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 U₂O₃ core, but either trans,-cis- or trans,-trans-OUOUOUO 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, [UO₂]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 U⁴ 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 [AnO₂]⁵⁻ (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 oxo-metalation,10–13 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 U⁵⁻ to U⁴ oxo-metalation,15–19 vs. oxo-silylation.20,21 Only very rarely does reduction to U⁴ occur, recently seen using oxophilic, highly reducing U⁴⁰ cations to form [[UO₂I₁][UIICl(py)₂]²⁻, for example.22 Also, exhaustive deoxygenation can convert simple uranyl salts to U⁴ 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 U₂O₃ motif with trans,-cis- or trans,-trans-OUOUOUO linkages.

The dinuclear uranyl(vi) complex [[UO₂(py)]₂[LA]⁺ (py = pyridine) reacts with two equivalents of the diborane B₂Pin₂ (pin = pinacolate) at 80 °C in pyridine to yield the new paramagnetic complex [[py][pinBO]UO(UBpin)₄[py][LA]²⁻ (Scheme 1, and ESI†). Both [UO₂]²⁻ ions in 1 have undergone U⁵⁻→U⁴ 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 ¹⁷B NMR spectrum of the reaction solution, in which the highest frequency chemical shift is attributed to the pyridine adduct of O(Bpin)₂ (see Fig. S16 and S18, ESI†), and accurately identified via an independent synthesis of O(Bpin)₂ from B₂pin₂ and Me₃N 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 CO₂.28 To our knowledge, this is the first example of their use to deoxygenate a metal complex. Reactions of uranyl with hydrosilanes such as HSiEt₃ can produce oxo-silylated U⁴⁺–OSiR₃ products such as [U(OSiR₃)₂(L)₂(PDI)], (PDI is a redox non-innocent pyridinedilimine),29 usually requiring a strong Lewis acid activator such as B(C₆F₅)₃, e.g. to form the intermediate [UOB(C₆F₅)₃(OSiR₃)(dbm)₂(THF)] (dbm = OC(Ph)CH(Ph)O)³⁰ and deoxygenation usually requires more aggressive reagents such as halosilanes.²⁴,²⁹ Complex 1 also reacts with HBpin, forming 2, H₂ 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 OOU stretching frequency is observed, from 912 cm⁻¹for the uranyl group in ¹¹ to 566 cm⁻¹ in 2. Complex 1 also reacts with the...
Similarly to the formation of \( \text{HBcat} (10 \text{ equiv.}) \), that one shows it comprises two exogenous boroxide ligands and from slow evaporation of a toluene solution at room temperature two U IV centres (Scheme 1); upon the addition of a third dikations to form the new tetracations \([\text{OUO}_2]\)\(^+\) (verified via \(\text{diborane } \text{B}_2\text{cat}_2 \) at 80 \(\text{°C}\)), the other has rearranged to a cis-OUO configuration with a \(\text{OUO}_2\)-angle of 96.51(7)\(^\circ\). The trans-cis- configurations of 2 and 3 are retained in solution – the \(^{11}\text{B} \) NMR spectrum of 2 shows two resonances at 475 and 221 ppm (496 and 126 ppm for 3), and two sets of Bpin–CH\(_3\) resonances are seen in the \(^1\text{H} \) 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 U(1)-O(1)-O(3) and U(2)-O(3) bond lengths are 170.7(1) and 99.2(1)\(^\circ\), 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-Oexo bond length in the py-solvated half of the structure, \((\text{U}(1)-\text{O}(1) = 2.092(2) \, \text{Å}; \text{U}(2)-\text{O}(2) = 2.219(2) \, \text{Å})\), and elongation of the B-Oexo bond lengths \((\text{B}(1)-\text{O}(1) = 1.400(5) \, \text{Å}; \text{B}(2)-\text{O}(2) = 1.315(5) \, \text{Å})\) and of the U-Oexo bond length \((\text{U}(1)-\text{O}(3) = 2.176(2) \, \text{Å}; \text{U}(2)-\text{O}(3) = 2.068(2) \, \text{Å})\), 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 \(\text{OBcat}\), which would presumably form an insoluble boroxide polymer. Both complexes 3 and 4 have paramagnetically shifted \(^1\text{H} \) 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 \((\text{O}(3))\) positioned on the mirror plane. It possesses a short U(1)-O(3) bond length of 2.090(2) \(\text{Å}\) and U(1)-O(1)/O(1') bonds to the
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 UV centres and a dianionic catecholate ligand. The U–Oendo–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, PPh3, HSnPh3, Sn2Me6, SmPh3), it reacts with the silane Ph3SiH2 over 24 h at 125 °C to form [[py][HPh3SiO]UO2(OSiPh3)2(py)[L2]] (5; Scheme 1).33 Complex 5 also reacts with PhSiH3, SiMe3, Ph5SiH and Si2Ph2Me4. Reactions with the former two silanes lead to the formation of unidentified, insoluble precipitates, whereas the latter two resulted in decomposition into [UO2(py)[H2L]2] and unidentified 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 hydride (except for H[Bn] and H[80]) of 5 py, the 50% occupancy disorder of the methyl carbon atom C(8) of 4.55THF, and lattice solvent are omitted. Atoms with a prime (’) character in the atom labels are located at equivalent positions: (x, 1/2 – y, z) for 4.55THF (a) and (1 – x, y, 3/2 – z) for 5 py (b).

