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-UOOUUO 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 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 complexes better models for the heavier, highly radioactive transuranic metal actinyl cations [AnO2]3+ (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,15–19 and rules that govern U VI to U V oxo-metalation,14–19 vs. U VI to U V reductive 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.20,21

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-UOOUUO linkages.

The dinuclear uranyl(vi) complex [[UO2(py)]2(LA)] (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]UO(UO)(py)[L]2] (Scheme 1, and ESI†). Both [U(V)O2]3+ ions in 1 have undergone U VI to 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 OB(pin)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 hydroxilanes such as HSiEt3 can produce oxo-silylated U V OSiR3 products such as [U(OSiR3)2/] (PDI) (PDI is a redox non-innocent pyridinedimine)29, usually requiring a strong Lewis acid activator such as B(C6F5)3, e.g. to form the intermediate [UO(B(C6F5)3)][OSiR3][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, 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 ODU stretching frequency is observed, from 912 cm−1 for the uranyl group in 11 to 566 cm−1 in 2. Complex 1 also reacts with the...
forming a fused \( U^{IV} \cdot O \cdot U^{IV} \) core that is essentially linear (\( U(1)\)–\( O(3) \)=\( U(2) \)= 176.2(1)). The \( U\)-\( O(3) \) 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 dications 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 \( ^{11} B \) 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 \( ^{1} H \) NMR spectra of \( 2 \).

X-ray quality crystals of \( 3\) \( \cdot \)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 \( U\)-\( O(3) \) 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 \( B\)-\( O(3) \) bond lengths (\( B(1)\)-\( O(1) \)= 1.400(5) Å; \( B(2)\)-\( O(2) \)= 1.315(5) Å) and of the \( U\)-\( O(3) \)= 1.762(2) Å; \( U\)-\( O(3) \)= 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 \( O\)\( B\)cat, which would presumably form an insoluble boroxide polymer. Both complexes \( 3 \) and \( 4 \) have paramagnetically shifted \( ^{1} H \) 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 OOU 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...
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 bond lengths in complexes 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 [UO₂⁴] complexes (~1.85–1.95 Å).34,35 and are similar to those in the [UO₂] complexes [(H₂HSiO)₂UCl₂(OPPh₃)₂] (2.120(5) Å),36 [(Me₃SiO)₂U₂(bipy)₂] (2.084(4) Å; bipy = 4,4’-bipyridine),36 [Cp₂Co[[[(Cp₂)₂BO(Me₃SiO)]U₄(acnac)] (U-O(silox) = 2.173(8) Å; Ar = C₆H₄-3,5-Bu₂),37 [(UO₂I₄){DyI(py)₅}₂] (2.058(3) and 2.068(3) Å), [(UO₂I₄)UCl(py)₃] (2.166(5) Å)38 and [(Cp₂CIMO₂UCl(L)] (2.062(7) and 2.066(7) Å; L = a monoanionic acyclic diimino-diPyrrin ligand),2 all of which derive from UIV–OBR₂ and releasing BR₂ which can either abstract an uranyl(v) ion. Furthermore, the average U-Npyrrolide/imine bond for one endo-oxo–bridge that now have greater oxo-basici y, facilitating the electron transfer required for one endo-oxo to form a covalent μ-oxo-bridge between the two U centres. The proposed di(boroxide),di(μ-oxo) intermediate is an analogue of the [Me₃SiOU(O)₂UOSiMe₃]⁴⁺ core seen previously.21 The catecholate dianion in Bcat enables a reductive deoxygenation of the uranyl(vi) ion. Communication

The reductive deoxygenation of U 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 U⁵–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, U⁵ intermediate [B₂O(μ-O)₂–UO₂BR₂]⁺ ion with elongated U=O exo bonds that now have greater oxo-basici ty, facilitating the electron transfer required for one endo-oxo to form a covalent μ-oxo-bridge between the two U centres. The proposed di[(boroxide),di(μ-oxo)] intermediate is an analogue of the [Me₃SiOU(O)₂UOSiMe₃]⁴⁺ core seen previously.24 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 P₃H₅ allows presumably 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 macr ocycle L₄ to enforce proximal co-linearity in uranyl(vi) coordination31 has enabled the first r eflective fusion of two uranyl dications into a single, double-uranium containing cation, and the diboranes B₃P₃H₅ and B₄C₄H₇ 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(\(\text{V}\)) 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 o xo-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 PhSiH\(_3\) or Si\(_2\)Me\(_6\) to yield unidentified, insoluble precipitates. Reactions with either PhSiH\(_3\) or B\(_3\)SiH or Si\(_2\)Ph\(_2\)Me\(_4\) result in the loss of one of the uranyl ions from, affording poor yields of the known mono-substituted [UO\(_2\)(py)(H\(_2\)LA)] reported previously by us.