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Single-Electron Uranyl Reduction by a Rare-Earth Cation**

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Supporting information:
Available at http://www.angewandte.org or from the author. CCDC codes 789825 & 789826 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Graphical abstract:
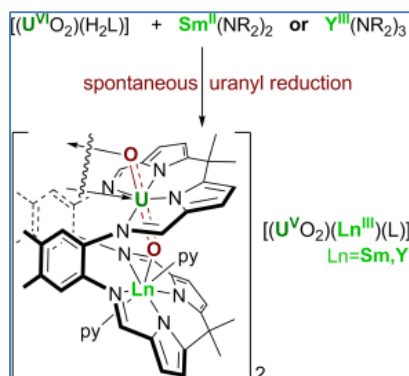
Keywords:

macrocycles; magnetic coupling; nitrogen ligands; single-electron reduction; uranyl complex

Abstract

Reducing the irreducible: Incorporation of a lanthanide cation into the vacant coordination pocket of a uranyl Pacman complex results in single electron reduction to form stable pentavalent uranyl–rare-earth complexes with uranyl–oxo–rare-earth bonds (see scheme; py=pyridine, R=SiMe$_3$).

Main text

Unlike their transition metal analogues, the oxo groups of the uranyl dication, $[UO_2]^{2+}$, which has a linear geometry and short, strong U-O bonds are traditionally considered inert.[1] Very little Lewis base character has been demonstrated for the uranyl oxo groups,[2, 3] which makes them poor models for the heavier, highly radioactive transuranic actinyl cations such as neptunyl $[NpO_2]^{n+}$ (n = 1, 2).[4, 5] The heavier actinyls are important components in nuclear waste and demonstrate oxo basicity that can give rise to poorly understood cluster formation and problems in nuclear waste PUREX separation processes.[6] However, it has been shown recently that the more Lewis basic, pentavalent uranyl cation, $[UO_2]^+$ can be stabilised indefinitely using suitable equatorial-binding ligands and anaerobic conditions.[7, 8] Usually the $[UO_2]^+$ cation decomposes by disproportionation, which is also a poorly understood process, but is important in the precipitation of uranium salts out of aqueous environments.[9, 10] The disproportionation is suggested, by analogy with the transuranic metal oxo-Lewis base behaviour, to involve the formation of cation-cation interactions, CCIs,[11, 12] in which the oxo groups ligate to adjacent actinyl centres forming diamond (**A**) or T-shaped (**B**) dimers or clusters which can then allow the transfer of protons and electrons between metals, such as in **C**.[13]

A
An = actinide

B

C
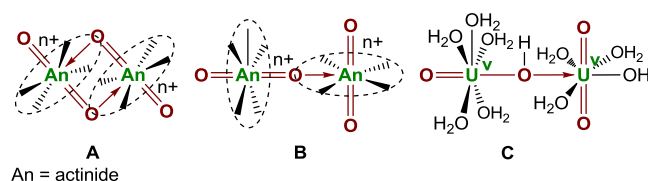
We reported that the use of rigid, Pacman-shaped macrocycles can allow the isolation of heterobimetallic uranyl-transition metal complexes that form an oxo-interaction with the transition metal in the solid state and solution,[14] and how the inclusion of more than one metal cation alongside the uranyl cation led to isolable, stable pentavalent uranyl complexes with a covalently functionalised oxo group.[15] More recently pentavalent uranyl complexes with Group 1 cation oxo-coordination,[16] and a doubly silylated complex[17] have been isolated. Here, we report the first uranyl-4f metal

interaction, prepared by either standard, or sterically induced reduction procedures, and demonstrate strong magnetic coupling between the 4f- and 5f electrons.

