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Double uranium oxo cations derived from uranyl by borane or silane reduction

Bradley E. Cowie, Gary S. Nichol, Jason B. Love* and Polly L. Arnold*

A new type of double uranium oxo cation \([\text{O-U-O-U}]^{4+}\) 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 \(\text{U}_2\text{O}_3\) core, but either trans-, cis- or trans-, trans- \(\text{OUO}_2\text{UO}\) 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, \([\text{UO}_2]^2+\), 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 states. Reduction reactions increase the oxo basicity, generating oxo-donor interactions to other Lewis acids ions. This makes reduced uranium oxo compounds better models for the heavier, highly radioactive transuranic metal actinyl cations \([\text{AnO}_2]^{n+}\) (An = Np, Pu; \(n = 1, 2\)) for which clustering behaviour is problematic in PUREX separation processes for civil nuclear waste treatment.

We originally reported reductive silylation as a route to the first covalent bond formation reaction of a molecular uranyl complex, and, with others, have developed generic systems and rules that govern U(VI) to U(V) oxo-metalation, vs. oxo-silylation. Only very rarely does reduction to U(IV) occur, recently seen using oxophilic, highly reducing U(III) cations such as to form \([\text{UO}_2\text{I}_4]\)(\text{UICl}(\text{py})_4)_2\), for example. Also, exhaustive 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.

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 \(\text{U}_2\text{O}_3\) motif with trans-, cis- or trans-, trans- \(\text{OUO}_2\text{UO}\) linkages.

\(^*^{a}\)EsSICHEM School of Chemistry, The University of Edinburgh, Joseph Black Building, The King’s Buildings, Edinburgh, EH9 3FJ, UK.

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J. Name., 2013, 00, 1-3 | 1
The dinuclear uranyl(VI) complex \([\{\text{UO}_2(\text{py})\}_2(L^2)\}] (1; \text{py} = \text{pyridine}) reacts with two equivalents of the diborane \(B_3\text{pin}_2\) (\(\text{pin} = \text{pinacolato}\)) at 80 °C in pyridine to yield the new paramagnetic complex \([\{\text{py}B\text{pinBO(UO)}(\text{O}B\text{pin(py)})\}_2(L^4)\}] (2) (Scheme 1, and Supporting Information). Both [U\(^{15}\)O\(^{18}\)]\(^{2+}\) ions in 1 have undergone U\(^{15}\)O\(^{18}\)\text{\(\rightarrow\)}U\(^{19}\)O\(^{17}\) reduction and borylation, and a single oxo-atom abstraction, resulting in extrusion of O(Bpin). The O(Bpin) byproduct gives rise to singlets at 23 and 16 ppm in the \(^{1}H\) NMR spectrum of the reaction solution, in which the highest frequency chemical shift is attributed to the pyridine adduct of OB(pin)\(_2\) (see Figures S16 and S18), and accurately identified via an independent synthesis of O(Bpin)\(_2\) from B\(_3\)pin\(_2\) and Me\(_2\)N=O in pyridine (see SI). 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,\(^{25,26}\) p-nitrostyrenes,\(^{27}\) and CO\(_2\). To our knowledge, this is the first example of their use to deoxygenate a metal complex. Reactions with hydroxilanes such as HSiEt\(_3\) can produce oxo-silylated U\(^{18}\)O\(^{17}\)SiEt\(_3\) products such as U(OSiEt\(_3\))(L)(PDI) (PDI is a redox non-innocent pyridinediimine),\(^{29}\) usually requiring a strong Lewis acid activator such as B(C\(_6\)F\(_5\))\(_3\), e.g. to form the intermediate U(OB(C\(_6\)F\(_5\))\(_3\))(OSiEt\(_3\))(dbm\(_3\))\(_2\) (THF) (dbm = OC(Ph)(CH\(_2\))Ph)(O),\(^{30}\) and deoxygenation usually requires more aggressive reagents such as halosilanes.\(^{24,29}\) Complex 1 also reacts with HBpin, forming 2, H\(_2\) and O(Bpin)\(_2\). However, this reaction requires an excess of HBpin (10 equiv.) and elevated temperatures (125 °C).

