



Double uranium oxo cations derived from uranyl by borane or silane reduction†

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A new type of double uranium oxo cation $[O-U-O-U-O]^{4+}$ is prepared by selective oxygen-atom abstraction from macrocyclic uranyl complexes using either boranes or silanes. A significant degree of multiple $U=O$ bonding is evident throughout the U_2O_3 core, but either *trans*-, *cis*- or *trans*-, *trans*-OUOUO motifs can be isolated as boron- or silicon-capped oxo complexes. Further controlled deoxygenation of the borylated system is also possible.

Until recently, the oxo groups of the uranyl(vi) dication, $[UO_2]^{2+}$, which has a linear geometry and short, strong U–O bonds were considered to be very inert.¹ However, under anaerobic conditions, one electron reduction of uranyl compounds is now recognised to form uranyl(v) complexes that do not disproportionate, although the reactions rarely proceed further to lower U^{IV} oxidation state.² Reduction reactions increase the oxo basicity, generating oxo-donor interactions to other Lewis acidic ions. This makes reduced uranium oxo compounds better models for the heavier, highly radioactive transuranic metal actinyl cations $[AnO_2]^{n+}$ ($An = Np, Pu$; $n = 1, 2$) for which clustering behaviour is problematic in PUREX separation processes for civil nuclear waste treatment.^{3–6} Actinide oxo-bridges also facilitate electron-transfer reactions in environmental waste remediation,^{7–9} enrich the coordination chemistry of actinides in minerals,¹⁰ and can generate interesting electronic and magnetic structures.^{11–13}

We originally reported reductive silylation as a route to the first covalent bond formation reaction of a molecular uranyl complex,¹⁴ and, with others, have developed generic systems and rules that govern U^{VI} to U^V oxo-metalation,^{15–19} vs. oxo-silylation.^{20,21} Only very rarely does reduction to U^{IV} occur, recently seen using oxophilic, highly reducing U^{III} cations to form $[(UO_2I_4)\{UICl(py)_4\}_2]$, for example.²² Also, exhaustive

deoxygenation can convert simple uranyl salts to U^{IV} halides when combinations of alkali metal and Group 1 alkyl reductants, and excesses of halosilanes are used.^{23,24}

Here we show for the first time how simple diboranes are effective reagents for metal oxo-abstraction chemistry and how borane and silane-mediated uranyl reduction, oxo-functionalisation and abstraction, can afford a new U_2O_3 motif with *trans*-, *cis*- or *trans*-, *trans*-OUOUO linkages.

The dinuclear uranyl(vi) complex $[(UO_2(py))_2(L^A)]$ (**1**; $py =$ pyridine) reacts with two equivalents of the diborane B_2pin_2 ($pin =$ pinacolate) at 80 °C in pyridine to yield the new paramagnetic complex $[(py)(pinBO)UOU(OBpin)(py)(L^A)]$ **2** (Scheme 1, and ESI†). Both $[U^{VI}O_2]^{2+}$ ions in **1** have undergone $U^{VI} \rightarrow U^{IV}$ reduction and borylation, and a single oxo-atom abstraction, resulting in extrusion of $O(Bpin)_2$. The $O(Bpin)_2$ byproduct gives rise to singlets at 23 and 16 ppm in the ^{11}B NMR spectrum of the reaction solution, in which the highest frequency chemical shift is attributed to the pyridine adduct of $OB(pin)_2$ (see Fig. S16 and S18, ESI†), and accurately identified *via* an independent synthesis of $O(Bpin)_2$ from B_2pin_2 and $Me_3N=O$ in pyridine (see ESI†). In spite of the strength of B–O bonds, diboranes have only rarely been used to deoxygenate molecules, such as pyridine-oxides and phosphine-oxides,^{25,26} *o*-nitrostyrenes,²⁷ and CO_2 .²⁸ To our knowledge, this is the first example of their use to deoxygenate a metal complex. Reactions of uranyl with hydrosilanes such as $HSiEt_3$ can produce oxo-silylated U^V -OSiR₃ products such as $[U(OSiR_3)_2(I)_2(PDI)]$, (PDI is a redox non-innocent pyridinediimine),²⁹ usually requiring a strong Lewis acid activator such as $B(C_6F_5)_3$, *e.g.* to form the intermediate $[U(OB\{C_6F_5\}_3)(OSiR_3)(dbm)_2(THF)]$ ($dbm = OC(Ph)CHC(Ph)O$),³⁰ and deoxygenation usually requires more aggressive reagents such as halosilanes.^{24,29} Complex **1** also reacts with $HBpin$, forming **2**, H_2 and $O(Bpin)_2$. However, this reaction requires an excess of $HBpin$ (10 equiv.) and elevated temperatures (125 °C).

