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Strongly coupled binuclear uranium–oxo complexes from uranyl oxo rearrangement and reductive silylation**

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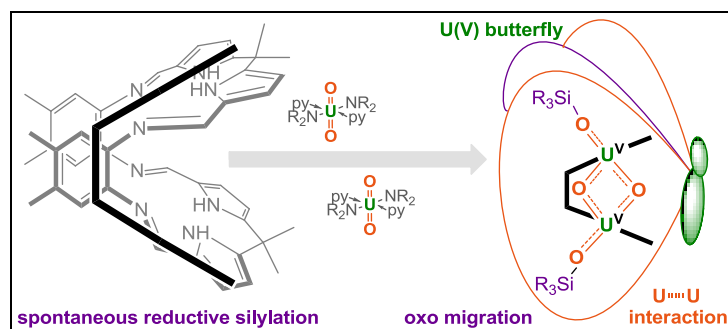
[*]These authors contributed equally to this work.

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Correspondence and requests for materials should be addressed to P.L.A. and J.B.L. (polly.arnold@ed.ac.uk, jason.love@ed.ac.uk). X-ray crystallographic coordinates for [UO₂{N(SiMe₂Ph)₂}₂(py)₂], **2a**, **2b**, and **4** have been deposited at the Cambridge Crystallographic Database, numbers CCDC 837886 - 837889.

Supplementary information is linked to the online paper at <http://www.nature.com/nchem>

Graphical abstract:



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Abstract

The most common motif in uranium chemistry is the d^0f^0 uranyl ion $[\text{UO}_2]^{2+}$ in which the oxo groups are rigorously linear and inert. Alternative geometries, such as the *cis*-uranyl have been identified theoretically and implicated in oxo-atom transfer reactions that are relevant to environmental speciation and nuclear waste remediation. Single electron reduction is now known to impart greater oxo-group reactivity, but with retention of the linear OUO motif, and reactions of the oxo groups to form new covalent bonds remain rare. Here we describe the synthesis, structure, reactivity, and magnetic properties of a binuclear uranium oxo complex. Formed through a combination of reduction and oxo-silylation and migration from a *trans* to a *cis*-position, the new butterfly-shaped Si-OUO₂UO-Si molecule shows remarkably strong U^V-U^V coupling and chemical inertness, suggesting that this rearranged uranium oxo motif might exist for other actinide species in the environment, and have relevance to the aggregation of actinide oxide clusters.

Main text

The linear uranyl dication $[\text{O}=\text{U}=\text{O}]^{2+}$ is present in the majority of known uranium compounds. It contains strongly covalently bound, rigorously axial oxo groups that exhibit almost no chemistry¹. Like its heavier, highly radioactive neptunyl and plutonyl congeners, the singly-reduced pentavalent uranyl cation $[\text{O}=\text{U}=\text{O}]^+$ retains the linear, strongly covalent metal dioxo core, but exhibits an enhanced oxo basicity²⁻⁴. This results in the formation of cation-cation clusters through the coordination of the oxo groups to other uranyl centres⁵ and causes unwanted precipitation in nuclear waste processing streams⁶. The enhanced oxo-basicity also facilitates electron transfer between U^V cations in disproportionation reactions, allowing the desirable removal of uranium from groundwater as insoluble U^{IV} salts⁷. The pentavalent uranyl cation, $[\text{UO}_2]^+$ ^{2,8} is unstable in water and so has been hard to study, but recent investigations under anaerobic conditions have allowed both T-shaped and diamond-shaped cation-cation interactions (CCIs) in $[\text{UO}_2]^+$ complexes to be stabilised^{9,10}, and have also allowed the coordination of other metal cations by the uranyl oxo groups.

We reported previously the syntheses of Pacman-shaped mono-uranyl complexes of the Schiff-base polypyrrolic macrocycle L, $[\text{UO}_2(\text{S})(\text{H}_2\text{L})]$ **1** (Figure 1, S = THF or pyridine (py)), from transamination reactions of H₄L and the uranyl silylamide $[\text{UO}_2\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$. We attributed our inability to coordinate a second uranyl group in the vacant N₄-donor pocket to the lack of space remaining in the macrocyclic cleft for another *trans*-dioxo group¹¹. However, the presence of this compartment allowed us to make a variety of heterobimetallic complexes by substitution of the remaining two acidic hydrogens with d- and 4f- metals with no axial ligand requirements^{12,13}. Furthermore, we demonstrated that potassium or lithium base activation of the uranyl oxo groups

promoted unprecedented UO-Si and UO-H bond forming reactions¹⁴⁻¹⁶. Outside of these examples, the formation of covalent oxygen-element bonds in uranyl chemistry remains restricted to a few discrete silyl complexes^{17,18}.

In contrast to the ubiquitous *trans*-arrangement of the uranyl oxo groups, the *cis*- motif presents a fascinating synthetic target which is as yet unseen in any experimental uranium chemistry^{19,20}. The *cis*- isomer appears to play a particularly important role in ligand exchange processes between uranium centres in uranyl hydroxides and aquo complexes²¹⁻²⁵, species that are prevalent in high pH nuclear wastes²⁶⁻²⁸. In acid solutions, both T-shaped tris(oxo) and *cis*-uranyl geometries have been invoked as intermediates in proton transfer reactions that lead to uranyl oxo-group exchange, a process which remains poorly-understood²⁹⁻³². Also, uranium lies directly below the Group 6 transition metals whose dioxo complexes are widespread in both enzymatic and industrial oxidation catalysis³³ and can adopt either the *cis*- or *trans*-dioxo geometry, depending on *d*-electron configuration. Regardless of electron count, all actinyl structures reported to date have linear AnO₂^{nt} geometries. However, theoretical work has shown that the *cis*- uranyl should be energetically accessible at 18 kcal.mol⁻¹ above the *trans* isomer.

