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 \(\text{U}_2\text{O}_3\) 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, \([\text{UO}_2]^{2+}\), which has a linear geometry and short, strong U–O bonds were considered to be very inert. However, under anaerobic conditions, one electron reduction of uranyl compounds is now recognised to form uranyl(V) complexes that do not disproportionate, although one electron reduction of uranyl compounds is now recognised to form uranyl(V) complexes that do not disproportionate, although reduction reactions rarely proceed further to lower U IV oxidation state. Reduction reactions increase the oxo basicity, generating oxo-donor interactions to other Lewis acidic ions. This makes reduced uranium oxo complexes better models for the heavier, highly radioactive transuranic metal actinyl cations \([\text{AnO}_2]^ {n+}\) (An = Np, Pu; \(n = 1, 2\)) for which clustering behaviour is problematic in PUREX separation processes for civil nuclear waste treatment. Actinide oxo-bridges also facilitate electron-transfer reactions in environmental waste remediation, and can generate interesting electronic and magnetic structures.

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

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 \(\text{U}_2\text{O}_3\) motif with trans-,cis- or trans-,trans-OUOUO linkages.

The dinuclear uranyl(VI) complex \([[[\text{UO}_2\text{py}]_2][\text{La}]](1)\); py = pyridine reacts with two equivalents of the diborane \(\text{B}_2\text{pin}_2\) (pin = pinacolate) at 80 °C in pyridine to yield the new paramagnetic complex \([[[\text{py}[\text{pinBO}]/\text{UO}]/\text{OBpin}]/\text{py}]/[\text{La}]\) (Scheme 1, and ESI†). Both \([\text{U}^{3+}\text{O}_2]^{2+}\) ions in 1 have undergone \(\text{U}^{VII}\) to \(\text{U}^{IV}\) reduction and borylation, and a single oxo-atom abstraction, resulting in extrusion of \(\text{O}(/\text{Bpin})_2\). The \(\text{O}(/\text{Bpin})_2\) byproduct gives rise to singlets at 23 and 16 ppm in the \(\text{^1B}^\text{NMR}\) spectrum of the reaction solution, in which the highest frequency chemical shift is attributed to the pyridine adduct of \(\text{O}(/\text{Bpin})_2\) (see Fig. S16 and S18, ESI†), and accurately identified via an independent synthesis of \(\text{O}(/\text{Bpin})_2\) from \(\text{B}_2\text{pin}_2\) and \(\text{Me}_3\text{N}=\text{O}\) 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, \(\text{o-nitrostyrenes}\), and \(\text{CO}_2\). To our knowledge, this is the first example of their use to deoxygenate a metal complex. Reactions of uranyl with hydrosilanes such as \(\text{HSiEt}_3\) can produce oxo-silylated \(\text{U}^\text{V} /\text{SiR}_3\) products such as \([\text{U}/\text{OSiR}_3]_2(\text{I})_2(\text{PDI})]\), (PDI is a redox non-innocent pyridinediimine), usually requiring a strong Lewis acid activator such as \(\text{B}/\text{C}_8\text{F}_8\), e.g. to form the intermediate \([\text{U}/\text{OB}[\text{C}_6\text{F}_5]_3]/[\text{OSiR}_3]/[\text{dbm}]_2(\text{THF})]\) (dbm = \(\text{OC}(/\text{Ph})/\text{CHC}(/\text{Ph})/\text{O}\)) and deoxygenation usually requires more aggressive reagents such as halosilanes. Complex 1 also reacts with \(\text{HBpin}\), forming \(2\) and \(\text{O}(/\text{Bpin})_2\). However, this reaction requires an excess of \(\text{HBpin}\) (10 equiv.) and elevated temperatures (125 °C).

Resonances in the \(\text{^1H}^\text{NMR}\) spectra of 2 range from +29 to –41 ppm and a significant reduction in the asymmetric OOU stretching frequency is observed, from 912 cm \(^{-1}\) for the uranyl group in 1 to 566 cm \(^{-1}\) in 2. Complex 1 also reacts with the...
diborane B2cat (cat = catecholate) at 80 °C in pyridine, forming a catecholboron-analogue of 2, [[py][([py]catBO)UOUCatO(py)(L)]]. 3

Similarly to the formation of 2, 3 is the product of U^IV→U^VI 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 (singlets at 15 and 9 ppm, Fig. S23 and S25, ESI†). The further deoxygenation of 3 to afford the UOU-containing 4.

