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–O–U]=+ is prepared by selective oxygen-atom abstraction from macrocyclic uranyl complexes with 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-UO₂UO₂O⁻ 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 uranil[V] complexes that do not disproportionate, although one electron reduction of uranyl compounds is now recognised to form uranil(V) complexes that do not disproportionate, although 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 ¹B 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, and ⁶-nitrostyrenes, ⁶-nitrostyrenes, and CO₂. 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(I)₂(PDI)] (PDI is a redox non-innocent pyridinediimine), usually requiring a strong Lewis acid activator such as B(C₆F₅)₃, e.g. to form the intermediate [U(OC(Ph)CH(C(Ph)O)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 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 to 566 cm⁻¹ in 2. Complex 1 also reacts with the 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. 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-UO₂UO₂O⁻ linkages.

The dinuclear uranyl[VI] complex [[UO₂(py)]₂(I)²⁺] (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]UO₂O[py][py]²⁺] (Scheme 1, and ESI†). Both [UΟ₂]²⁺ ions in 1 have undergone U⁴⁺–U⁴⁺ reduction and borylation, and a single oxo-atom abstraction, converting uranyl(V) to uranyl(IV) (see ESI†).

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Similarly to the formation of frequency singlet is due to the pyridine adduct of O(Bcat)\(^2\) (singlets at 15 and 9 ppm, Fig. S23 and S25, ESI†). Whereas complex 2 is the product of U\(^{IV}\) → U\(^{IV}\) reductive borylation of both U centres, and O-atom extrusion forming O(Bcat)\(^2\) which was identified by \(^{11}B\) 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 B2cat and Me2N=O in pyridine, see ESI†). Whereas complex 2 can be isolated cleanly on a preparative scale, 3 transforms slowly into the new catecholboroxy-analogue of \(\text{[C}_6\text{H}_4\text{O}_2\text{]}\)\(^-\) (formed cleanly on a preparative scale, (U(1)–O(1) = 2.092(2) Å; U(2)–O(2) = 2.219(2) Å), and of the U–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 exo bond lengths are significantly longer than the U–Oex = U(2) = 176.2(1)°. The U–Oexo bond lengths are significantly longer than the U–Oexo 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 OOU dication retains the trans-cis-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 \(^1H\) 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–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-Oexo (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 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.

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 U IV centres and a dianionic catecholate ligand. 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 reactants aside from diboranes, driven by the formation of strong Si–O bonds, and release of H2 and O(SiHPh2)2 as reaction by-products. Indeed, when monitoring the C(64)–O(1) bond length of 1.340(6) Å, indicate two U IV coordination31 has enabled the first reductive fusion of two uranyl(IV) reductive functionalisation of the uranyl(vi) ion. Furthermore, the average U–Narylside/imine bond length in complexes 2–5 is 2.548 Å, which is longer than those in uranyl(vi)–(2.525 Å)14,16,19,20 and uranyl(vi)–pcam 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 V−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, U IV intermediate [R2BOU(O2)−U OBr2]3+ ion with elongated U3−O endo 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[boroxide],di[μ-oxo] intermediate is an analogue of the [Me2SiO(μ2-O)OSiMe2]1+ 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 Ph3SiH2 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 macrocycle L A to enforce proximal co-linearity in uranyl(vi) coordination31 has enabled the first rreductive fusion of two uranyl dications into a single, double-uranium containing cation, and the diboranes B2Pi2 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 [OUOOU]+ core existing in either trans-trans-linear, or trans-cis-bent conformation. The reaction
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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 o xo-ion fusion chemistry is possible for the actinyl cations of neptunium and plutonium, \([\text{AnO}_2^+\]).

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Conflicts of interest

There are no conflicts to declare.

Notes and references

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33 Complex 1 also reacts with PhSSiH or Si₂Me₆ to yield unidentified, insoluble precipitates. Reactions with either Ph₂SiH, B₂SiH or Si₂Ph₂Mg result in the loss of one of the uranyl ions from 1, affording poor yields of the known mono-substituted [UO₂(py)[H₂LA]] reported previously by us.