3

Supporting Information

Pentavalent Uranyl Stabilized by a Dianionic Bulky Tetradentate Ligand

Pawel Horeglad, Grégory Nocton, Yaroslav Filinchuck, Jacques Pécaut, and Marinella Mazzanti*.

Laboratoire de Reconnaissance Ionique et Chimie de Coordination, Service de Chimie Inorganique et Biologique (UMR-E 3 CEA-UJF), INAC,
CEA-Grenoble, 38054 GRENOBLE, Cedex 09, France,

* To whom correspondence should be addressed. E-mail: marinella.mazzanti@cea.fr

General

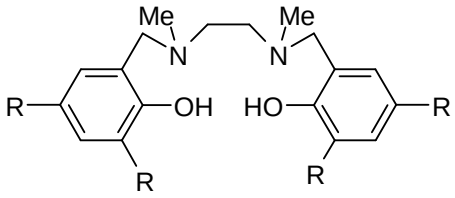
All manipulations were carried out under an inert argon atmosphere using Schlenk techniques and a MBraun glovebox equipped with a purifier unit. The water and oxygen levels were always kept at less than 1 ppm. The solvents were purchased from Aldrich in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (pyridine, hexane, diisopropylether and toluene) or P_2O_5 (CD_2Cl_2). Commercial anhydrous dmso-d_6 was further dried over molecular sieves preliminary heated at 220°C. Depleted uranium turnings were purchased from the "Société Industrielle du Combustible Nucléaire" of Annecy (France). *N*,*N*'-bis(2-hydroxybenzyl-3,5-ditertbutyl)-1,2-dimethylaminomethane H_2salan-^{t}Bu$_2$ and *N*,*N*'-bis(2-hydroxybenzyl-3,5-dimethyl)-1,2-dimethylaminomethane H_2salan-Me_2, were prepared according to the literature procedures[1] and dried under vacuum at 80 ºC for 5 days prior to use. 18-crown-6 were purchased from Aldrich and dried under vacuum at 50 ºC for 7 days. [(UO_2Py_5)(KI_2Py_2)], (**1**) was prepared as previously described.[2]

Elemental analysis were performed under argon by Analytische Laboratorien GMBH at Lindlar, Germany. FTIR spectra were recorded with a Perkin Elmer 1600 Series FTIR spectrophotometer. UV-Visible measurements were carried out with a Varian Cary 50 Probe spectrophotometer in quartz cells (optical path lengths: 1 mm and 1cm) adapted with Young valves.

^{1}H NMR spectra were recorded on Varian UNITY and MERCURY 400 MHz spectrometer. NMR chemical shifts are reported in ppm with solvent as internal reference. NOESY and COSY 2DNMR experiments allowed the assignment of proton signals of **2** and **3**.

Magnetic moments in pyridine solution were determined using the Evans method.[3]

Mass spectra were obtained with a Finnigan LCQ-ion trap equipped with an electrospray source in a pyridine/acetonitrile mixture 1:5 which was filtrated on microporous filters. The experimental isotopic profile was compared in each case to the theoretical ones.



R = ^{t}Bu - **H_2salan-^{t}Bu$_2$**

R = Me - **H_2salan-Me$_2$**

Synthesis of K_2salan-R_2

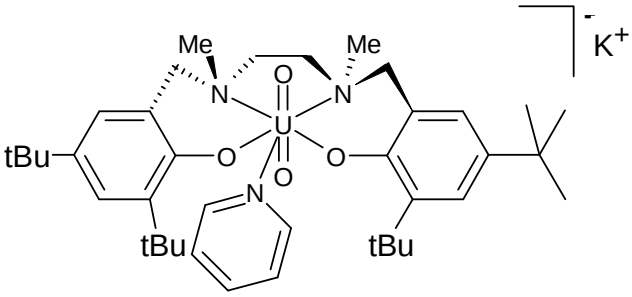
A solution of H_2salan-R_2 (1 equiv.) in thf (3 mL) was added to a suspension of KH (>2 equiv.) in thf (1 mL). The mixture was stirred for 5 hours to afford a colourless solution. After removal of the excess of KH by filtration, the solvent was evaporated under vacuum. The resulting solid was washed with 3 mL of hexane.

K_2salan-^{t}Bu$_2$: H_2salan-^{t}Bu$_2$ (200.0 mg, 0.38 mmol, 1 equiv.), KH (32.1 mg, 0.80 mmol, 2.03 equiv.) Yield: (209 mg , 91.6 %) ^{1}H NMR: (dmso-d_6, 298K, 200MHz): 1.17 (s, 9H); 1.32 (s, 9H); 1.89 (s, 3H); 2.42 (s, 2H); 3.14 (br, 2H); 6.61 (s, 1H); 6.81 (s, 1H).

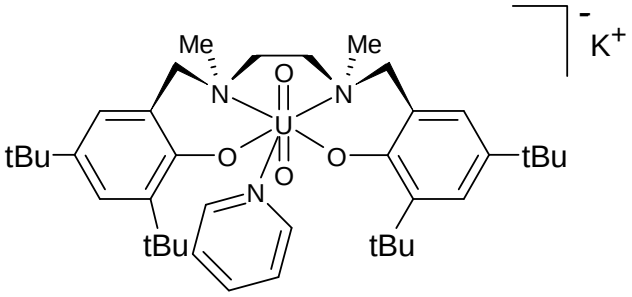
K_2salan-Me$_2$: H_2salan-Me$_2$ (192.4 mg, 0.54 mmol, 1 equiv.), KH (45.5 mg, 1.13 mmol, 2.1 equiv.) Yield: (191.2 mg , 81.9 %) ^{1}H NMR: (dmso-d_6, 298K, 200MHz): 1.88, 1.89 (s, 6H); 2.00 (s, 3H); 2.37 (s, 2H); 3.01 (s, 2H); 6.36 (br. D, 1H), 6.50 (br. D, 1H).

[UO_2(salan-^{t}Bu$_2$)(Py)μK]n (2)

^{1}H NMR (Pyridine-d_5; 333 K; 400MHz, 12.62 mM) two sets of signals corresponding to isomers **I** and **II*** (presented below) in the ratio 100:11 were found. First set (**I**): -10.08 (br, 2H, -NCH_2-); -7.41 (br, 2H, -NCH_2-); -6.56 (s, 6H, -$N(CH_3)$-); -4.71 (br, 2H, -NCH_2-Ph); -3.84 (s, 18H, -*t*Bu); 0.29 (s, 18H, -*t*Bu); 3.54 (s, 2H, -CH-$_{aromatic}$); 5.09 (s, 2H, -CH-$_{aromatic}$); 10.29 (br, 2H, -NCH_2-Ph). Second set (I**I**): -9.91 (br, 2H, -NCH_2-); -4.71 (br, 2H, -NCH_2-); -4.59 (s, 3H, -$N(CH_3)$-); -2.46 (s, 18H, -*t*Bu); 0.41 (s, 18H, -*t*Bu); 3.47 (s, 2H, -CH-$_{aromatic}$); 4.24 (br, 2H, -NCH_2-Ph); 5.46 (s, 2H, -CH-$_{aromatic}$).