Resonances in the 1H NMR spectra of **2** range from +29 to –41 ppm and a significant reduction in the asymmetric OUO stretching frequency is observed, from 912 cm^{-1} for the uranyl group in **1**³¹ to 566 cm^{-1} in **2**. Complex **1** also reacts with the

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Scheme 1 Diborane or silane-mediated deoxygenation of co-axial uranyl dications to form the new tetracations [OUOUO]⁴⁺ **2**, **3**, and **5**, with either *trans*-, *cis*- (for boron) or *trans*-, *trans*- (for silicon) geometry, and the further deoxygenation of **3** to afford the UOU-containing **4**.

diborane B_2cat_2 (cat = catecholate) at 80 °C in pyridine, forming a catecholboroxo-analogue of **2**, [(py){(py)catBO}UOU(OBcat)(py)(L^A)] **3**. Similarly to the formation of **2**, **3** is the product of U^{VI} → U^{IV} reductive borylation of both U centres, and O-atom extrusion forming O(Bcat)₂ which was identified by ¹¹B NMR spectroscopy (singlets at 15 and 9 ppm, Fig. S23 and S25, ESI†); the highest frequency singlet is due to the pyridine adduct of O(Bcat)₂ (verified *via* an independent synthesis from B_2cat_2 and $\text{Me}_3\text{N}=\text{O}$ in pyridine, see ESI†). Whereas complex **2** can be isolated cleanly on a preparative scale, **3** transforms slowly into the new catecholate-bridged complex [(py)UOU(μ-O₂C₆H₄)(py)(L^A)] **4** which is the product of loss of both boroxo ligands and the addition of a catecholate ligand, [C₆H₄O₂]²⁻, that bridges the two U^{IV} centres (Scheme 1); upon the addition of a third equivalent of B_2cat_2 and heating for 48 h at 80 °C, **3** is converted exclusively into **4** in 77% yield. Only very small quantities of **3** have been isolated cleanly by fractional crystallisation. Complexes **3** and **4** may also be obtained from **1** and HBcat and, as with the formation of **2** from HBpin, these reactions require an excess of HBcat (10 equiv.).

An X-ray diffraction study on single crystals of **2** obtained from slow evaporation of a toluene solution at room temperature (Fig. 1a) shows it comprises two exogenous boroxide ligands and that one *endo*-oxo atom has been eliminated, with the remaining

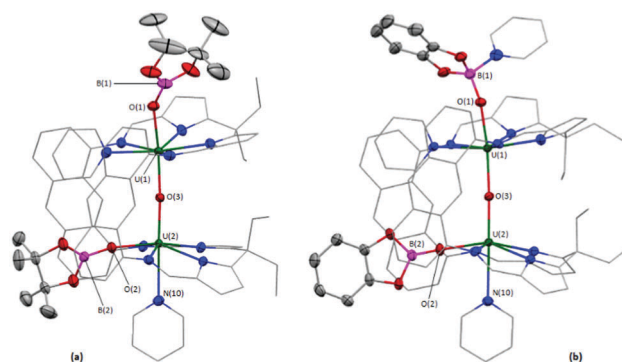


Fig. 1 Solid-state structures of **2·toluene** (a) and **3·THF** (b). Displacement ellipsoids are drawn with 50% probability, and carbon atoms of L^A and U-coordinated solvent molecules drawn wireframe. For clarity, hydrogen atoms, lattice solvent, and lower-fractional occupancy disorder components of the OBpin ligand (B(1)), and L^A ethyl groups of **2·toluene** are omitted.