Here we show that mixing solutions of the binucleating macrocycle H₄L and excess quantities of uranyl silylamide complexes results in an unprecedented butterfly-shaped U^V oxo dimer. This compound displays a new structural motif for high-valent uranium in which one of the four traditionally inert uranyl oxo groups in the reagents has moved into a *cis*-site, affording a tightly-bound U₂O₂ core. Also, the two exogenous oxo groups of this molecule are silylated during the synthesis to form a bis(U^VU^V) dioxo core of remarkable air-stability and with an extremely strong U-U electronic interaction.

Results and Discussion

Synthesis of reductively silylated binuclear uranium-oxo complexes

Reactions between pyridine solutions of the mono(uranyl) Pacman complex **1** and 1.5 molar equivalents of the uranyl silylamides [UO₂{N(SiR₃)₂}₂(py)₂] (SiR₃ = SiMe₃, SiMe₂Ph; py = pyridine) at 120 °C for twelve hours afford the brown, toluene soluble, paramagnetic binuclear pentavalent uranium complexes [(R₃SiOUO)₂(L)] **2** (SiR₃ = SiMe₃ **2a**, 25 %; SiMe₂Ph **2b**, 22%) and the poorly soluble material **3** (SiR₃ = SiMe₃ **3a**; SiMe₂Ph **3b**, ca. 30%, Figure 1). A similar reaction between the macrocycle H₄L and 2.5 equivalents of [UO₂{N(SiMe₃)₂}₂(py)₂] also generated **2a** (37 %) and reactions in the absence of pyridine (THF solvent) also generated **2a**, albeit at a much slower rate.

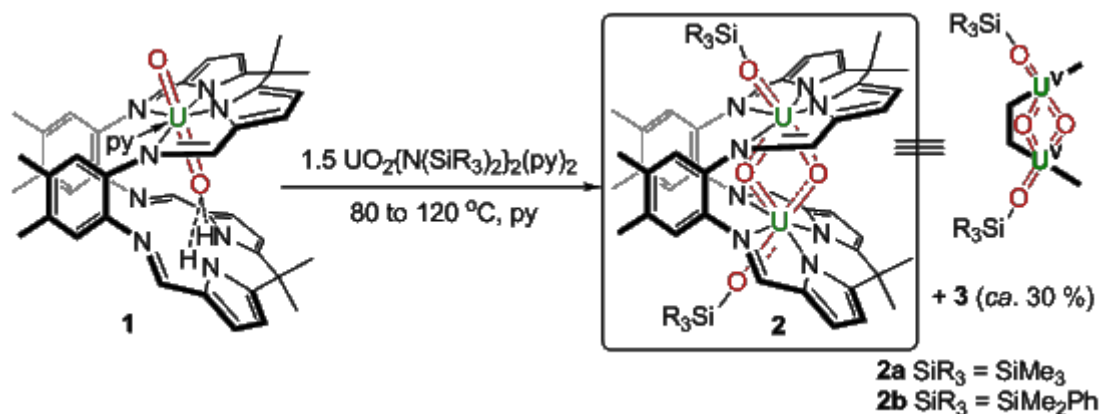


Figure 1 The new butterfly-shaped binuclear U^V complexes are formed from addition of excess uranyl amide salts to the wedge-shaped uranyl macrocyclic complex as a result of oxo-silylation and oxo-migration from a *trans* to a *cis*-position. The reactions between [UO₂(py)(H₂L)] **1** and [UO₂{N(SiR₃)₂}₂(py)₂] (py = pyridine) that result in the new binuclear U^V complexes **2** (SiR₃ = SiMe₃ **2a**, SiMe₂Ph **2b**) which incorporate two closely-bound uranium oxo groups in the Schiff-base macrocyclic framework resulting from oxo-group rearrangement, reduction and silylation.

The ¹H nuclear magnetic resonance (NMR) spectrum of **2a** is consistent with its high symmetry and paramagnetism, displaying eight resonances between +14.8 and –11 ppm. Furthermore, a resonance at 160 ppm in the ²⁹Si NMR spectrum can be tentatively assigned to the SiMe₃ group of the newly-silylated oxo group. The FTIR spectrum of **2a** contains bands at 862 and 802 cm⁻¹ assigned to U-O stretches that are weakened and desymmetrised with respect to **1** (ν U=O 908 cm⁻¹), and a Si-O stretch at 1100 cm⁻¹; these data support the assignment of the pentavalent oxidation state.

A single crystal X-ray diffraction study on **2a** (crystals grown from pyridine solution) shows a new structural type in uranium oxo chemistry with a butterfly-type core geometry (Figure 2, see Figure SI.23 for **2b**). Interestingly, it is similar to that predicted by Schreckenbach and co-workers in a recent computational study as being energetically accessible for two U^{VI} uranyl ions in the Pacman macrocycle^{34,35}, and is notable in that the normally robust *trans*-uranyl geometry has been lost on the formation of the U₂O₄ core. Whilst the majority of singly reduced uranyl complexes show interaction of one or both oxo groups with another metal cation, this is the first case in which the same yl-derived-oxo group is shared by two uranium centres in a mutually *trans* geometry, as a result of the migration of one oxo group to a mutually *cis*-position.