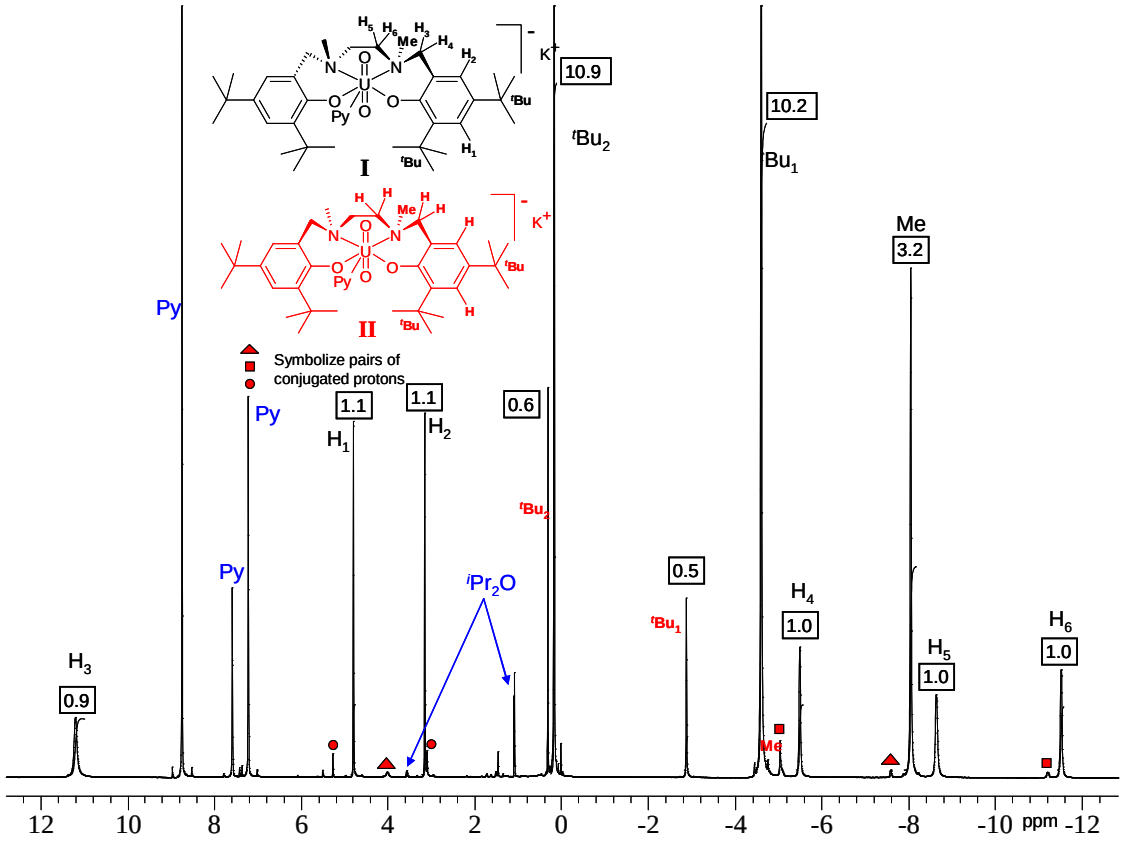
I



II

*The signals of the major species could not be assigned unequivocally (to isomer **I** or **II)**. However, as the crystallized isomer (isomer **I,** with methyl groups in trans to each other) is expected to be the more stable isomer in solution, we have assigned it as the major species.

Figure S1. ^{1}H NMR spectrum of [UO_2(salan-$^{t}Bu_2$)(Py)μK]n **(2)** in pyridine-d_5 at 298K (Integrals are given only for the major isomer).



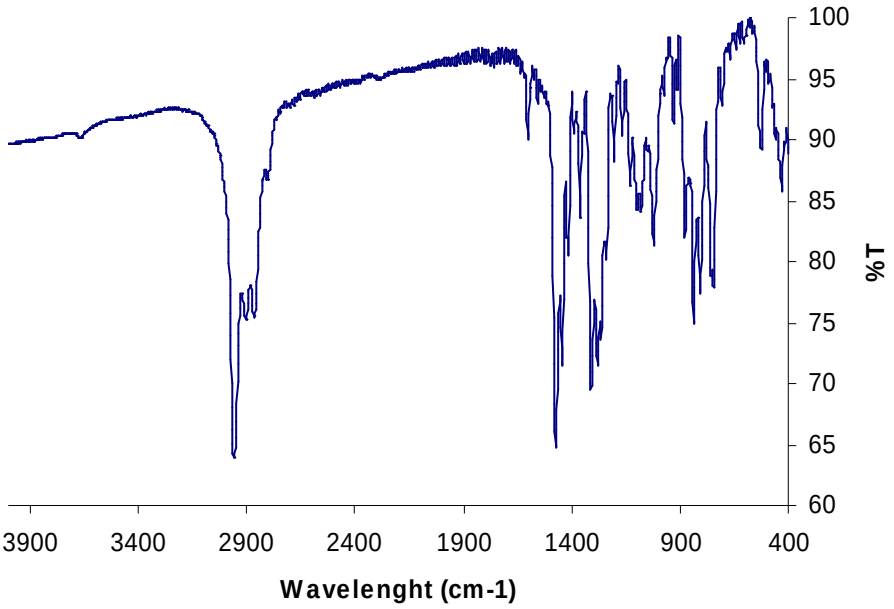
^{1}H NMR (dmso-d_6; 298 K; 400MHz, 6.03 mM) two sets of signals corresponding to two different isomers in the ratio 100:23 were found. First set (major species): -12.30 (br, 2H, -NCH_2-); -11.04 (br, 2H, -NCH_2-); -8.52 (s, 6H, -$N(CH_3)$-); -6.88 (br, 2H, -NCH_2-Ph); -4.52 (s, 18H, -*t*Bu); 0.06 (s, 18H, -*t*Bu); 3.06 (s, 2H, -CH-$_{aromatic}$); 4.23 (s, 2H, -CH-$_{aromatic}$); 9.87 (br, 2H, -NCH_2-Ph). Second set (minor species): -12.04 (br, 2H, -NCH_2-); -8.14 (br, 2H, -NCH_2-Ph) -7.95 (br, 2H, -NCH_2-); -5.93 (s, 3H, -$N(CH_3)$-); -3.14 (s, 18H, -*t*Bu); 0.26 (s, 18H, -*t*Bu); 3.06 (s, 2H, -CH-$_{aromatic}$); 3.85 (br, 2H, -NCH_2-Ph); 4.80 (s, 2H, -CH-$_{aromatic}$). Signals of pyridine: 7.34, 7.49, 8.55.