formal oxidation state. The trans-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 py (see the ESI† for the THF solvate) was obtained. 5 py possesses a 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 exo-oxo-siloxides both remain 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 R2BO–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 [UO2]2+ (shorter than 1.80 Å) and [UO2]2+ complexes (~1.85–1.95 Å).34,35 and are similar to those in the [UO2]2+ complexes [[Ph2HSiO2]UCl2(OPPh3)]2+ (2.120(5) Å),23 [[Me2SiO2][UCl2(bipy)]2] (2.084(4) Å; bipy = 4,4’-bipyridine),36 [[Cp2Co][((Cp,F3)3BO)[Me3SiO]U(4-acac)n]Cl3] (U–O(siloxy) = 2.173(8) Å; Ar = C6H5, 3,5′-Bu2),37 [[UO2I4]{DyI(py)5}2] (2.058(3) and 2.068(3) Å),38 [[UO2I4]{UCl2(ppy)2}2] (2.166(5) Å)17 and [[Cp2Cl2O2]{UCl2[L]}2] (2.062(7) and 2.066(7) Å; L = 1-monoanionic acyclic diimino-dipyrind ligand),39 all of which derive from UO2→UV reductive functionalisation of the uranyl(vi) ion. Furthermore, the average U–N(silyl/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 exo-oxo ligands, with B–B bond homolysis forming U–OBR2 and releasing BR2 which can either abstract H atoms from solvent, or react with the other uranyl exo-oxo. This will result in a reduced, UOintermediate [R2BO(UO2–OBR2)+ ion with elongated UOendo–Oendo bonds that now have greater oxo-basicity, facilitating the electron transfer required for one endo-oxo to form a covalent μ-oxo-bridge between the two U centres. The proposed dioxaboroxide,diμ-oxo intermediate is an analogue of the [Me2SiO2(UO2)2(OSiMe3)]2+ core seen previously.21 The catecholate dianion in Bcat enables a further deoxygeneration by the B atoms resulting in the conversion of 3 to 4. The reaction of 1 with Ph3SiH2 presumably involves activation of the oxo group as a Lewis base through hypervalent silicate formation.20,38

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 fission of two uranyl dications into a single, double-uranium containing cation, and the diboranes B2pin2 and B2cat2 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 [OOOUO]3+ core existing in either trans-trans-linear, or trans-cis-bent conformation. The reaction
that transforms complex 3 into the catechol-bridged diuranium(\(\nu\)) 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, \([\text{AnO}_2]^+\).

The authors thank the EPSRC-UK grants EP/N022122/1 and EP/M010534/1, the European Commission Directorate General and Actinet JRC Userlab (ACTINET-I3-CP-CSA-JRP-232631) and the Natural Sciences and Engineering Research Council of Canada for an NSERC Post-Doctoral Fellowship (BEC). This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No. 740311).

Conflicts of interest
There are no conflicts to declare.

Notes and references
33 Complex 1 also reacts with \(\text{PhSH}_3\) or \(\text{SiMe}_3\) to yield unidentified, insoluble precipitates. Reactions with either \(\text{PhSH}_3\), \(\text{EtSH}\) or \(\text{SiMe}_3\) result in the loss of one of the uranyl ions from 1, affording poor yields of the known mono-substituted \([\text{UO}_2(\text{py})(\text{H}_2\text{LA})]\) reported previously by us.