The formation of 4 could occur via the extrusion of two equivalents of [O(Bcat), 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 OOU stretches by comparison with 2.

The 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 170.3(1)°, respectively. However, the catBO-ligand that is axially coordinated to U(1) in 3 contains an additional pyridine donor. The [Bpin–CH3]2+ resonances are seen in the 1H NMR spectra of 2.

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.
bridging catecholate ligand of 2.128(3) Å which, combined with the C(64)–O(1) bond length of 1.340(6) Å, indicate two U IV centres and a dianionic catecholate ligand.32 The U–O endo–U angle in 4 (142.3(3)°) is significantly more acute than that in 2 and 3, resulting in a close approach of the two U centres (3.956 Å in 4 versus 4.248 and 4.243 Å in 2 and 3, respectively).

It was envisaged that 1 could react with other p-block reactants aside from diboranes, driven by the formation of strong new O–E bonds (E = p-block element). While 1 does not react with phosphines and stannanes (HPPh2,P2Ph4, HSnPh3, \( \text{Ph}_3\text{SiH} \) and \( \text{Si}_2\text{Ph}_2\text{Me}_4 \), it reacts with the silane \( \text{Ph}_3\text{SiH}_2 \) over 24 h at 125 °C to form \( [\text{py}][\text{HPh}_2\text{SiO}]\text{UO\text{O}}\text{OSiPh}_2\text{H}[\text{py}][\text{H}L] \) (5; Scheme 1).33 Complex 1 also reacts with \( \text{Ph}_2\text{SiH}_3 \), \( \text{Si}_2\text{Me}_6 \), \( \text{Ph}_3\text{SiH} \) and \( \text{Si}_2\text{Ph}_2\text{Me}_4 \). Reactions with the former two silanes lead to the formation of unidentified, insoluble precipitates, whereas the latter two resulted in decomposition into \( [\text{UO}_2(\text{py})][\text{H}_2\text{L}] \) and unidentifed uranyl-containing species.

Complex 5 is a siloxy-analogue of 2 and 3 and is only formed in the presence of a catalytic amount (25 mol%) of an alkali-metal salt such as \( \text{KN(SiMe}_3\text{)}_3 \), \( \text{Li}[\text{SiMe}_3\text{]}_2 \) or \( \text{KO} \text{Bu} \), which is suggestive of a hypervalent silicate facilitating bond homolysis. The simple Lewis acids such as \( \text{BF}_3(\text{OEt}_2) \) or \( \text{B} \text{(C}_6\text{F}_5)\text{}_3 \) do not catalyse these reactions (see ESI†). The formation of 5 likely occurs in an analogous fashion to 2 and 3, but with Si–H bond homolysis driven by the formation of strong Si–O bonds, and release of \( \text{H}_2 \) and \( \text{OSiPh}_2\text{H} \) as reaction by-products. Indeed, when monitoring the reaction by \(^1\text{H} \) NMR spectroscopy, \( \text{H}_2 \) was observed (4.31 ppm in \( \text{d}_7\text{-pyridine} \) although it was not possible to identify Si-containing by-products in the \(^29\text{Si} \) NMR spectrum, so these may be undergoing further condensation/catenation reactions.

The chemical shifts in the \(^1\text{H} \) 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 formal oxidation state. The \( \text{trans},\text{trans} \)-symmetry of this silyl-capped ion is retained in the solution, but may be enforced by an inability of the large silyl-groups to fit between the anthracenyl spacers of L4.

The solid-state structure of the pyridine solvate of 5 \( \text{py} \) (see the ESI† for the THF solvate) was obtained. 5 \( \text{py} \) possesses crystallographically imposed two-fold symmetry, with the central oxygen O(3) positioned on the two-fold axis, and shows a near linear U–O–U bond angle of 173.1(2)° (Fig. 2b), similar to 2 and 3. However, in contrast to the B-capped compounds, the \( \text{exo} \)-oxo-siloxides both remain \( \text{trans} \) with nearly linear O(1)–U(1)–O(3) and O(1)–U(1)–O(3) angles (172.09(9)°). The U(1)–O(1) and U(1)/U(1)–O(3) bond lengths are 2.142(2) and 2.1486(3) Å, in good agreement with the \( \text{B}_2\text{O} \)-U bond lengths in 2 and 3, and with the U–O bond lengths in 4.