^{1}H NMR (dmso-d_6; 333 K; 400MHz, 6.03 mM) two sets of signals corresponding to two different isomers in the ratio 100:29 were found. First set (major species): -11.32 (br, 2H, -NCH_2-); -10.03 (br, 2H, -NCH_2-); -7.07 (br, 6H, -$N(CH_3)$-); -6.54 (br, 2H, -NCH_2-Ph); -3.95 (s, 18H, -*t*Bu); 0.12 (s, 18H, -*t*Bu); 2.96 (br, 2H, -CH-$_{aromatic}$); 4.41 (br, 2H, -CH-$_{aromatic}$); 8.38 (br, 2H, -NCH_2-Ph). Second set (minor species): -11.19 (br, 2H, -NCH_2-); -7.51 (br, 2H, -NCH_2-Ph); -5.31 (br, 3H, -$N(CH_3)$-); -2.84 (br, 18H, -*t*Bu); 0.28 (br, 18H, -*t*Bu); 3.14 (br, 2H, -CH-$_{aromatic}$); 3.91 (br, 2H, -NCH_2-Ph); 4.86 (br, 2H, -CH-$_{aromatic}$). Signals of pyridine: 7.33, 7.48, 8.52.

No significant change was observed in the ^{1}H NMR spectra after 36 days in pyridine and dmso.

The proton NMR spectrum shows only one set of signals for the coordinated and solvent pyridine probably due to their rapid exchange on the NMR time scale.

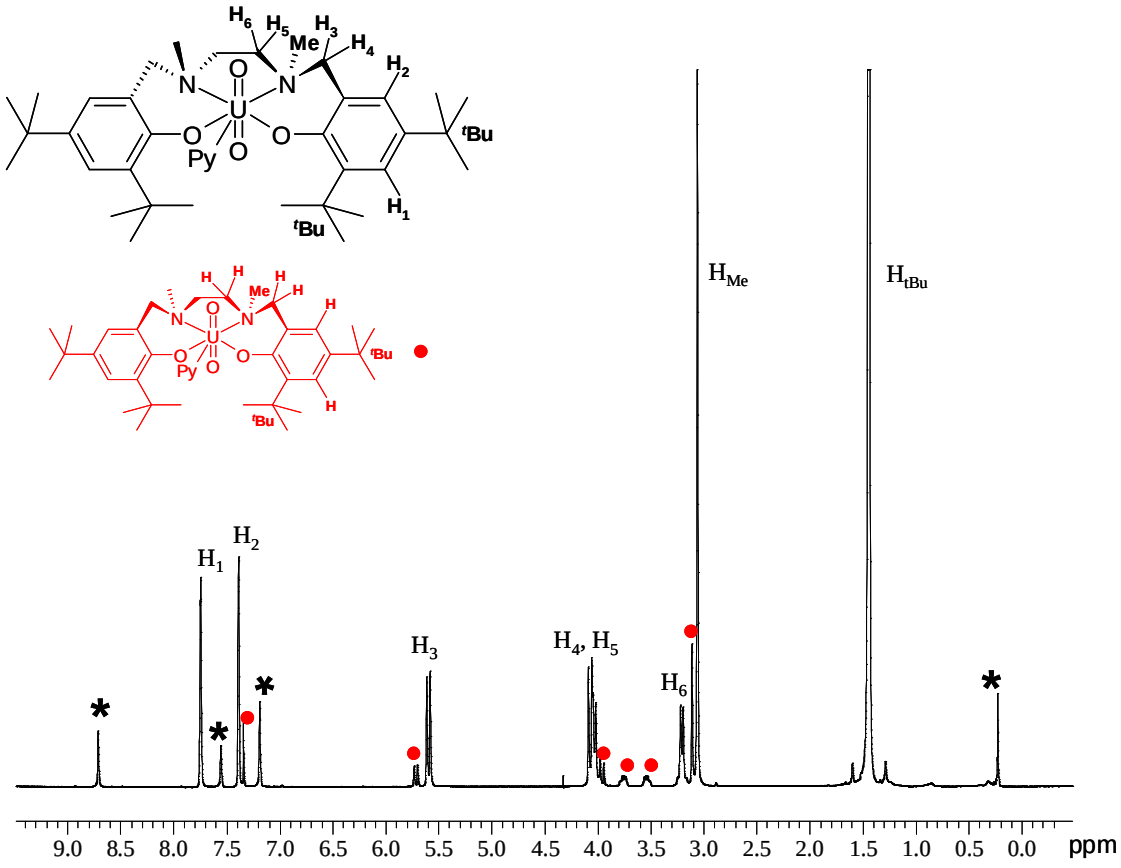
Figure S2. FTIR of $[UO_2(salan\text{-}^tBu_2)(Py)\mu K]_n$ **(2)** in KBr pellets performed under argon.



2953 (w), 2899 (m), 2860 (m), 2800 (s), 1601 (s), 1471 (w), 1442 (w), 1414 (m), 1360 (m), 1309 (w), 1277 (w), 1238 (w), 1203 (s), 1165 (s), 1128 (m), 1093 (m), 1078 (m), 1018 (m), 929 (s), 912 (s), 874 (m), 835 (w), 804 (w), 766(w), 750 (m), 743 (m), 702 (s), 523 (m), 428 (m).