The reaction between the divalent samarium silylamide $[Sm(THF)_2\{N(SiMe_3)_2\}_2]$ and the uranyl Pacman complex $[UO_2(py)(H_2L)]$ **1** in pyridine resulted in the deposition of the new uranyl-samarium complex $[UO_2Sm(py)_2(L)]_2$ **2** as a very poorly soluble, thermally stable, red crystalline powder in good yield (Scheme 1), and containing crystals suitable for single crystal X-ray diffraction studies (Figure 1).
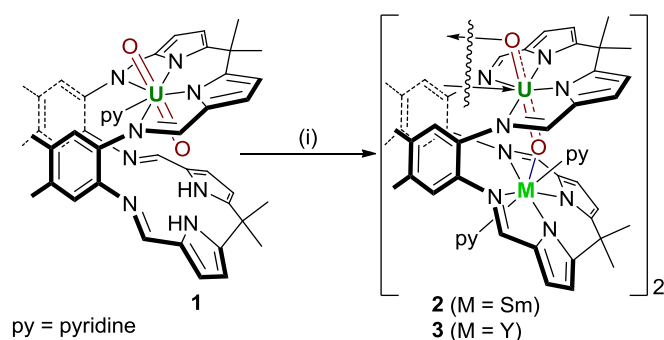
Scheme 1 Synthesis of uranyl-rare earth compounds of the macrocycle H_4L (M = Sm, Y). Reagents and conditions: (i) $[Sm(THF)_2\{N(SiMe_3)_2\}_2]$, py; or $[Y\{N(SiMe_3)_2\}_3]$, py.

The ^1H NMR spectrum of **2** in $[D_5]$-pyridine reveals the presence of paramagnetically-shifted resonances between 12.4 and −21.5 ppm, the number and integrals of which are consistent with the retention of a wedged, Pacman structure in solution of C_s-symmetry. In the solid state, the molecular structure shows that **2** is dimeric (Figure 1) and the unit cell contains two similar molecules. Focusing on one molecule of **2**, both the uranium and samarium centres are seven coordinate with approximate pentagonal bipyramidal geometry, but a greater distortion at Sm. This primarily results from the bond between the uranyl *endo*-oxo and the Sm cation, which at 2.238(5) Å is indicative of a single bond,[18, 19] and represents the first example of a 4f-element to uranyl oxo bonding interaction. The Sm1-O1-U1 angle is effectively linear (174.5(3)°), as is O1-U1-O2 (174.4(2)°), and the U1-O1 (1.890(5) Å) and U1-O2 (1.941(5) Å), respectively *endo*- and *exo*-oxo uranium bond distances are elongated compared to those in the hexavalent uranyl complex **1**, and close to those in other pentavalent uranyl complexes.[2] The Sm-O bond length of 2.238(5) Å,[20] compares well with other seven-coordinate Sm^{III}-O-Ar bond lengths. These data are therefore consistent with single electron reduction by Sm^{II} to afford pentavalent uranyl and Sm^{III}. The N_4-macrocyclic donor set contributes four equatorial N atoms to each metal coordination sphere. The fifth site at U1 is occupied by the *exo*-oxo O2' of an adjacent

molecule, which gives rise to the dimeric structure [UO$_2$Sm(py)$_2$(L)]$_2$ and a diamond-shaped (UO$_2$)$_2$ core (a type A CCI). The diamond motif is asymmetric with U1-O2' 2.345(4) Å and acute and obtuse angles of 72.2(2)° for O2-U1-O2' and 107.8(2)° for U1-O2-U1', and a U1···U1' separation of 3.4706(4) Å. These data compare favourably to those reported for the pentavalent **A**-shaped [UO$_2$(dbm)$_2$K(18C6)]$_2$,[21] and reflect the propensity of pentavalent uranyl to form cation-cation interactions due to the increased Lewis basicity of the U^V oxo groups. The samarium centre Sm1 also has two approximately axial pyridine nitrogen donors to complete the coordination sphere.
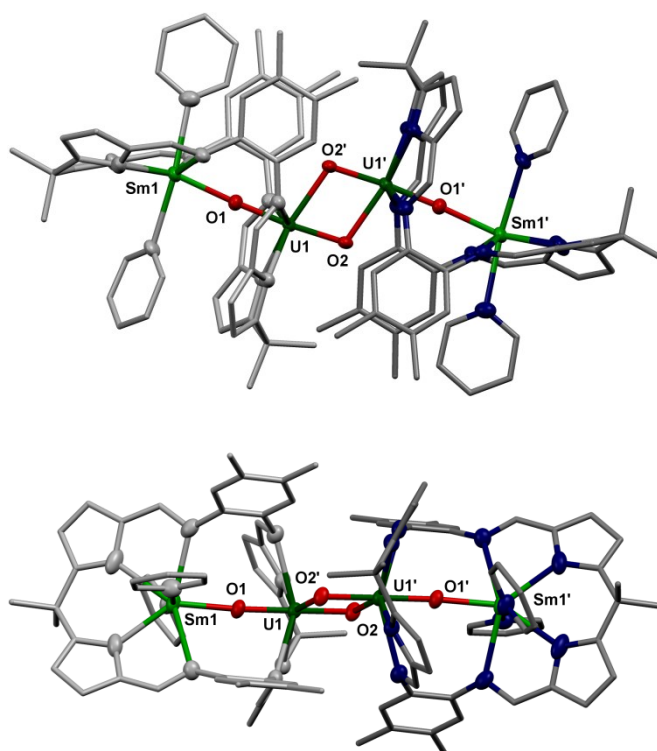
Figure 1 The solid state structure of [{UO$_2$Sm(py)$_2$(L)}$_2$], **2**. One molecule from the unit cell is shown, with hydrogen atoms and pyridine disorder components omitted, (50 % probability displacement ellipsoids where drawn).

