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-UO2OUO2 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. 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. 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]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,14 and, with others, have developed generic systems for this reaction. We now show that 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-UO2OUO2 linkages.

The dinuclear uranyl(vi) complex [[UO2(py)]2(L A)] (1; 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]UO2[OBpin][py][L A]] 2 (Scheme 1, and ESI†). Both U IV ions in 1 have undergone U VI → 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 11B 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, or nitroso- and CO2. To our knowledge, this is the first example of their use to deoxygenate a metal complex. Reductions of uranyl with hydrodilanes such as HSiEt3 can produce oxo-silylated U V OSiR3 products such as [U(OSiR3)2][d(bnf)2PDI], (PDI is a redox non-innocent pyridinedilimine) usually requiring a strong Lewis acid activator such as B(C6F5)3, e.g. to form the intermediate [UOB(C6F5)2][O(SiR3)(dbn)2THF]] (dbn = OC(Ph)CHC(Ph)O) and deoxygenation usually requires more aggressive reagents such as halosilanes. 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 2H 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 to 566 cm–1 in 2. Complex 1 also reacts with the...
Scheme 1. Diborane or silane-mediated deoxygenation of co-axial uranyl dications to form the new tetracations [OUOUO]₄⁺ using B₂cat₂ and heating for 48 h at 80 °C. Whereas complex 2 can be isolated cleanly on a preparative scale, 3 transforms slowly into the new tetracations [OUOUO]₄⁺ via (verified via an independent synthesis from B₂cat₂ and Me₃N=O in pyridine, see ESI). Whereas complex 2 can be isolated cleanly on a preparative scale, 3 transforms slowly into the new tetracations [OUOUO]₄⁺, Fig. 1a, possessing axial and equatorial boroxides; the U(1)–O(1) and U(2)–O(2) bond lengths are 2.092(2) Å; U(2)–O(2) bond lengths are 2.219(2) Å, respectively. Of greatest interest is that one reduced OUO dication retains 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.

Diborane B₂cat₂ (cat = catecholate) at 80 °C in pyridine, forming a catecholborox-analogue of 2, [[py][py]catBO][OU(O)Bcat][py](L³) 3, with either trans-cis- (for boron) or trans-trans- (for silicon) geometry, and 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 O=O stretches by comparison with 2.

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 forming a fused UIV-O–UIV core that is essentially linear (U(1)–Oendo–U(2) = 176.2(1)°). The U–Oexo bond lengths are significantly longer than the U–Oendo 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-cis-configuration of a U(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(5) 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–Oexo 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-Oexo bond lengths (B(1)-O(1) = 1.400(5) Å; B(2)-O(2) = 1.315(5) Å) and of the U-Oendo (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).
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 UIV 

centres and a dianionic catecholate ligand.32 The U–O_inclined–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 reagents 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 (HPPh3, P2Ph3, HSnPh3, Sn2Me6, SnPh2Me), it reacts with the silane Ph2SiH2 over 24 h at 125 °C to form [[py][HPh2SiO]UOU(OSiPh2H)[py][L2]] (5; Scheme 1).33 Complex 1 also reacts with PhSiH3, Si2Me6, 

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)[HJL2]] 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 salt such as K2SiMe3, Li2SiMe3 or KOBu, which is suggestive of a hypervalent silicate facilitating bond homolysis. The simple Lewis acids such as BF3(OEt2) or B(C6F5)3 do not catalyse these reactions (see ESIF). 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 H2 and O(SiPh2H)3 as reaction by-products. Indeed, when monitoring the reaction by 1H NMR spectroscopy, H2 was observed (4.31 ppm in d4-pyridine) although it was not possible to identify Si-containing by-products in the 29Si NMR spectrum, so these may be undergoing further condensation/catenation reactions.

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 UIV 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 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) 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]+ (shorter than 1.80 Å) and [UO2]2+ complexes (~1.85–1.95 Å)34,35 and are similar to those in the [UO2] complexes [Ph2H5SiO]UCl2(OPPh3) (2.120(5) Å),23 [(Me2SiO)2UI(bipy)_2] (2.084(4) Å; bipy = 4,4’-bipyridine),36 

[CP2Co][((CP2F)3BO)(Me2SiO)U4(acac)] (U–O(silox) = 2.173(8) Å; Ar = C6H6,3.5-’Bu3),37 [(UO2)3][DyI(py)5] (2.058(3) and 2.068(3) Å), 

[(UO2)]2[UCl(py)5] (2.166(5) Å)38 and [(CP2ClTiO)2UCl(L)] (2.062(7) and 2.066(7) Å; L = I monomeric acyclic dirimo-dipyrrin ligand),39 all of which derive from UVI reductive functionalisation of the uranyl(vi) ion. Furthermore, the average U–N_symidoiline/imine 

bond length in complexes 2–5 is 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

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 voyeur–BR2 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, UIV intermediate [R2BOU(O)2– 

UO2BR2]+ ion with elongated U–=–O_inclined 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 di[borate],di[μ-oxo] intermediate is an analogue of the [Me2SiO(U(μ-oxo)O)SiMe3]+ core seen previously.31 The catecholate dianion in Bcat enables a further deoxygenation by the B atoms resulting in the conversion of 3 to 4. The reaction of 1 with Ph5SiH2 presumably involves activation of the oxo group as a Lewis base through hypervalent silicate formation.20,38

Significantly, the use of a larger spacer in the compartmental macroring 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 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 [OUO2]+ core existing in either trans-trans-linear, or trans-cis-bent conformation. The reaction
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-ioxo fusion chemistry is possible for the actinyl cations of neptunium and plutonium, [\(\text{An}_2\text{O}_6\text{]^m}\)].

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Conflicts of interest

There are no conflicts to declare.

Notes and references

33. Complex 1 also reacts with Ph₅SiH or Si₅Me₅ to yield unidentified, insoluble precipitates. Reactions with either Ph₅SiH, B₃SiH or Si₅Ph₃Me₅ result in the loss of one of the uranyl ions from 1, affording poor yields of the known mono-substituted [UO₂(µ-H)L₄] reported previously by us.