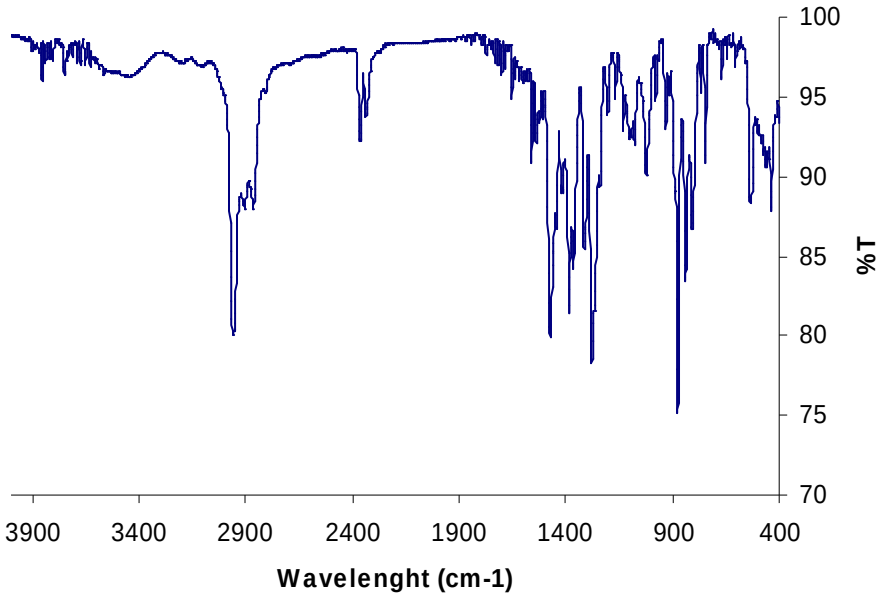
Synthesis of $[UO_2(salan\text{-}^tBu_2)(Py)]$(3): A light yellow pyridine solution (2 mL) of $UO_2(NO_3)_3 \cdot 5H_2O$ (100.9 mg, 0.201 mmol, 1 equiv.) was added to a pyridine suspension (2 mL) of $H_2salan\text{-}^tBu_2$ (114 mg, 0.218 mmol, 1.1 equiv.). The resulting deep red solution was stirred for 1h at room temperature. The solvent was removed under vacuum and the resulting residue was dissolved in warm hexane (60°C), filtrated and cooled at -20°C for 16h (overnight). A red microcrystalline powder formed and was filtrated to yield 98 mg (56 %) of $[UO_2(salan\text{-}^tBu_2)(Py)]$. ^1H NMR (Pyridine-d_5; 298 K; 400MHz): 7.72 (s, 2H) ; 7.42 (s, 2H); 5.62 (d, 2H, J = 12.4 Hz) ; 4.09 (d, 2H, J = 13.2 Hz) ; 4.06 (m, 2H) ; 3.23 (m, 2H) ; 3.00 (s, 6H) ; 1.47 (s, 36H). ESI/MS (CH_2Cl_2) m/z = 827 $\{[UO_2(salan\text{-}^tBu_2)(Cl)\}^-$

Figure S3. ^{1}H NMR spectrum of [UO_2(salan-$^{t}Bu_2$) (Py)](**3**) in pyridine-d5 at 298K.



* grease and solvent signals, red dots mark the signals of the minor isomer.

Figure S4. FTIR of [UO_2(salan-^{t}Bu_2)(Py)] **(3)** Br pellets.



2954 (m), 2900 (m), 2861 (m), 2361 (m), 2332 (m), 1653 (m), 1558 (m), 1539 (m), 1519 (m), 1471 (s), 1443 (m), 1419 (m), 1413 (m), 1385 (s), 1362 (s), 1313 (s), 1277 (s), 1238 (w), 1201 (m), 1167 (w), 1128 (w), 1099 (w), 1076 (w), 1018 (m), 977 (m), 931 (m), 914 (w), 887 (m), 873 (s), 834 (s), 806 (s), 766 (w), 743 (m), 667 (w), 644 (w), 603 (w)), 530 (m), 440 (m).

Figure S5. Comparison between the FTIR spectra of [UO_2(salan-^{t}Bu_2)(Py)] **(3)** (blue line) and [UO_2(salan-^{t}Bu_2)(Py)µK]n **(2)** (red line).

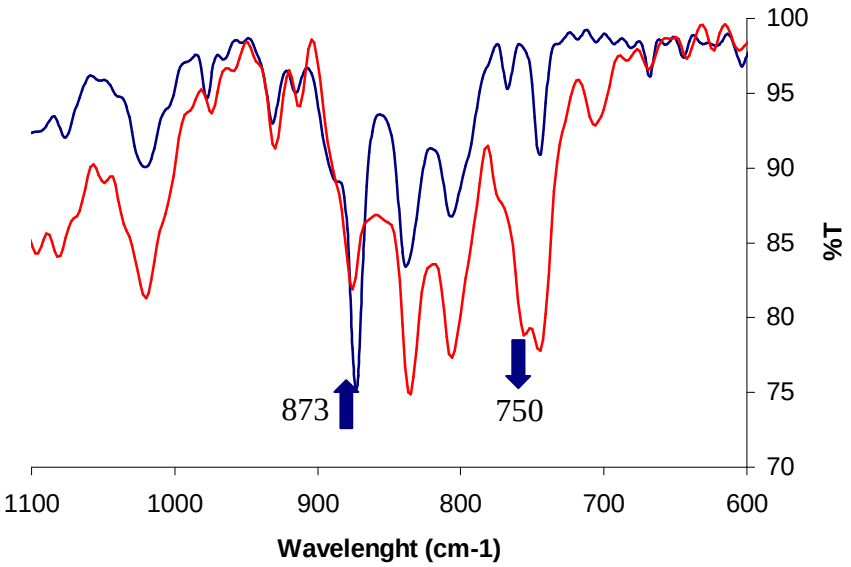
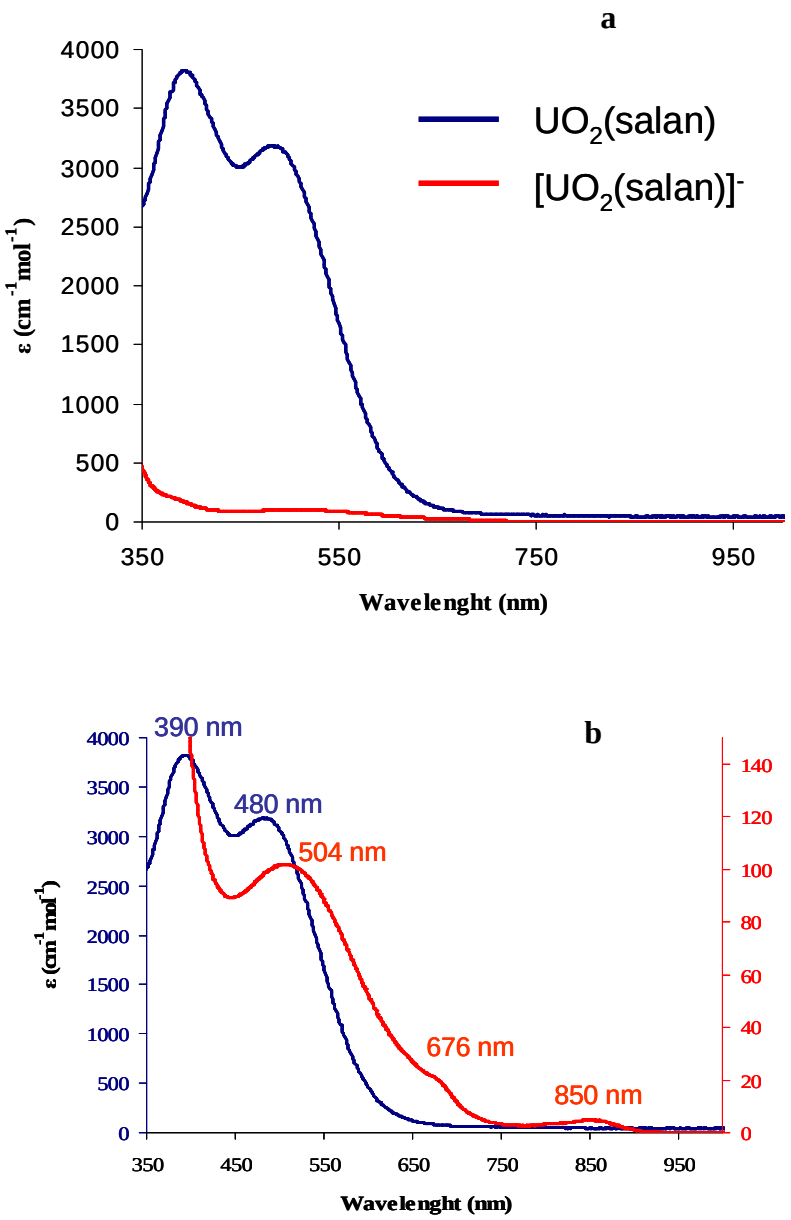