The single-electron reduction of **1** (U$^{VI/V}$ −0.54 V *vs*. NHE) observed on the introduction of the Sm^{II} cation into the vacant pocket may be rationalised by both the strong reduction potential and the oxophilicity of Sm^{II} (Sm$^{III/II}$ −1.55 V *vs*. NHE).[22] The transition metal- incorporated complexes [UO$_2$(THF)M(THF)(L)] (M = Mn, Fe, Co) that we reported previously did not show single-electron

reduction, these d-block cations being less strongly reducing, and exhibiting only a strong dative bond between the endogenous uranyl oxo and the metal cation.[14]

To our surprise, this uranyl reduction chemistry to form **2** can also occur by treatment of **1** with *trivalent* [Ln{N(SiMe$_3$)$_2$}$_3$] in pyridine; the reaction between **1** and the redox-inactive [Y{N(SiMe$_3$)$_2$}$_3$] generates cleanly the new pentavalent uranyl-yttrium complex [{UO$_2$Y(py)$_2$(L)}$_2$] **3** as a red/brown solid in good yield, again a result of the single electron reduction of the uranyl dication. No Y$^{III/II}$ reduction potential, either experimental or calculated, is available. As with **2**, the ^{1}H NMR spectrum of **3** in [D$_5$]-pyridine reveals the presence of paramagnetically-shifted resonances between 21 and −9 ppm, the number and integrals of which are consistent with the retention of a wedged, Pacman structure in solution and is supported by multinuclear, two-dimensional NMR spectroscopy. The compound is thermally stable to at least 110 ^{o}C in solution without decomposition. Crystals of **3** were grown from pyridine and an X-ray diffraction study shows **3** to be isostructural to **2** (Supporting Information). In **3**, the exo (1.919(4) Å) and endo (1.965(4) Å) U-O bond distances are again indicative of single-electron reduction of **1** to pentavalent uranyl. The O1-U1-O2 (175.3(2)^o) and U1-O1-Y1 (177.3(3)^o) angles are linear, and the Y1-O1 bond distance (2.155(4) Å) supports a single bond between the yttrium and uranyl cations. As **3** is marginally more soluble in pyridine than **2**, the NIR spectrum was recorded and shows a well-defined absorption at 1571 nm (ε 169 dm^{3}mol^{-1}cm^{-1}) consistent with [UO$_2$]$^+$; a similar feature is seen in the NIR spectrum of pentavalent uranyl carbonate [UO$_2$(CO$_3$)$_3$]$^{5-}$ 1600 nm.[23] In the FTIR spectrum of **3**, a strong band at 724 cm^{-1} is assigned as the U=O asymmetric stretch (ν$_3$). This compares with 908 cm^{-1} in [UO$_2$(THF)(H$_2$L)], and supports reduction to [U^{V}O$_2$]$^+$.[24]