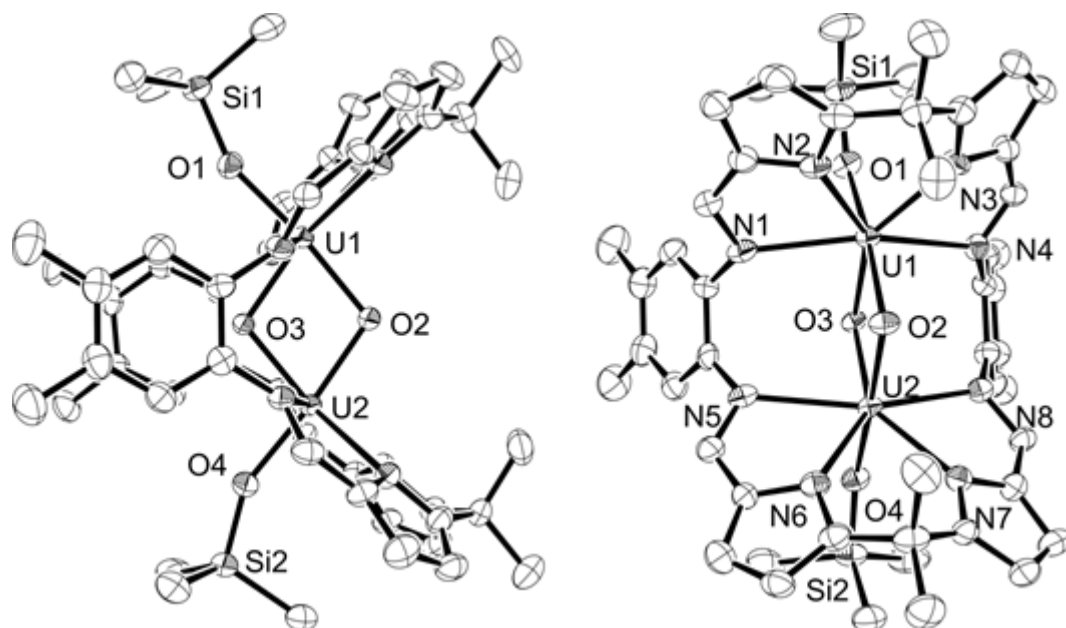


Figure 2 Side on (a) and face on (b) views of the solid state structure of the binuclear silylated uranium oxo complex $[(\text{Me}_3\text{SiOUO})_2(\text{L})]$ **2a**. The butterfly shape has not been observed before in uranyl or uranium chemistry, and both *exo*-oxo groups have undergone spontaneous silylation, affording a dinuclear $\text{U}^{\text{V}}\text{U}^{\text{V}}$ complex with a very short $\text{U}\cdots\text{U}$ separation, and a symmetrical, tightly-bound U_2O_2 diamond core. For clarity, all hydrogen atoms and solvent of crystallisation are omitted (displacement ellipsoids are drawn at 50 % probability). Selected distances (\AA) and angles ($^\circ$): $\text{U1}\cdots\text{U2}$ 3.3557(5), U1-O1 2.034(4), U1-O2 2.099(4), U1-O3 2.098(4), O1-Si1 1.666(4), U1-O2-U2 106.6(2), U1-O3-U2 106.3(2), O2-U1-O3 73.3(2), O1-U1-O2 173.4(2), Si1-O1-U1 157.7(3).

In the structure of **2a** the U_2O_2 core is a C_{2v} -symmetrical, diamond shape with an average U-O distance of 2.094 \AA and range of 0.012 \AA ; the related phenyldimethylsilylated complex **2b** displays an average U-O distance of 2.081 \AA . This diamond-shaped core has precedence in a few lower-oxidation state uranium complexes, notably in pentavalent uranyl complexes, but also in the oxo-bridged U^{IV} dimer $[(\text{Cp}^\ddagger)_2\text{U}(\mu\text{-O})]_2$ ($\text{Cp}^\ddagger = \text{C}_5\text{H}_3^t\text{Bu}_2$) in which one U-O bond distance of 2.096(6) \AA is similar to that of the two *endo*-oxo atoms in **2**. The butterfly shape however, has not been observed before in uranyl or uranium chemistry. The silylated *exo*-oxygen atoms, now formally siloxides, retain evidence of U-O multiple bonding with U1-O1 and U2-O4 distances of 2.034(4) and 2.040(4) \AA , respectively^{10,12,36}. Each uranium cation adopts a pentagonal bipyramidal geometry with axial oxo/siloxide ligands and the N_4 -donor set of the macrocycle equatorial. The fifth equatorial site, in which a solvent donor atom is usually seen, is occupied instead by an oxo group that was originally bound in an axial position of the adjacent uranyl. The other notable feature is that both *exo*-oxo groups have undergone spontaneous silylation, affording a $\text{U}^{\text{V}}\text{U}^{\text{V}}$ dimer with a very short $\text{U}\cdots\text{U}$ separation of 3.3557(5) \AA .