Figure S6. UV-Vis spectra of a 2mM pyridine solution of $[UO_2(salan\text{-}^tBu_2)(Py)]$ **(3)** (blue) and a 40mM pyridine solution of $[UO_2(salan\text{-}^tBu_2)(Py)\mu K]_n$ **(2)** (red) presented at the same scale (a) and presented at different scales (red scale for U(V) and blue scale for U(VI)) (b).



The absorption spectra of the pentavalent complex **2** show absorptions consistent with f-f transitions (850 and 676 nm) which display very low absorptivities similar to what observed for the carbonate complex $[UO_2(CO)_3]^{5-}$.[4]

Crystal Structure Determination

Synchrotron radiation and the use of the low-noise image-plate detector were needed because the crystals of **2** diffracted weakly (only up to 20° theta). More divergent laboratory X-ray beam and relatively noisy CCD camera would not allow the data measurement in the highest resolution shell. Given the lower diffraction power of **2** with respect to **3**, the use in the former case of the synchrotron source + image plate detector was essential for the successful structure characterization.

The reason of such weak scattering power is probably the high thermal motion of the weakly associated hexane solvent molecule. The asymmetric unit contains four tert-butyl groups, which show pronounced atomic displacements even at 100 K (usual behaviour for this group). The carbon atoms of methyl groups show expectedly big and anisotropic thermal ellipsoids. Large thermal vibrations make crystals scatter to lower angles, and the smaller quantity of the experimental information affects the precision of the structure. In both complexes the refinement of the occupancy factors for the solvent molecule showed that they are partially occupied (~50%) and the occupancy was fixed to 50% at the final refinement stage. The partially occupied atoms were refined isotropically in both structures. In the refined of structure **2** a total of 432 restraints was applied. DELU restraints defined all bonds in the connectivity list: the components of the (anisotropic) displacement parameters in the direction of the bond are restrained to be equal. SIMU restraints were applied with the default standard deviation for all covalently bound atoms to have the same Uij components. Thus, the Uij values on neighbouring atoms in larger molecules tend to be both similar and significantly correlated with one another. Finally three bond restraints were imposed in the refinement of the solvent molecule (C51-C52, C52-C53 and C51-C53 which automatically restraints the angle C51-C52-C53). In the refinement of the structure of complex **3** three bond restraints were imposed in the refinement of the solvent molecule (C51-C52, C52-C53 and C51-C53 which automatically restraints the angle C51-C52-C53). Hydrogen atoms for all complexes were included in calculated positions.

Table S1. Crystallographic data of **2** and **3**

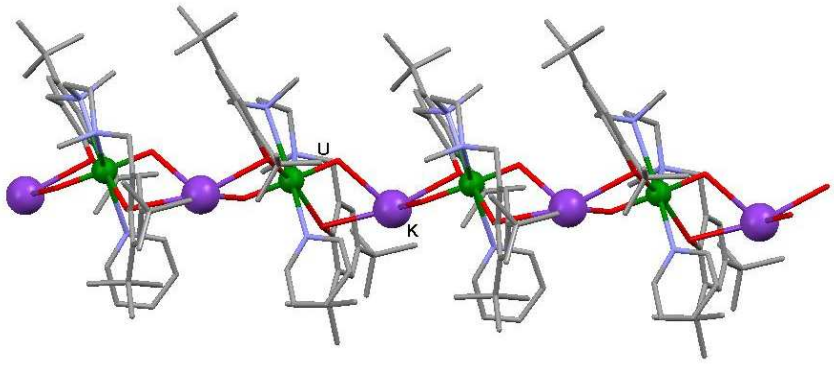
	{[UO_2(salan-^{t}Bu$_2$)(Py)μK]·0.25C_6H_{14}}n **(2)**	[UO_2(salan-^{t}Bu$_2$)(Py)]·0.25C_6H_{14} **(3)**
Formula	C40.5 H62.5 K N3 O4 U	C40.5 H62.5 N3 O4 U
Crystal size (mm)	0.3x0.04x0.03	0.38 x 0.03 x 0.02
cryst syst	Monoclinic	monoclinic
space group	P2(1)/c	P2(1)/c
volume (Å^3)	4536.26(17)	4422.1(2)
a (Å)	11.7846(3)	19.6726(6)
b (Å)	30.2442(5)	20.0780(6)
c (Å)	13.0298(3)	11.4096(3)
α(deg)	90	90
β(deg)	102.368(2)	101.116(3)
γ(deg)	90	90
Z	4	4
formula weight (g/mol)	932.57	893.47
density (calcd) (g cm^{-3})	1.365	1.342
absorption coefficient (mm^{-1})	3.707	3.708
F(000)	1878	1802
temp (K)	100(1)	150(2)
total no. reflections	12949	25664
unique reflections	3824	9620
Final R indices [$I > 2\acute{o}(I)$]	R1 = 0.0641, wR2 = 0.1726	R1 = 0.0403, wR2 = 0.0690
Largest diff. peak and hole (e.A^{-3})	1.783 and -0.962	1.907 and -0.882
GOF	1.218	0.808

Synchrotron radiation with λ= 0.69408 Å and MAR345 detector were used for data collection (SNBL at the ESRF).

Table S2. Selected structural parameters for **2** and **3**. (#2 = x,-y+1/2,z+1/2; distances are given in Å, angles in deg.)