We suggest that this latter reaction is a result of the initial coordination of the Y^{III} cation in the vacant macrocyclic compartment, forming the silylamide intermediate [UO$_2$(py)Y{N(SiMe$_3$)$_2$}(py)(L)] which contains a sterically-crowded Y^{III} centre. To avoid implicating divalent yttrium centre in the formation of **3**, we can now invoke a sterically induced reduction, or 'SIR' mechanism for these reactions, based on the homolysis of the metal-N(SiMe$_3$)$_2$ bond. Crowded f-block organometallic complexes such as LnCp*$_3$ (Cp* = C$_5$Me$_5$) can provide a reducing electron *via* the [Cp*]/[Cp*]$^-$ couple[25] allowing, for example, redox inactive complexes such as YCp*$_3$ to reduce dinitrogen to form, for example [{Cp*$_2$Y}$_2$(μ-N$_2$)]. SIR mechanisms have been observed in other organometallic f-block systems.[26-28] To confirm that Y-N bond homolysis is occurring in our case,[29] the reaction between **1** and [Y{N(SiMe$_3$)$_2$}$_3$] in the presence of dihydroanthracene (DHA) shows not only the rapid formation of **3** plus three equivalents of HN(SiMe$_3$)$_2$ by ^{1}H NMR spectroscopy, but also a stoichiometric quantity of anthracene (0.5 equivalents), formed by H-atom abstraction from DHA by the silylaminyl radical ·N(SiMe$_3$)$_2$, the SIR by-product.

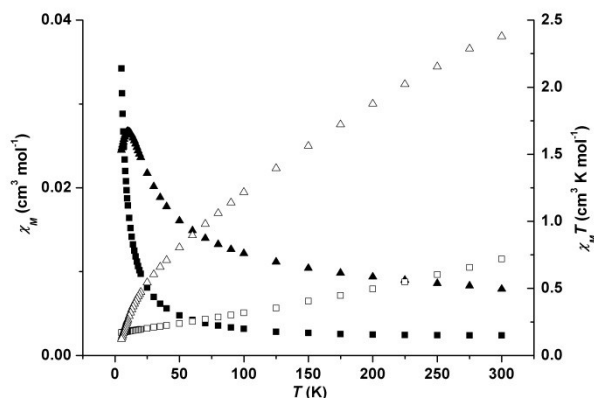**Figure 2** Variable temperature magnetic data for **2** ($\chi_{M,}$ black squares; $\chi_{M}T$, hollow squares) and **2** ($\chi_{M,}$ black triangles; $\chi_{M}T$, hollow triangles).

Variable temperature magnetic susceptibility data (SQUID) of both **2** and **3** show magnetic moments at all temperatures measured (Figure 2). The combination of pentavalent uranyl with a Sm^{III} cation in **2** generates a spin system comprising two dimerised oxo-bridged [5f^1-4f^5] ions, while in **3** this is simplified to a 5f^1-4f^0 spin system. For the Y complex **3**, the $\chi_{M}T$ value of 0.75 cm^3 K mol^{-1} (2.4 μ_B) at 300 K drops continually with decreasing temperature to a minimum value of 0.17 cm^3 K mol^{-1} (1.2 μ_B) at 5 K. For the Sm complex **2**, the room temperature $\chi_{M}T$ value of 2.38 cm^3 K mol^{-1} (4.36 μ_B) drops rapidly with decreasing temperature, reaching a minimum value of 0.12 cm^3 K mol^{-1} (1.0 μ_B) at 5 K. The behaviour in each case is consistent with the depopulation of excited crystal field states in the f-block cations with decreasing temperature.

The magnetism of f-element, and particularly, uranium-containing complexes is of considerable current interest;[30, 31] as such, in order to gain insights on the electronic ground states and magnetic interactions between the *f*-electron centres, a preliminary fit of the susceptibility measurements has been made using a spin-Hamiltonian model. The susceptibility of the Y complex **3** can be reproduced (as shown in the supplementary information) by assuming $|g_\parallel|$ = 1.6 and $g_\perp$ = 0, plus a small constant χ_0 value to account for the effect of unpopulated ligand field states. Fits of comparable quality can be obtained by considering other values for g$_\perp$ up to about 0.3, without significant changes in g$_\parallel$; this is particularly interesting because it suggests that the ligand-field ground state for **3** is very similar to that seen in the model used to account for the EPR data in an analogous [U^{V}O$_2$]$^+$ dimer.[16] Although the dominant superexchange interaction in **2** is between Sm and U and not between the two uraniums (which can be readily understood by observing that the distance between the two f centres and their bridging oxygens is larger for the latter pair), the presence of a weaker antiferromagnetic coupling between the two U centres cannot be excluded, although this would imply an upper limit for the coupling constant of about 2 cm^{-1}. In principle, it is also possible to reproduce the data by assuming a

