular to the four equatorial nitrogen donors of the Pacman macrocycle. The fifth and sixth equatorial donors to each metal center are provided by the bridging peroxide ligand, which lies sandwiched between the two aryl spacers of the wedge-shaped ligand in a μ-κ^2-κ^2 motif. The O5–O6 bond length is 1.433(7) Å and is characteristic of peroxide; charge balance is maintained by retention of the two potassium cations which coordinate to the *exo*-uranyl oxo atom O1, the bridging peroxide atoms O5 and O6, and the O2 and O4 atoms of separate Pacman molecules (see the Supporting Information). Although numerous uranyl peroxide complexes are known, they are formed exclusively by ligand exchange between uranyl(VI) precursors.[19] In contrast, compound **3** is the first uranyl peroxide complex formed by a redox reaction, adding to the wealth of small molecule activation chemistry known for uranium complexes.[20] Recently a uranyl(V) complex was shown to react with dioxygen, but in this case it formed an oxo-bridged uranyl(VI) complex.[7]

Oxidation of the U^{V} complex **2c** with pyridine-*N*-oxide instead of dioxygen yields the mono-oxo-bridged complex $K_2[(UO_2)(\mu\text{-}O)(UO_2)(L)]$ **4** in moderate yield (Scheme 2). The solid-state structure of **4** (Figure 2) is similar to that of **3**, with occupation of the Pacman ligand by two uranyl(VI) dications in adjacent N_4 donor pockets. In contrast to **3** however, the single oxide ligand O5, rather than peroxide, bridges U1 and U2 at the obtuse U1-O5-U2 angle of 136.4(3)°, resulting in pentagonal bipyramidal uranium geometries. In analogy with **3**, the mono-oxo structure exists as a crystallographic dimer maintained by uranyl/potassium CCIs (see the Supporting Information). In contrast to **3** however, the ^{1}H NMR spectrum of **4** displays 14 resonances for the Pacman ligand, indicating that the asymmetry in the solid-state structure due to K-coordination is retained in solution.

The uranyl(VI) complexes **3** and **4** form only the second and third examples of cofacial, binuclear uranyl Pacman complexes, the first reported by us using an expanded, anthracene-derived Pacman macrocycle.[21] More importantly however, the isolation of both complexes provides further insight into the nature and stability of the binuclear U^{V} precursors **A** and **2c**. While **A** is a highly unusual example of an air-stable U^{V} complex, desilylation of the oxo ligands to form **2c** uncovers underlying reactivity. Furthermore, oxidation of the desilylated complex **2c** causes oxo-group rearrangement to occur, re-forming the traditional uranyl(VI) bonding motif from which **A** was originally derived. Treatment of **2c** with chlorotrimethylsilane allows the clean transformation back to **A**, upon which its stability against oxidation is restored, suggesting that the oxo-bound SiR_3 groups in **A** are responsible for its remarkable redox stability. As such, the trialkylsilyl group may be viewed as an effective protecting group for the uranyl oxo and therefore analogous to the well-documented silyl-group protection of functional groups in organic synthesis. Unlike the latter, we have been unable to deprotect **A** using common reagents such as fluoride.

The desilylated complex $[(OUO)_2(L)]^{2-}$ **2**, is highly reactive towards oxidation, resulting in preferential formation of compounds that contain two discrete uranyl dications and not the elusive *cis*-uranyl. This is surprising, as DFT calculations show only a circa 16 kcal mol^{-1} difference in energy between the two forms,[22] and the macrocyclic framework has distorted appreciably to accommodate the two *trans*-uranyl motifs. Even so, the more yl-like nature of the desilylated complex **2** than **A** means that it is a more realistic model of the actinyl(V) CCI complexes that are proposed to exist in nuclear waste mixtures and which participate in redox processes and are disruptive to fuel reprocessing. Overall, the synthesis and characterization of these complexes demonstrate our ability to exploit the Pacman macrocyclic framework to manipulate uranyl oxo group bonding and reactivity through control of the uranium oxidation state and oxo-group functionalization.

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