Resonances in the \(^{1}H\) NMR spectra of 2 range from +29 to −41 ppm and a significant reduction in the asymmetric O\(_1\)O\(_2\)O\(_3\)O\(_4\) 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 diborane B\(_3\)cat\(_2\) (cat = catecholate) at 80 °C in pyridine, forming a catecholboroxy-analogue of 2, \([\{\text{py}B\text{pinBO(UO)}(\text{O}B\text{pin(py)})\}_2(L^4)\}] \) 3. Similarly to the formation of 2, 3 is the product of U\(^{19}\)O\(^{17}\)\text{\(\rightarrow\)}U\(^{19}\)O\(^{18}\) reductive borylation of both U centres, and O–atom extrusion forming O(Bcat\(_2\)), which was identified by \(^{1}B\) NMR spectroscopy (singlets at 15 and 9 ppm, Figures S23 and S25). The highest frequency singlet is due to the pyridine adduct of O(Bcat\(_2\)) (verified via an independent synthesis from B\(_3\)cat\(_2\) and Me\(_2\)N=O in pyridine, see SI). Whereas complex 2 can be isolated cleanly on a preparative scale, 3 transforms slowly into the new catecholate-bridged complex \([\{\text{py}UO\mu-\text{O}_2\text{C}_2\text{H}_4\text{O}_2\}(\text{py})\}_2(L^4)\}] 4 which is the product of removal of both borony ligands and the addition of a catecholate ligand, \([\text{C}_6\text{H}_4\text{O}_2]^{-}\), that bridges the two U\(^{3+}\) centres (Scheme 1); upon the addition of a third equivalent of B\(_3\)cat\(_2\) and heating for 48 h at 80 °C, 3 is converted exclusively into 4 in 77 % yield. Only very small quantities of 3 have been isolated cleanly by fractional crystallisation. Complexes 3 and 4 may also be obtained from 1 and HBcat. As with the formation of 2 from HBpin, these reactions require an excess of HBcat (10 equiv.).

An X-ray diffraction study on single crystals of 2 obtained from slow evaporation of a toluene solution at room temperature (Figure 1a) shows it comprises two exogenous boroxide ligands and that one endo-oxo atom has been eliminated, with the remaining forming a fused U\(^{19}\)O\(^{18}\)–U\(^{19}\)O\(^{18}\) core that is essentially linear (U(1)–O\(_{\text{endo}}\)–U(2) = 176.2(1)°). The U–O\(_{\text{endo}}\) bond lengths are significantly longer than the U–O\(_{\text{bend}}\) 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)–U(3) bond lengths are 2.139(2) and 2.112(2) Å, respectively. Of greatest interest is that one reduced UO\(_{\text{II}}\) dication retains the trans-(pin)O\(_{\text{II}}\)O\(_{\text{I}}\) geometry (O(1)–U(1)–O(3) = 169.05(8)°), but the other has rearranged to a cis-UO\(_{\text{II}}\) configuration with a O(2)–U(2)–O(3) angle of 96.51(7)°. The trans,cis-structures of 2 and 3 are retained in solution – the \(^{1}H\) 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-THF were obtained by diffusion of hexanes vapour into a THF solution of a dried, crude reaction product mixture containing ca 90 % 3, Figure 1b. The core is similar to 2, Figure 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\(_{\text{endo}}\) 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\(_{\text{endo}}\) bond lengths (B(1)–O(1) = 1.400(5) Å; B(2)–O(2) = 1.315(5) Å) and of the U–O\(_{\text{endo}}\) (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 [OBcat], 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 O\(_{\text{II}}\)-O\(_{\text{I}}\) stretches by comparison with 2.

In the solid-state (Figure 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) 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\(^{19}\)O\(^{18}\) centres and a dianionic catecholate ligand.\(^{32}\) The U–O\(_{\text{endo}}\)–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 1 does not react with phosphines and stannanes (HPPH\(_3\), P\(_2\)PH\(_3\), HSnPH\(_3\), Sn\(_2\)Me\(_6\), Sn\(_2\)PH\(_3\)), it reacts with the silane Ph\(_3\)SiH\(_2\) over 24 h at 125 °C to form \([\{\text{py}HPPH_3\text{Si]}\text{UO(UO)}(\text{OSiPh}_3\text{py})\}_2(L^4)\}] \) (5; Scheme 1).\(^{33}\) Complex 1 also reacts with Ph\(_3\)SiH\(_2\), Si\(_2\)Me\(_6\), Ph\(_3\)SiH and Si\(_2\)PH\(_2\)Me\(_4\). Reactions with the former two silanes lead to the formation of unidentified, insoluble precipitates, whereas the latter two resulted in...
decomposition into [UO₂(py)(H₂L₄)] 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 KN(SiMe₂)₄, LiN(SiMe₂)₂ or KO'Bu, which is suggestive of a hypervalent silicon intermediate facilitating bond homolysis. The simple Lewis acids such as BF₃(OEt₂) or B(C₆F₅)₃ do not catalyse these reactions (see SI). 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(SiHPh₂)₂ as reaction by-products. Indeed, when monitoring the reaction by ¹H NMR spectroscopy, H₂ was observed (4.31 ppm in d₅-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 U⁰ formal oxidation state. The trans,trans- symmetry of this siloxy-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.