The U–O bond lengths in 2–5 range from 2.068(2)–2.219(2) Å, which are significantly elongated relative to the U–O bond length anticipated for \( [\text{UO}_2^2+ \] (shorter than 1.80 Å) and \( [\text{UO}_2]^2+ \) complexes (~1.85–1.95 Å),34,35 and are similar to those in the \( [\text{UO}_2]^2+ \) complexes \( [\text{Ph}_2\text{HSiO}]_4\text{UCl}_2(\text{OPPh}_3)_2 \) (2.120(5) Å),23 \( [(\text{Me}_3\text{SiO})_2\text{U}]_2(\text{bipy})_2 \) (2.084(4) Å; bipy = 4,4′-bipyridine),36 \( [\text{Cp}_2\text{Co}][((\text{C}_5\text{F}_5)_3\text{BO})(\text{Me}_3\text{SiO})\text{U}^{2+}\text{acncac}] \) (U–O(silox) = 2.173(8) Å; \( \text{Ar} = \text{C}_6\text{H}_3-3,5-\text{Bu}_2 \)),37 \( [(\text{UO}_2)\text{I}(\text{Dy}L)_5]_2 \) (2.058(3) and 2.068(3) Å), \( [(\text{UO}_2)L_2(\text{UCl})_2(\text{bipy})_2] \) (2.166(5) Å)27 and \( [(\text{Cp}_2\text{CIO})_2\text{UCl}(\text{L})] \) (2.066(7) and 2.066(7) Å; \( \text{L} = \) a monoanionic acyclic dlimino-dipyrin ligand),2 all of which derive from U IV to U IV reductive functionalisation of the uranyl(vi) ion. Furthermore, the average U–N(pyridine/imine) bond length in complexes 2–5 is 2.548 Å, which is longer than those seen in uranyl(vi) (2.525 Å)14–16,19,20 and uranyl(vi)–pacman complexes (2.487 Å).12,15

The reductive deoxygenation of 1 by the diborane is a new reaction type and a mechanism would likely involve reaction at the most accessible \( \text{exo} \)-oxo ligands, with B–B bond homolysis forming \( \text{U}^\text{V} \)-\( \text{B} \text{R}_2 \) and releasing \( \text{BR}_2 \) which can either abstract H atoms from solvent, or react with the other uranyl \( \text{exo} \)-oxo. This will result in a reduced, \( \text{U}^\text{V} \) intermediate \( [\text{B}_2\text{O}]^\text{U}^\text{IV} \text{BO} \text{U}^\text{IV} \text{BO} \text{B}_2 \) with elongated U V–(2.525 Å)14–16,19,20 and U V–pacman bond lengths in complexes 2–5 (2.548 Å), which is longer than those see in uranyl(vi) (2.525 Å).14–16,19,20 and uranyl(vi)–pacman complexes (2.487 Å).12,15

Significantly, the use of a large spacer in the compartmental macrocycle L4 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 \( \text{B}_2\text{pin}_2 \) and \( \text{B}_2\text{cat}_2 \) have been shown to be powerful reductants for U IV–U IV reductive functionalisation of the uranyl(vi) ion. Further, the average U–N(pyridine/imine) bond length in complexes 2–5 is 2.548 Å, which is longer than those seen in uranyl(vi) (2.525 Å)14–16,19,20 and uranyl(vi)–pacman complexes (2.487 Å).12,15
that transforms complex 3 into the catechol-bridged diuranium(\(\text{VI}\)) 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, [\(\text{AnO}_2\)]\(^{m+}\).

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Conflicts of interest

There are no conflicts to declare.

Notes and references

33 Complex 1 also reacts with Ph5SiH or Si2Me6 to yield unidentified, insoluble precipitates. Reactions with either Ph5SiH or Si2Me6 result in the loss of one of the uranyl ions from 1, affording poor yields of the known mono-substituted [\(\text{UO}_2(py)(H_2LA)\)] reported previously by us.