ferromagnetic exchange between the two U centres; however, this intuitively seems less likely since the sign of the exchange interaction would be opposite to that of other U^{5+} uranyl dimers with similar geometries (see Fig. 13 of reference [21]). Further lower temperature magnetometric and EPR spectroscopic data will help elucidate this, and measurements are planned.

To conclude, the binding of large and oxophilic divalent or trivalent rare earth metal cations in the vacant coordination pocket of the uranyl-complexed Pacman macrocycle results in spontaneous reduction of the uranyl dication for the first time, forming unprecedented, and strongly magnetically coupled $5f^1$-$4f^n$ complexes. A sterically induced reduction route avoids the requirement for a divalent 4f-ion precursor, and should allow the controlled synthesis of $5f^1$-$4f^n$ bimetallic complexes, magnetically coupled systems, and new inter-f-block CCI motifs. We anticipate that the CCI interaction, which holds the two uranyl complexes together should be cleaved by the addition of a suitable Lewis acid to compete for the *exo*-UO group. Work is in progress to identify whether paramagnets such as uranium and manganese cations can cleave the U_2O_2 diamond motif to generate molecules with more complex magnetic and supramolecular structures.

Experimental Section

All manipulations were carried out under dry dinitrogen using standard Schlenk techniques or in an MBraun Unilab glovebox unless otherwise stated.

[UO$_2$Sm(py)$_2$(L)]$_2$ 2 A solution of Sm(THF)$_2${N(SiMe$_3$)$_2$}$_2$ (168 mg, 0.274 mmol) in pyridine (5 mL) was added dropwise to [UO$_2$(py)(H$_2$L)] (276 mg, 0.274 mmol) in pyridine (10 mL) at room temperature. The resultant dark red solution was stirred for 48 h, during which bright red-pink microcrystalline solid precipitated from the solution. These solids were isolated by filtration and dried to yield 140 mg, 41 % of [{UO2Sm(py)$_2$(L)}$_2$]. Analysis. Found: C, 48.54; H, 4.18; N, 10.98. C$_{94}$H$_{90}$N$_{18}$O$_4$Sm$_2$U$_2$ ([UO$_2$Sm(py)(L)]$_2$, i.e. loss of one Sm-bound pyridine) requires C, 48.82; H, 3.92; N, 10.90 %. IR (Nujol mull, cm^{-1}):v 724. χ_MT (300K) = 2.38 cm^3 K mol^{-1} (4.36 μ_B), χ_MT (5K) = 0.12 cm^3 K mol^{-1} (1.0 μ_B).

[UO$_2$Y(py)$_2$(L)]$_2$ 3 A solution of Y{N(SiMe$_3$)$_2$}$_3$(THF)$_{1.6}$ (86.4 mg, 0.126 mmol) in pyridine (5 mL) was added dropwise to [UO$_2$(py)(H$_2$L)] (127 mg, 0.126 mmol) in pyridine (10 mL) at room temperature. The resultant dark red solution was stirred for 4 weeks, after which the volatiles were removed under reduced pressure to afford a dark red solid, yield 147 mg, 100 % of [UO$_2$Y(py)$_2$(L)]$_2$. Analysis. Found: C, 57.12; H, 4.95; N, 12.97. C$_{134}$H$_{130}$N$_{26}$O$_4$Y$_2$U$_2$ ([UO$_2$Y(py)$_2$(L)]$_2$·6py, i.e. with three incorporated molecules of pyridine solvent) requires C, 57.02; H, 4.64; N, 12.90 %. IR (nujol mull, cm^{-1}): v 722. NIR (pyridine, 25 °C): 1571 nm (ε = 168.7 dm^{3}mol^{-1}cm^{-1}). χ_MT (300K) = 0.75 cm^3 K mol^{-1} (2.4 μ_B), χ_MT (5K) = 0.17 cm^3 K mol^{-1} (1.2 μ_B).

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