Similarly short U...U separations have been seen in the U^{III}U^{III} amido-bridged complex [U(η -C₈H₈)₂][μ - κ^4 : κ^4 -HN(CH₂)₃N(CH₂)₂N(CH₂)₃NH]³⁷ and also the U^{IV}U^V complex [K(dme)₄][$\{(\mu_3$ -N)K(dme)₂U₂(μ_4 - η^5 : η^3 : η^2 -octamethylcalix(4)pyrrole)₂]³⁸, although the uranium centres in these complexes are more reduced (i.e. larger) than in **2**. Pentavalent uranyl complexes that dimerise to form asymmetric U₂O₂ diamond cores of C_{2h}-symmetry have longer U...U separations such as *ca.* 3.43 Å in [$\{(\text{ArO})_3\text{-TACN}\}\text{U}_2(\mu\text{-O})_2$] (TACN = triazacyclononane)³⁹, 3.47 Å in [U^VO₂Sm(py)₂(L)₂] and 3.55 Å in [U^V₂(μ -OPrⁱ)₂(OPrⁱ)₈].^{10,12,36}

Electronic structure analysis of **2a**

Analysis of the bonding in the U₂O₄ core of **2a** was undertaken using density functional theory (DFT) and natural bond order (NBO) calculations. Single point calculations in a pyridine solvent continuum were carried out on a molecule of **2a** whose geometry had been optimised in the gas phase (see SI). Three possible arrangements of the two uranium-centred *f*-electrons were considered: triplet (ferromagnetically-coupled, f ^{α} f ^{α}); anti-ferromagnetic unrestricted broken-symmetry singlet (f ^{α} f ^{β} independently-localised orbitals); and restricted singlet (f ^{$\alpha\beta$} delocalised orbital over both uranium centres). The unrestricted singlet state was calculated to be more stable than the triplet and restricted singlet states by 1.4 and 42.7 kcal/mol, respectively, in pyridine when the B3LYP functional was employed with relativistic pseudopotentials. This is also the case when larger basis sets were employed. For the unrestricted singlet state of **2a**, the bonds between the uranium and the *endo*- and *cis*-oxo atoms were calculated to be between 2.092 and 2.099 Å while the U-O_{exo} bond lengths were calculated as 2.053 Å, within 0.01 Å of those obtained experimentally. The U...U separation was calculated as 3.366 and 3.379 Å in the unrestricted broken-symmetry singlet and triplet states respectively. The calculated Mayer and Wiberg (in parentheses) bond orders for the O_{exo}-Si, U-O_{exo}, U-O_{endo} and U-O_{cis} were calculated as 1.04 (0.57), 1.27 (0.79), 1.20 (0.79) and 1.19 (0.79), respectively. The bonds within the U₂O₄ core can therefore be considered formally as single bonds with some double bond character, although the U-O_{exo} bonds are slightly stronger. This is the case for both the electronic triplet and unrestricted singlet states.

The α -(HOMO-27) and β -(HOMO-27) orbitals obtained with the B3LYP functional for the unrestricted singlet state are depicted in Figure 3(a) and (b) and describe the primary σ -bonding interaction in the U₂O₄ core. The contributions from the *trans-endo*-oxo atom to these orbitals are significantly larger than those from the *cis*-oxo atom although the calculated Mulliken charges and spin densities on both atoms are essentially identical. There is another set of σ -type orbitals at slightly higher energy with greater contributions from the *cis*-oxo atom. Thus, although the σ -framework is weaker in **2a** than in the calculated structure of the hexavalent uranyl analogue³⁴, a strongly bound

cis-oxo component can be identified in **2a**. In addition, there is a weaker π -type bonding interaction in the U_2O_2 core. The π -type orbitals, Figure 3(c) and (d), are dominated by 2p-contributions from the *cis*-oxo atom and appear to be the only remnants of more prominent and stable π -interactions in the calculated structure of the hexavalent, non-silylated counterpart.³⁴