Structural parameters	**(2)**	**(3)**
U-O(1U)	1.819(12)	1.764(4)
U-O(2U)	1.830(12)	1.790(3)
U-O(1)	2.323(11)	2.201(4)
U-O(2)	2.379(11)	2.231(4)
U-N(1)	2.715(16)	2.641(5)
U-N(2)	2.690(14)	2.649(5)
U-N(3)	2.618(16)	2.593(5)
K-O(2U)#2	2.691(11)	-
K-O(1U)	2.663(13)	-
K-O(1)#2	2.695(15)	-
K-O(2)	2.697(13)	-
O(1U)-U-O(2U)	178.9(6)	178.37(18)

Figure S7. Side view of the 1D polymer **2**. (C atoms in grey, O in red, K in purple, and U in green).



Magnetic susceptibility measurements of 2

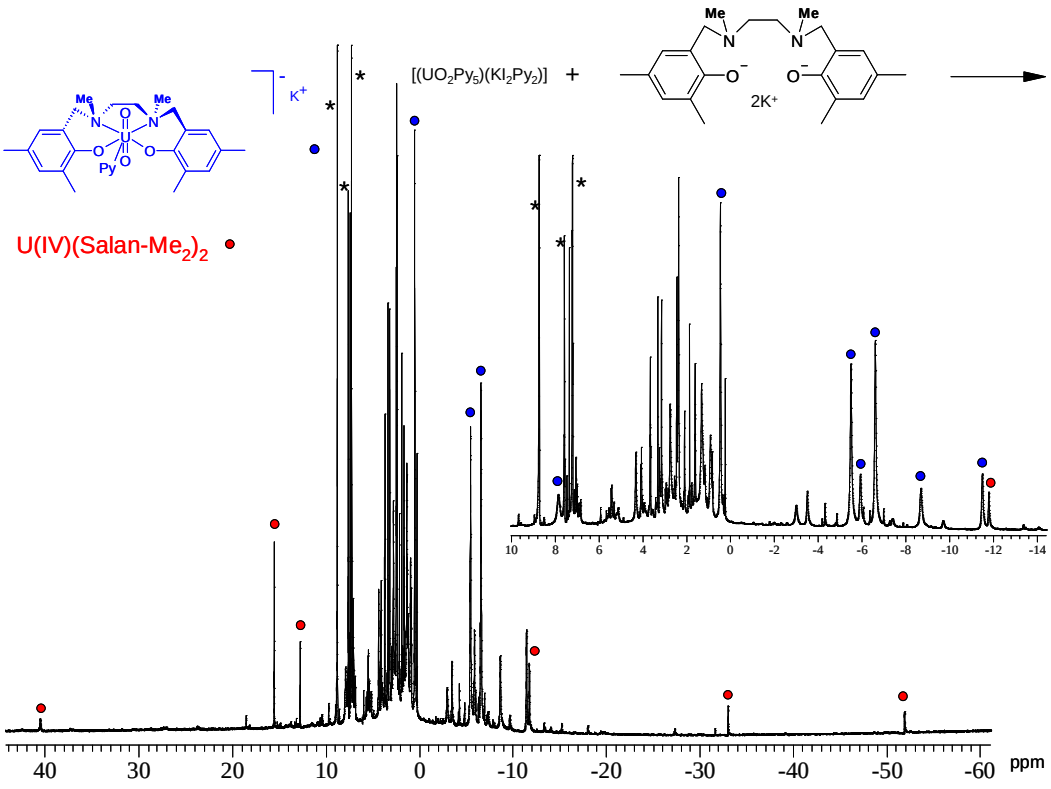
The high solution stability of **2** allowed us to measure the magnetic susceptibility in pyridine and dmso solution. The effective magnetic moments at 300K were found to be respectively μ_{eff} = 2.35(6) in pyridine solution and μ_{eff} = 2.2(2) in dmso solution. These values are in the range of a few U(V) complexes which were characterized by this method (1.64-2.57μ_B).[1]

Reaction of K_2salan-Me_2 with $[(UO_2Py_5)(KI_2Py_2)]_n$.

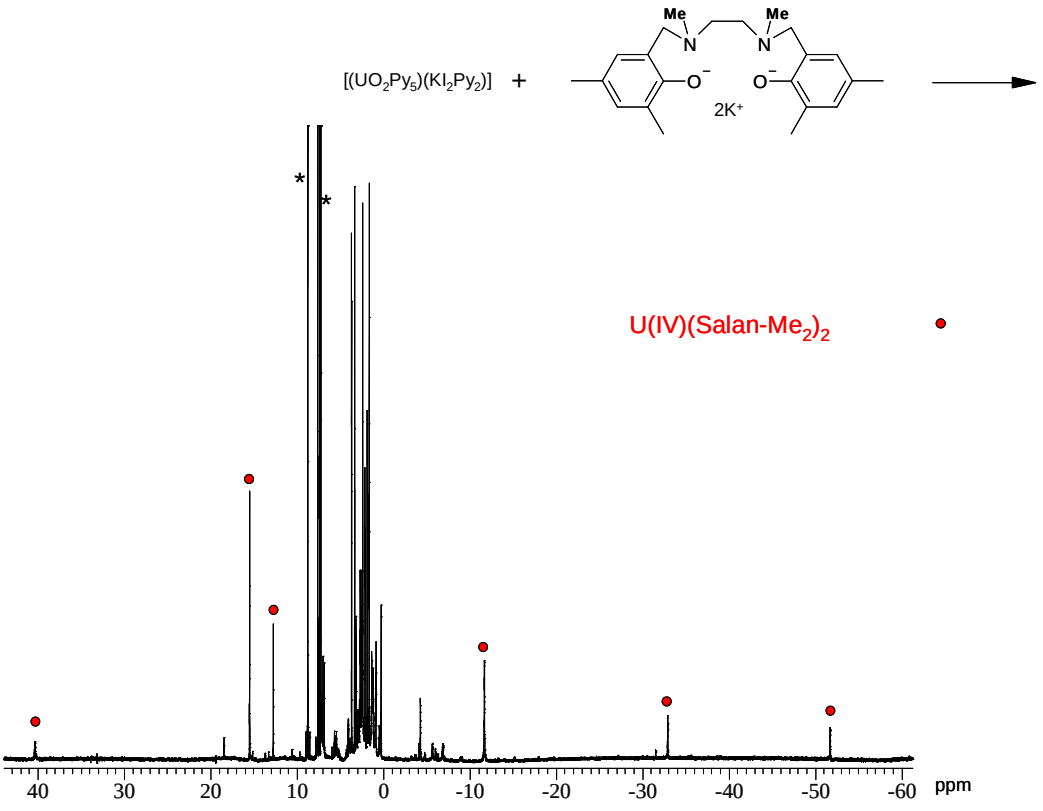
A solution of K_2salan-Me_2 (3.9 mg, 0.009 mmol, 1 equiv.) in pyridine (1.5 mL) was added to a suspension of **1** (10 mg, 0.009 mmol, 1 equiv.) in pyridine (1.5 mL). The resulting clear orange solution was stirred for an hour. ^{1}H NMR (Pyridine-d_5; 298 K; 400MHz) was complex. On the basis of U(V)O_2(salan-^{t}Bu$_2$)K, some signals corresponding to a U(V)O_2^+ species were identified (–Me and –NMe groups were found at -6.60, -5.50 and 0.47, three broad signals assigned to -N(Me)CH_2CH_2(Me)N- and -N(Me)CH_2-Ph were found at -11.49, -8.68 and -5.92). However, the complex nature of ^{1}H NMR spectrum and the fast decomposition prevented further assignment. The NMR show the presence of decomposition products assigned to uranyl(VI) and U(IV) species.