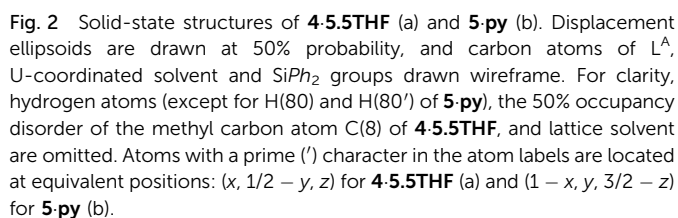
forming a fused U^{IV}–O–U^{IV} core that is essentially linear (U(1)–O_{endo}–U(2) = 176.2(1)°). The U–O_{exo} bond lengths are significantly longer than the U–O_{endo} bonds; the U(1)–O(1) and U(2)–O(2) bond lengths are 2.161(2) and 2.172(2) Å, respectively, whereas the U(1)–O(3) and U(2)–O(3) bond lengths are 2.139(2) and 2.112(2) Å, respectively. Of greatest interest is that one reduced OUO dication retains the *trans*-(pinB)OUO geometry (O(1)–U(1)–O(3) = 169.05(8)°), but the other has rearranged to a *cis*-OUO configuration with a O(2)–U(2)–O(3) angle of 96.51(7)°. The *trans*-, *cis*-configurations of **2** and **3** are retained in solution – the ¹¹B NMR spectrum of **2** shows two resonances at 475 and 221 ppm (496 and 126 ppm for **3**), and two sets of Bpin–CH₃ resonances are seen in the ¹H NMR spectra of **2**.

X-ray quality crystals of **3·THF** were obtained by diffusion of hexanes vapour into a THF solution of a dried, crude reaction product mixture containing *ca.* 90% **3**, Fig. 1b. The core is similar to **2**, Fig. 1a, possessing axial and equatorial boroxides; the O(1)–U(1)–O(3) and O(2)–U(2)–O(3) bond angles are 170.7(1) and 99.2(1)°, respectively. However, the catBO-ligand that is axially coordinated to U(1) in **3** contains an additional pyridine donor, hampering direct comparison with **2** and resulting in a relative contraction of the U–O_{exo} bond length in the py-solvated half of the structure, (U(1)–O(1) = 2.092(2) Å; U(2)–O(2) = 2.219(2) Å), and elongation of the B–O_{exo} bond lengths (B(1)–O(1) = 1.400(5) Å; B(2)–O(2) = 1.315(5) Å) and of the U–O_{endo} (U(1)–O(3) = 2.176(2) Å; U(2)–O(3) = 2.068(2) Å), presumably as a result of the lower Lewis acidity of B(1) than B(2).

The formation of **4** could occur *via* the extrusion of two equivalents of [OBcat], which would presumably form an insoluble boroxide polymer. Both complexes **3** and **4** have paramagnetically shifted ¹H NMR spectra (resonances ranging from *ca.* +70 to –60 ppm), and the FTIR spectrum of reaction solutions that contain predominantly **3** has bands at 580 and 531 cm^{–1}, which are tentatively assigned as OUO stretches by comparison with **2**.

In the solid-state (Fig. 2a), **4** has crystallographically imposed mirror symmetry, with the central oxygen atom of the complex (O(3)) positioned on the mirror plane. It possesses a short U(1)–O(3) bond length of 2.090(2) Å and U(1)–O(1)/O(1') bonds to the





The chemical shifts in the ^1H NMR spectrum of paramagnetic **5** span +64 to -41 ppm, and no obvious high-frequency asymmetric OUO stretch is found in the FTIR spectrum, consistent with a U^{IV}

Significantly, the use of a large spacer in the compartmental macrocycle L^A to enforce proximal co-linearity in uranyl(vi) coordination³¹ has enabled the first reductive fusion of two uranyl dications into a single, double-uranium containing cation, and the diboranes B_2pin_2 and B_2cat_2 have been shown for the first time to be capable oxo-atom abstraction reagents; this latter feature should have a widespread utility for the deoxygenation of d-block metal oxo complexes. Both borane and silane reagents have allowed an unusually high degree of uranyl reduction, with the $[OUOU]^{4+}$ core existing in either *trans*-, *trans*-linear, or *trans*-, *cis*-bent conformation. The reaction

that transforms complex 3 into the catechol-bridged diuranium(IV) complex 4 suggests that further reaction chemistry of these dinuclear uranium complexes will be possible. Work is in progress to explore the level of electronic coupling between the metal centres in all of these complexes, and to explore whether analogous oxo-ion fusion chemistry is possible for the actinyl cations of neptunium and plutonium, $[\text{AnO}_2]^{n+}$.

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Conflicts of interest

There are no conflicts to declare.

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