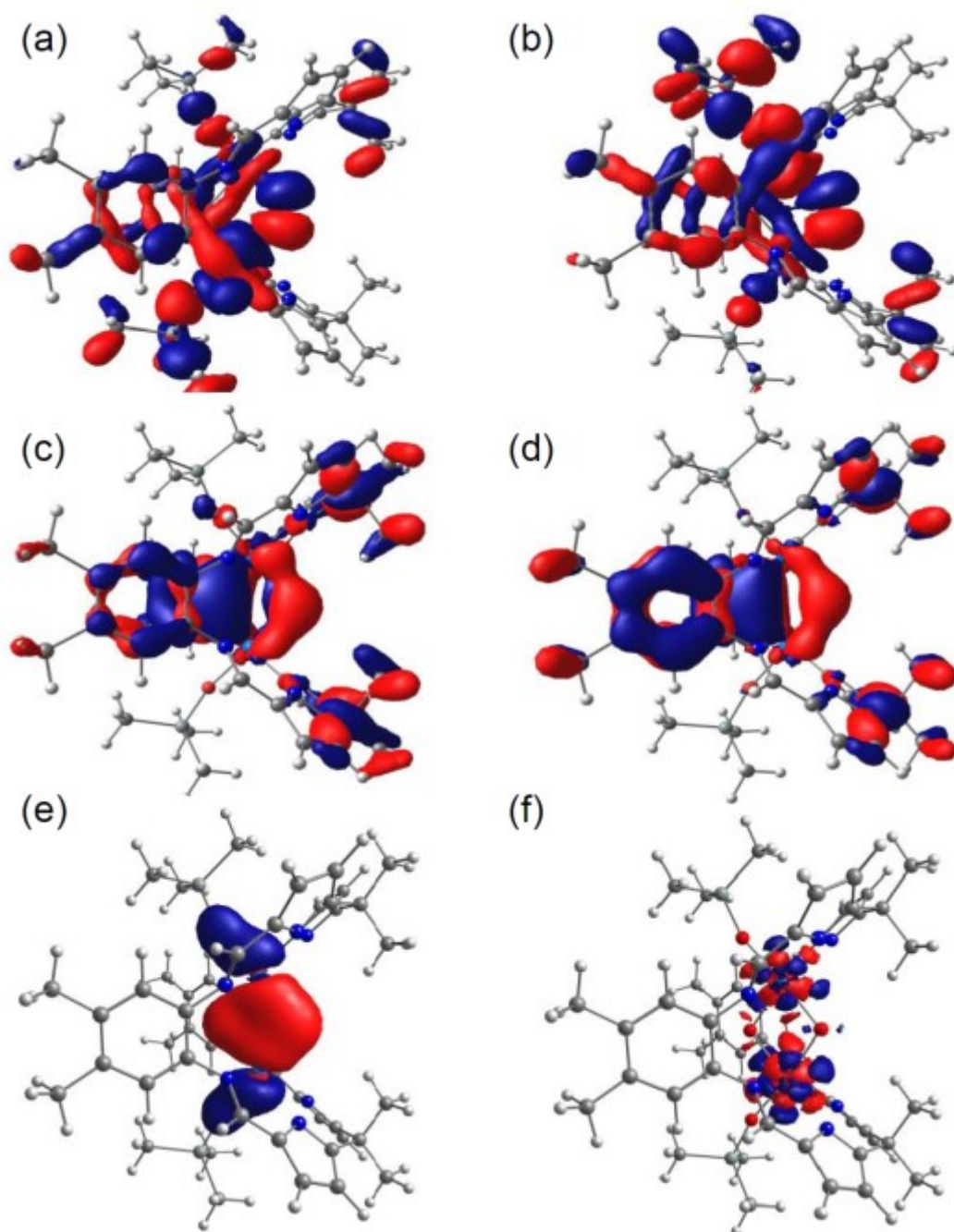


Figure 3 Molecular orbitals of primary σ - and π - character in the unrestricted singlet state of **2a**: (a) α -(HOMO-27) with energy of -0.333 a.u. and contributions of 27% *endo*-oxo 2p, 13 % *exo*-oxo 2p, 3

% *cis*-oxo 2p and 13 % U-5f; (b) β -(HOMO-27), with energy of -0.333 a.u. and contributions of 25 % *endo*-oxo 2p, 11 % *exo*-oxo 2p, 3 % *cis*-oxo 2p and 13% U-5f. These σ -type orbitals extend across the U_2O_2 core; (c) α -HOMO-28 with energy of -0.334 a.u. and contributions of 34 % *cis*-oxo 2p and 9 % *endo*-oxo 2p, 5% U-5f and 6 % U-6d; (d) β -HOMO-28, with energy of -0.334 a.u. and contributions of 37 % *cis*-oxo 2p, 9 % *endo*-oxo 2p, 5 % U-5f and 5 % U-6d. These orbitals depict the weaker π -type interaction across the U_2O_2 core. (e) HOMO-145 (bonding with respect to the two U atoms) with an energy of -1.094 a.u. and (f), the antibonding counterpart to HOMO-145, both predominantly U-5f, with very minor components from the O 2s orbitals.

The combined structural and computational data show that the butterfly $U_2O_4Si_2$ motif can be formulated as singly bonded uranium oxo and siloxide groups combined with a significant π -bonding contribution from the *cis*-oxo group. Formally, this has resulted from the rearrangement of two linear, pentavalent actinyls into a new bonding mode for uranium in which one oxo group is shared and *trans*- and one has adopted a *cis*-position.

The diamond U_2O_2 geometry adopted in **2a** has been observed in related Group 6 chemistry. For example, oxidation reactions of the quadruply metal-metal bonded Mo acetate dimer in the presence of good π -accepting ligands form $Mo^V(\mu-O)_2Mo^V$ complexes which have single M-M bonds.⁴⁰ It is therefore tempting to look for a direct metal-metal interaction in **2a** since no f-block metal-metal bonded complex has been reported. The calculated $U\cdots U$ separation of 3.366 Å is much shorter than twice the covalent radius of the uranium atom (3.92 Å) which may indicate some bonding interaction. This is reflected in the non-trivial calculated Mayer bond order of 0.34 between the uranium atoms, which is only slightly lower than those calculated for some of the U-N bonds in **2a** (range 0.38-0.55). NBO analysis allows the identification of a set of bonding and antibonding orbitals (Figure 3(e) and (f) respectively) with almost exclusively f-orbital based overlap between the uranium centres. However, **2a** is clearly paramagnetic at room temperature with spin-pairing occurring only at 17 K (see below). While there are no reported examples of molecular bonds between two f-block elements, multiple U-U bonds with distinctly different interactions compared to transition metals have been predicted by theory.⁴¹