Figure S8 ^{1}H NMR spectrum of the 1:1 reaction mixture of $[(UO_2Py_5)(KI_2Py_2)]_n$ (**1**) and H_2salan-Me_2 registered: a) right after the reaction, b) after 60 hours

a)



b)

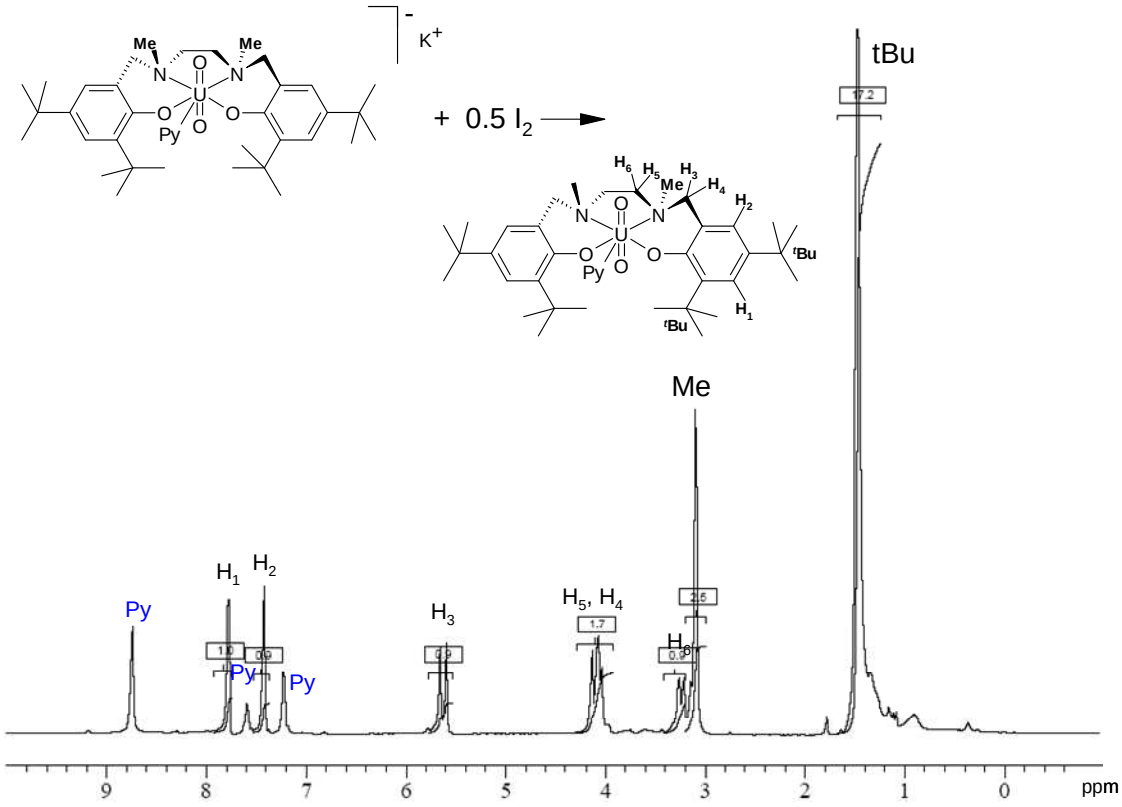


* solvent signals

The reaction of U(V)O_2(salan-^{t}Bu_2)(Py)K with I_2

I_2 (0.5 mg, 0.004 mmol, 0.49 equiv.) was added to a solution of **2** (10 mg, 0.008 mmol, 1 equiv.) in Py-D_5(0.5 mL) resulting in a colour change from pink to deep red. The ^{1}H NMR of this solution recorded after 5 minutes shows only the presence of the hexavalent uranyl complex. ^{1}H NMR (Pyridine-d_5; 298 K; 200MHz): 1.46 (s, 18H, -*t*Bu); 3.09 (s, 3H, -N(CH_3)-); 3.23 (d, 1H, $^3J_{HH}$ = 9.5 -N(Me)CH_2-Ph); 4.06 (m. 2H, -N(Me)CH_2CH_2(Me)N-); 5.62 (d, 1H, $^3J_{HH}$ = 12.7 Hz -N(Me)CH_2-Ph)), 7.42, 7.76 (s, 2H, -CH- $_{aromatic}$)

Figure S9. ^{1}H NMR spectra of the reaction mixture of **2** + **0.5 I_2** (Pyridine-d_5; 298 K; 400MHz)



The reduction of [U(VI)O_2(salan-^{t}Bu_2)(Py)] (prepared in situ) with $CoCp_2$.