**FIGURE 1.** Solid-state structures of 2-toluene (a) and 3-THF (b). Displacement ellipsoids are drawn with 50% probability, and carbon atoms of L⁴ and U-coordinated solvent molecules drawn wireframe. For clarity, hydrogen atoms, lattice solvent, and lower-fractional occupancy disordered components of the OIPpin ligand (B(1)), and L⁴ ethyl groups of 2-toluene are omitted.

**FIGURE 2.** Solid-state structures of 4–5.5THF (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)’ of 5-py), the 50% occupancy disorder of the methyl atom labels are located at equivalent positions: (x, 1/2-y, z) for 4-5.5THF (a) and (1-x, y, 3/2-z) for 5-py (b).

The solid-state structure of the pyridine solvate of 5-py (see the SI 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)° (Figure 2b), similar to 2 and 3. However, in contrast to the B-capped compounds, the exo-oxo-siloxyides 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)′–O(1)′ bond lengths are 2.142(2) and 2.1486(3) Å, in good agreement with the R₂B–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]⁴⁺ (shorter than 1.80 Å) and [UO₃]⁴⁺ complexes (~1.85–1.95 Å) and are similar to those in the [UO₂]⁴⁺ complexes [(Ph₃SiO₂)₂UCl₂(OPPh₃)] (2.120(5) Å), [(Me₅SiO₂)₂U₂(bipy)] (2.084(4) Å; bipy = 4,4′-bipyridine), [Cp₅Co][{(C₅F₅)₂(C₅F₅)}₂U₃⁺(acnac)] (U–Osiloxyl) = 2.173(8) Å; Ar = C₅H₅,5,5′-Bu₂,₂⁰ [(UO₄)₂(Dy(py)₃)] (2.058(3) and 2.068(3) Å), [(UO₄)₂(Dy(py)₃)] (2.166(5) Å)², and [(Cp₅TiO)₂UCl₂] (2.062(7) and 2.066(7) Å; L = a monoanionic acyclic diimino-dipyrrin ligand), all of which derive from U⁴⁺→U⁴⁺ reductive functionalisation of the uranyl(VI) ion. Furthermore, the average U–N₃pyridoxide/mino bond length in complexes 2–5 is 2.548 Å, which is longer than those see in uranyl(V)- (2.525 Å)², uranyl(VI)-pacman complexes (2.487 Å).²,₁²,₁₅

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 U⁴⁺-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⁻ intermediate [R₂BOU(O₂)₂UOBR₂]⁴⁻ ion with elongated U=O endo bonds that now have greater oxo-basicity, facilitating the electron transfer required for one endo-oxo to form a covalent oxo-bridge between the two U centres. The proposed d-(boroxide),((μ-oxo) intermediate is an analogue of the [Me₅SiO₂U(μ-oxo)UOSiMe₃]⁴⁺ core seen previously. The catecholate dianion in 3cat enables a further deoxygenation by the B atoms resulting in the conversion of 3 to 4. The reaction of 1 with Ph₂SiH₂ presumably involves activation of the oxo group as a Lewis base through hypervalent silicate formation.²,₁⁰

Significantly, the use of a large spacer in the compartmental macrocycle L⁴ to enforce proximal co-linearity in uranyl(VI) coordination²³ has enabled the first reductive fusion of two uranyl dications into a single, double-uranium containing cation, and the diboranes B₂pin₂ and B₂cat₁ 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 [OUO₄]²⁻ core existing in either trans-trans-linear, or trans-cis-bent conformation. The reaction 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 oxo-ion fusion chemistry is possible for the actinyl cations of neptunium and plutonium, [AnO₃]³⁺.

Conflicts of interest
There are no conflicts to declare.

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Notes and references
33. Complex 1 also reacts with P(SiH₃)₃ or SiMe₃ to yield unidentified, insoluble precipitates. Reactions with either Ph₂SiH or Si₂Me₃ result in the loss of one of the urany ions from 1, affording poor yields of the known mono-substituted [UO₂(py)](py)(H₂L) reported previously by us.