Allied with the proximate uranium cations in **2a**, the unusual properties of the 5f orbitals make actinide ions attractive building blocks for new nanomagnetic materials, but the fundamental understanding of the factors that govern the exchange interactions and electron delocalisation are poorly understood, a factor exacerbated by the rarity of 5f^I dimers which are the easiest to study.⁴² A variable temperature study of the magnetism of **2a** (Figure 4) shows Curie-Weiss behaviour down to 25 K with an effective moment of $1.53 \mu_B/U$ ion at 300 K. This value is lower than would be expected

for a single $U f^1$ ion ($\mu_{\text{eff}} = 2.54 \mu_{\text{B}}/U$ ion in the L-S coupling scheme). This reduction can be attributed neither to room-temperature antiferromagnetic coupling, nor to an orbital contribution from metal-ligand covalency (the latter argument for this observation having been disputed previously),⁴³ but instead arises from the strong ligand field typical of the uranyl-type geometry. Below these temperatures, a clear signature of anti-ferromagnetic coupling between the f^1 centres occurs, with the $\chi(T)$ curve peaking at a Néel temperature of 17 K, much higher than in other O-bridged di-uranium molecules for which the maximum observed was 5 K¹⁰, but similar to that seen for the singly-oxo bridged U^{IV} complex $[\{(\text{ArO})_3\text{-TACN}\}U_2(\mu\text{-O})]$ at 20 K.³⁹ For the latter example, it was postulated that the geometry of the oxo-group interaction and not the shortened $U\cdots U$ separation was the primary mediator of superexchange. The magnetic coupling due to superexchange across the two oxo groups was modelled by a spin Hamiltonian containing the Zeeman terms (one for each magnetic site) and the exchange interaction (see SI). The resulting exchange interaction, $J_{\text{ex}} = -33 \text{ cm}^{-1}$, is particularly large, suggesting that the butterfly geometry could be of use in the building of more complex magnetic architectures through replacement of the silyl groups with further metal ions.

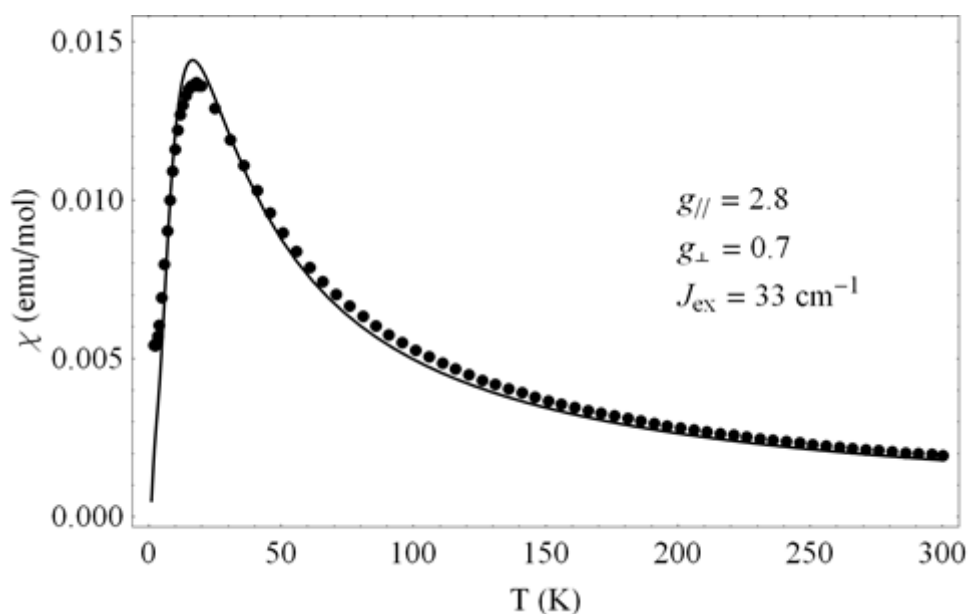


Figure 4 Solid-state magnetic behaviour of **2a** between 2 and 300 K that displays spin pairing as high as 17 K. The dots are the experimentally measured temperature dependence of the magnetic susceptibility (χ vs T) and the line shows the calculated fit to the data, using a spin model based on superexchange across the two bridging oxo groups.

Mechanistic insight into the formation of **2**

The low yields of **2** and lack of obvious reducing agent in the synthetic procedure led us to investigate reactions at lower temperatures (Figure 5). It is clear from these investigations that two competing reactions occur, one at lower temperature that involves metallation of the uranyl oxo, and one at elevated temperature that results in reductive silylation. Reaction of H_4L and 2.5 equivalents of $[UO_2\{N(SiMe_3)_2\}_2(py)_2]$ for two weeks at 20 °C formed the insoluble paramagnetic product **3a** and $HN(SiMe_3)_2$. Compound **3** forms more quickly and equally cleanly at temperatures up to 80 °C, while above 80 °C both **2** and **3** are formed, along with a small quantity of decomposition products. Significantly, **3** was found to react with $ClSiR_3$ to form **2** in high yields. This secondary treatment of **3a** thus allows for the two-step synthesis of **2a** directly from the macrocyclic ligand in overall 73 % yield in gram quantities.

