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]+ is prepared by selective oxygen-atom abstraction from macroyclic 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. 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 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.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[π] complex [[UO2(py)2][L1]] (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)[L1]] (Scheme 1, and ESI†). Both [UO3]2+ ions in 1 have undergone U V 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 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,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 U V-OSiR3 products such as [U(OSiR3)21](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)2(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 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
Similarly to the formation of \( \text{O(Bcat)}_2 \) (singlets at 15 and 9 ppm, Fig. S23 and S25, ESI), 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 catecholate ligand, \([\text{C}_6\text{H}_4\text{O}_2]\) which is the product of loss of both boroxy ligands and the reductive borylation of both U centres, and O-atom extrusion forming \( \text{O(Bcat)}_2 \) which was identified by \(^{11}\text{B} \) NMR spectroscopy (verified via an independent synthesis from \( \text{B}_2\text{cat}_2 \) and \( \text{Me}_3\text{N} \) at 80 °C, 48 h, py). Whereas complex 1, which has paramagnetically shifted \(^1\text{H} \) NMR spectra (resonances ranging from -10 to 70 ppm), and the FTIR spectrum of reaction solutions that contain predominantly 3 has bands at 580 and 315 cm \(^{-1} \), which are tentatively assigned as OUO stretches by comparison with 2.

The formation of 4 could occur via the extrusion of two equivalents of [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) Å and U(1)–O(1)/O(1’)

forming a fused U IV–O–U IV core that is essentially linear (U(1)–O \(_{\text{endo}}\)–U(2) = 176.2(1)°). The U–O \(_{\text{exo}}\) bond lengths are significantly longer than the U–O \(_{\text{endo}}\) 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 dication 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 \(^{11}\text{B} \) 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, 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 \(_{\text{exo}}\) 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 \(_{\text{exo}}\) bond lengths (B(1)–O(1) = 1.400(5) Å; B(2)–O(2) = 1.315(5) Å) and of the U–O \(_{\text{endo}}\) bond (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).

Fig. 1. Solid-state structures of 2/toluene (a) and 3/THF (b). Displacement ellipsoids are drawn with 50% probability, and carbon atoms of L \(_3\) and U-coordinated solvent molecules drawn wireframe. For clarity, hydrogen atoms, lattice solvent, and lower-fractional occupancy disorder components of the OBpin ligand (B(II)), and L \(_4\) ethyl groups of 2/toluene are omitted.
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 bond length anticipated for [UVIO2]2+ (shorter than 1.80 Å) and [UO2O4] complexes (~1.85–1.95 Å),34,35 and are similar to those in the [UO2O4] complexes [Ph2H5SiO]UCl2(OPPh3)2 (2.120(5) Å),23 [(Me3SiO)2Ui(bipy)2] (2.084(4) Å; bipy = 4,4′-bipyridine),36 [Cp5Co][[(C6F5)3BO(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(µ-py)2] (2.166(5) Å)32 and [(Cp5C5H5)3UCl(L)] (2.062(7) and 2.066(7) Å; L = a monoanionic acyclic diimino-dipyrindin ligand),2 all of which derive from U IV–U IV reductive functionalisation of the uranyl(v) ion. Furthermore, the average U–N pyridine/imine bond length is 2.548 Å, which is longer than those see in uranyl(v)–(2.525 Å)14–16,19,20 and uranyl(v)–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 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 V intermediate [R2BOU(O)2–U V–OBR2]++ ion with elongated U V–OBR2 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 [Me5SiO2U(μ-oxO)3OSiMe5]++ core seen previously.21 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 L4 to enforce proximal co-linearity in uranyl(v) coordination31 has enabled the first reductive fission of two uranyl dications into a single, double-uranium containing cation, and the diboranes B2Ph3 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]4+ core existing in either trans-, trans-linear, or trans-, cis-bent conformation. The reaction

Fig. 2  Solid-state structures of 4.5THF (a) and 5 py (b). Displacement ellipsoids are drawn at 50% probability, and carbon atoms of L4, U–coordinated solvent and SiPh2 groups drawn wireframe. For clarity, hydrogen atoms (except for H(80) and H(80′)) are omitted. Atoms with a prime (′) character in the atom labels are located at equivalent positions: (x, 1/2 − y, z) for 4.5THF (a) and (1 − x, y, 3/2 − z) for 5 py (b).
that transforms complex 3 into the catechol-bridged diuranium(IV)
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-o xo fusion chemistry is possible for the

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Conflicts of interest

There are no conflicts to declare.

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insoluble precipitates. Reactions with either Ph5SiH3 or Si2Me6 result in the loss of one of the uranyl ions from 1, affording
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