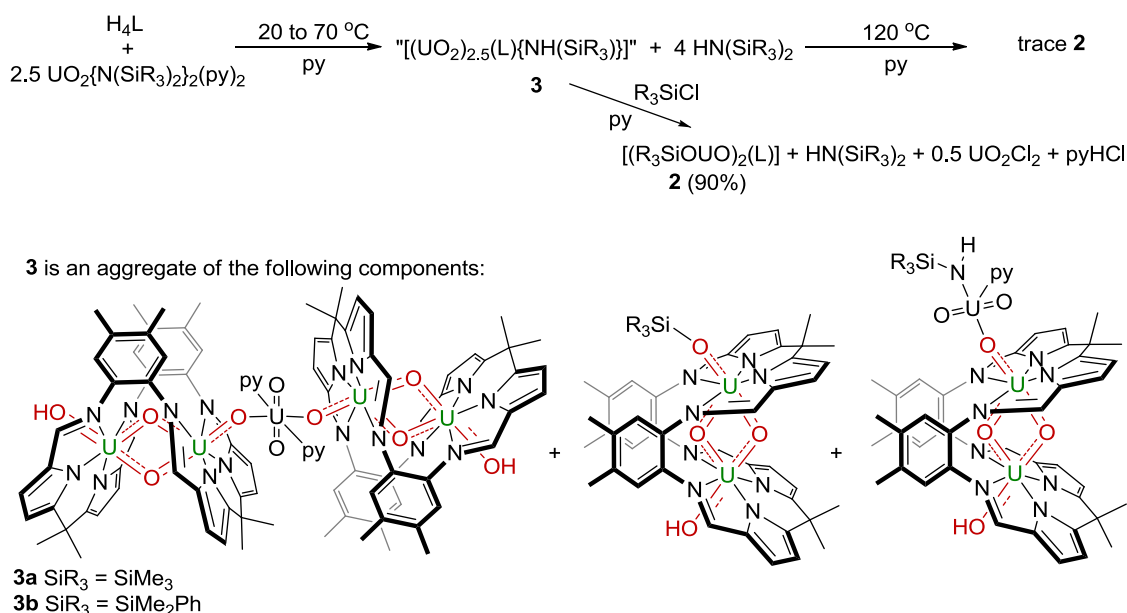


Figure 5 Reactions between uranyl silylamides and H_4L to afford the butterfly-uranyl complexes **2** and **3** and the probable structures of the constituent parts of **3**. At low temperatures, the same ratio of 2.5 UO_2^{2+} to one macrocycle ligand is observed, and although reduction processes are occurring, the product precipitates. Addition of trialkylchlorosilane generates **2** from the precipitate, and releasing other fragments that made up the complex structure of **3**, including silylamine and the remaining 0.5 equivalents of UO_2^{2+} .

We have been unable to determine crystallographically the structure of **3**. However, calibrated NMR-scale reactions show that four equivalents of by-product $HN(SiR_3)_2$ are generated during the reaction

between H_4L and $[UO_2\{N(SiR_3)_2\}_2(py)_2]$ and that 2.5 equivalents of UO_2^{2+} are consumed per Pacman ligand. One further equivalent of $HN(SiR_3)_2$ is liberated on reaction of **3** with $ClSiMe_3$ (Figure 5). This therefore suggests that **3** has an aggregated structure based on $[(UO_2)_{2.5}(L)\{NH(SiR_3)\}(py)]$, an empirical formula supported by elemental analysis. Furthermore, a reaction between **3b** and an excess of Me_3SiCl generated a mixture of **2a** (75%), the mixed silylated $[(Me_3SiOUO)(Me_2PhSiOUO)(L)]$ (25%), and no **2b**. Knowing that the silyl groups do not rearrange in these conditions, this suggests that only some of oxo groups in **3** are silylated.

The laser desorption ionisation (LDI) mass spectrum of **3** (Figure SI.15) contains a number of peaks that support an oligomeric structure. The highest ion visible is at 3173 amu and is assigned as a hexakis uranium dioxo complex of two Pacman ligands that incorporates silylamide. In turn, the series of ions in the range 2300 -3200 amu are related to each other by the loss of silylamide, UO_2 , or UO_3 groups. More intense features occur at 2096 amu for a combination of two uranium oxo Pacman compounds, at 1239 amu for a mono(silylated) complex, and the base peak at 1167 amu due to a bis(uranium oxo)Pacman complex. No assignable parent or daughter ions were observed in the electron impact or electrospray ionisation mass spectra of **3**. From these data it is clear that **2** and **3** have related, butterfly uranium oxo core structures which is also supported by the reaction of **3** with R_3SiCl to form **2**. Further support for an aggregated structure for **3** was suggested from the X-ray structure of $[\{(Me_3SiOUO)(UO_2)(L)\}UO_2(thf)_2(\mu-OH)_2]_2$ **4** (Figure SI. 24), isolated as a result of adventitious air ingress to a solution of **3a**. This compound contains the core U_2O_4 butterfly unit of **2a** already installed, with one *exo*-oxo group silylated, and the other oxo participating in a cation-cation interaction with a uranyl hydroxide dimer.

The source of the silyl group in **2** can be traced to the uranyl silylamide, and not the by-product silazane $HN(SiR_3)_2$. The reaction between **1** and $[UO_2\{N(SiMe_2Ph)_2\}_2(py)_2]$ to form **2b** was carried out in the presence of the silylamine $N(SiMe_3)_3$. No evidence for **2a** or the mixed silyl complex $[(Me_3SiOUO)(Me_2PhSiOUO)(L)]$ was found in the 1H NMR spectrum, confirming that the oxo-silyl groups derive from a metal-bound silylamido or amino group. This observation contrasts with the DFT calculations pertaining to our previous reductive silylation chemistry of Pacman uranyl complexes in which it was shown that model compounds with K cations bound to a uranyl oxo group can undergo S_N2 -type homolytic bond cleavage reactions with aminosilanes.^{44,45} While a detailed evaluation of the mechanism of formation of **2** is ongoing, the observations described above suggest that two competing, reductive pathways occur that involve either U-N or N-Si bond homolysis (for a speculative mechanism see Figure SI. 19). The nature of the bridging groups that form **3** is unclear, although the presence of OH groups is implicit to this mechanism and would facilitate aggregation¹⁶. It is likely that initial single-electron reduction of **1** occurs on addition of uranyl silylamide with concomitant loss of aminyl radical (i.e. homolytic U-N scission), and that further uranyl silylamide is

required to promote subsequent reduction and silylation reactions (i.e. N-Si homolysis). We have seen similar reduction chemistry during the formation of lanthanide-incorporated pentavalent uranyl complexes¹², and coordination of a Lewis acid to the uranyl oxo group can facilitate reduction.^{15,46} Unfortunately, our efforts to probe the nature of the radical species in these reactions have as yet proved inconclusive.

Reactivity of **2**

Almost all of the recently isolated $[U^V O_2]^+$ complexes are relatively unstable towards redox decomposition, so it is remarkable that, on exposure to air for 48 hours, a wet benzene solution of **2a** shows virtually no change in its ¹H NMR spectrum. Furthermore, after five days, only 20 % decomposition of **2a** cleanly to free ligand H₄L is observed. Solution cyclic voltammetry experiments display no oxidation processes within the window of study afforded by the THF solvent. In accordance, no reactions are observed between **2a** (or **3a**) and chemical oxidants such as iodine or cerium(IV) triflate. Complex **2a** is also very thermally robust and unreactive towards the exchange of the O-SiR₃ group. For example, **2a** can be recovered unchanged after 12h in boiling pyridine, while the addition of excess quantities of Me₃SiCl, Ph₂SiHCl, or $[UO_2\{N(SiMe_3)_2\}_2(py)_2]$ gave no reaction, even at elevated temperatures.

Conclusions

We have shown that the facile rearrangement of a *trans*-uranyl oxo into a mutually *cis*-position between two high-oxidation state uranium ions occurs on reduction so forming a new butterfly-shaped uranium oxo motif with remarkable stability and strong U-U electronic coupling. The formation of this *f^l-f^l* motif is possibly facilitated by the rigid constraints of the macrocyclic framework that disfavour the complexation of two linear uranyl cations. However, due to the redox stability exhibited by this compound, it is of interest to consider whether this motif has been perhaps overlooked in favour of its linear congener in actinyl chemistry outside the laboratory.

The mechanisms of the two competing pathways to **2** and **3** are as yet unknown. It remains unclear how the reduction and silylation processes occur, although the reactions of **3** and the isolation of **4** implies that the interaction of the extra half equivalent of uranyl silylamide with the U₂O₄(L) core is requisite. Further investigation into the mechanism is required to determine to what extent this work bears relevance to the proton, electron transfer and oxo group exchange reactions that occur in aqueous uranyl systems, and if it is possible to draw analogies to transition metal oxo chemistry.

The extremely short U-U separation, magnetic coupling, and broken-symmetry singlet ground state exhibited by **2a** evidence strong communication between the two f^1 centres⁴¹ and suggest that the precise details of the electronic and magnetic structure will be of widespread interest.

Methods summary

Working under a dry, oxygen-free dinitrogen atmosphere, with reagents dissolved or suspended in aprotic solvents, and combined or isolated using cannula and glove box techniques, we heated pyridine solutions of the hinged macrocyclic complex $[\text{UO}_2(\text{py})(\text{H}_2\text{L})]$ (py = pyridine), in which one compartment binds the uranyl dication and the other still contains two pyrrolic H atoms with 1.5 equivalents of a uranyl bis(silylamide) complex $[\text{UO}_2\{\text{N}(\text{SiR}_3)_2\}_2(\text{py})_2]$ at 120 °C for 12 hours to afford the new, reduced and silylated bimetallic uranium oxo complexes $[(\text{R}_3\text{SiOUO})_2(\text{L})]$ for two different SiR_3 derivatives. The poorly-soluble byproduct could be converted into the target compound by treatment with R_3SiCl , with presumed elimination of a uranyl-containing material. At temperatures below 70 °C, the poorly-soluble byproduct is now the dominant product, and can be converted very cleanly, in high yields, to the same bimetallic $[(\text{R}_3\text{SiOUO})_2(\text{L})]$. Repetitions of the reaction with different silylamides and silylamines were carried out to confirm that the reducing electron derives from the cleavage of a U-N(SiR_3)₂ bond, and the silyl group derives from a metal-bound UN-SiR₃ group. All compounds were characterised by a variety of methods, including elemental analysis, FTIR spectroscopy, magnetic moment measurements, mass spectrometry, NMR spectroscopy, and single crystal X-ray diffraction studies.

The geometry of **2a** was optimised in the gas phase using DFT calculations in three different spin states: antiferromagnetic broken-symmetry singlet, restricted singlet, and ferromagnetic triplet states. Single point DFT calculations in a model pyridine solvent were carried out on the optimised structures by employing a polarisable continuum solvation model. The uranium atom was described with the Stuttgart relativistic pseudopotential^{46,47} while all other atoms were described with the 6-31G** basis set. Single point calculations were carried out with the 6-311++G** basis to check for the basis set dependency of the relative energies of the three electronic states considered. These calculations were performed with the Gaussian 03 suite of programs⁴⁸. The molecular orbitals obtained are plotted with isosurface contours of 0.02. Scalar relativistic calculations with all-electron basis sets using a four-component approach were also carried out with the Priroda program^{49,50}. The PBE functional was employed in these calculations while using a triple- ζ (cc-pVTZ) basis set. The small-component portion was described using appropriate kinetically balanced basis sets. Mayer bond orders were calculated after the geometry optimization.

Competing Interests statement The authors declare that they have no competing financial interests.

Author Contributions G.M.J. synthesised and characterised the compounds. P.L.A. and J.B.L. generated and managed the project, helped characterise the complexes, analysed the data, and wrote the manuscript. G.S. and S.O.O. carried out and interpreted the computational analyses of bonding. N.M. performed the ligand-field and magnetic superexchange calculations.

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