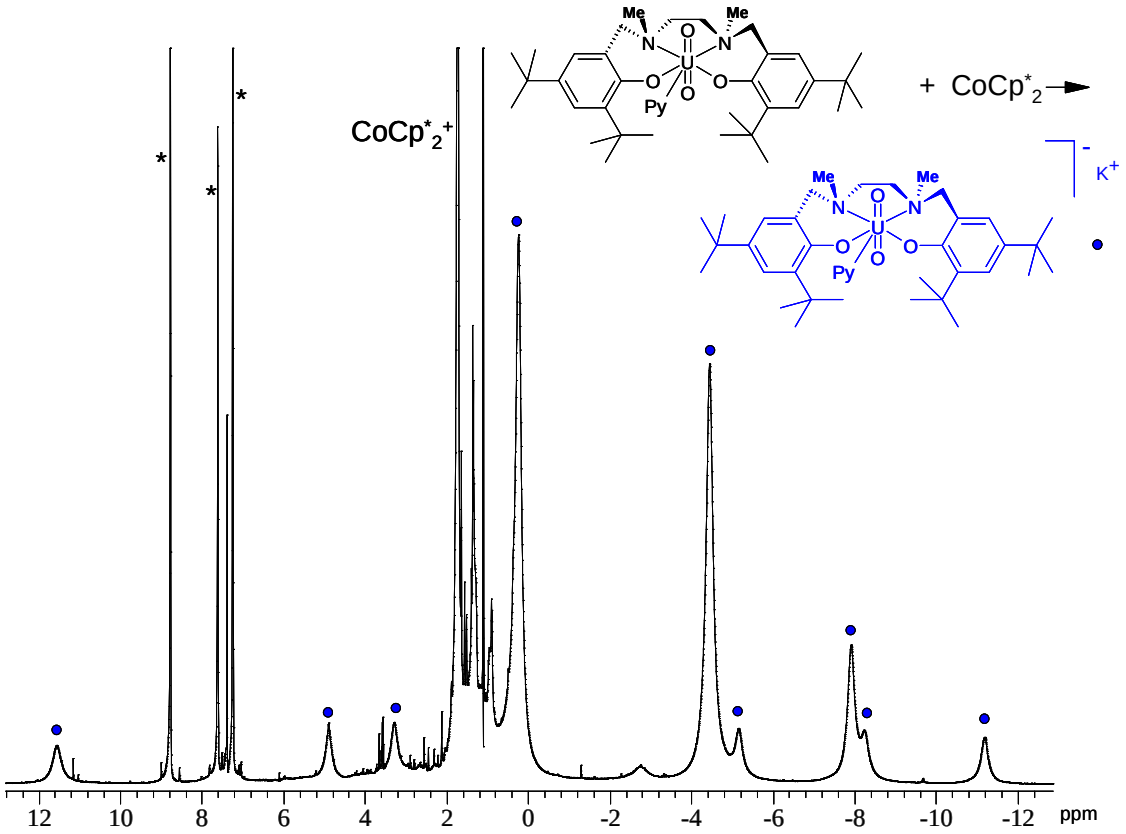
I_2 (1 mg, 0.004 mmol, 0.49 equiv.) was added to a solution of **2** (10 mg, 0.008 mmol, 1 equiv.) in pyridine-d_5(0.5 mL) resulting in a colour change from pink to deep red. 2.9 mg (2 equiv.) of $CoCp_2$ were added to the resulting pyridine solution of [U(VI)O_2(salan-^{t}Bu_2)(Py)]. No change was observed. The only change in the ^{1}H NMR spectrum was the presence of the peak assigned to $CoCp_2$ at -50.4 ppm.

The reduction of [U(VI)O_2(salan-^{t}Bu_2)(Py)] (prepared in situ) with $CoCp^*_2$.

I_2 (1 mg, 0.004 mmol, 0.49 equiv.) was added to a solution of **2** (10 mg, 0.008 mmol, 1 equiv.) in pyridine-d_5(0.5 mL) resulting in a colour change from pink to deep red. 3.0 mg (1.13 equiv.)

$CoCp^*_2$ were added to the resulting pyridine solution of [U(VI)O_2(salan-^{t}Bu$_2$)(Py)]. The proton NMR of the resulting orange solution shows only the signals assigned to complex **2**.

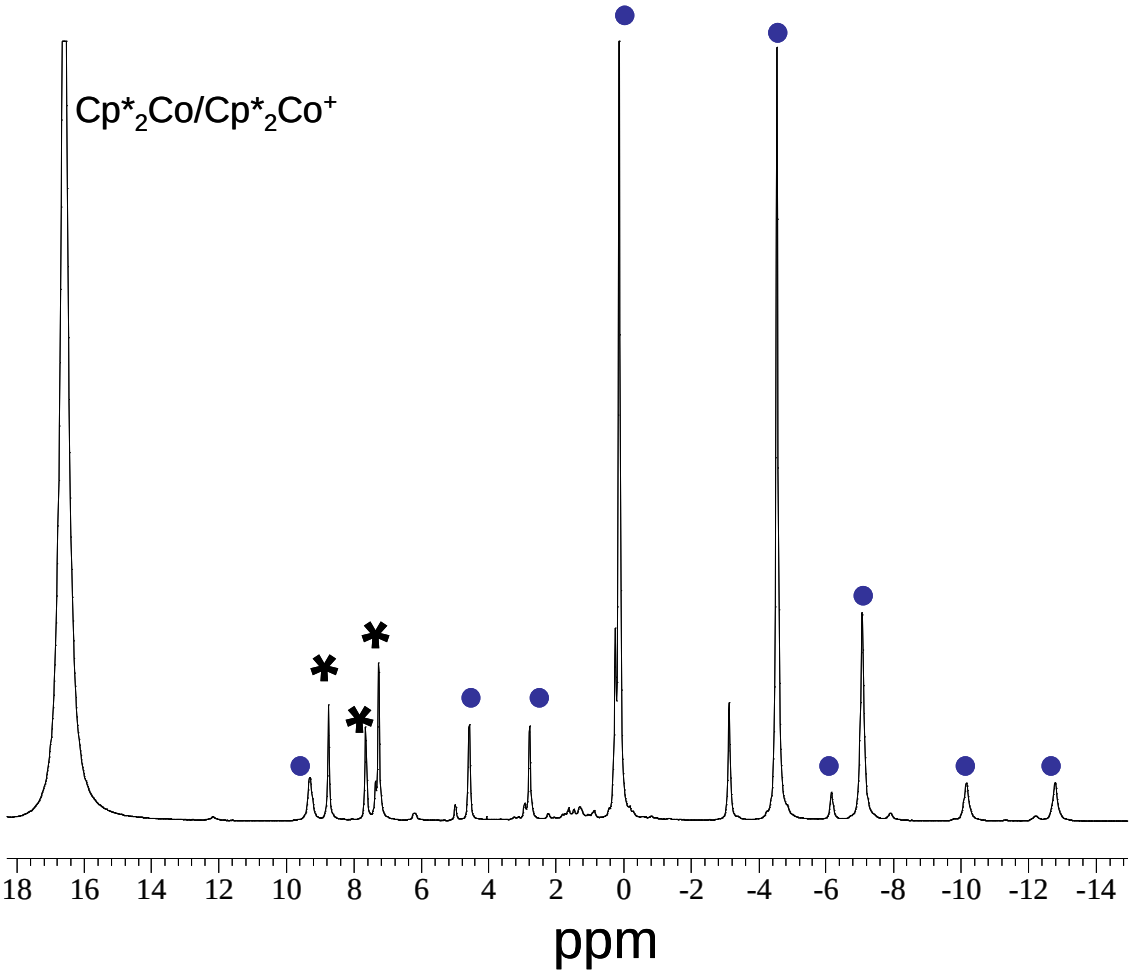
Figure S10 ^{1}H NMR spectra of reaction mixture of [U(VI)O_2(salan-^{t}Bu$_2$)(Py)] (prepared in situ by oxidation of U(VI)O_2(salan-^{t}Bu$_2$)K(Py) with 0.5 I_2) reduced with with 1.1 equiv. $CoCp^*_2$



* solvent signals

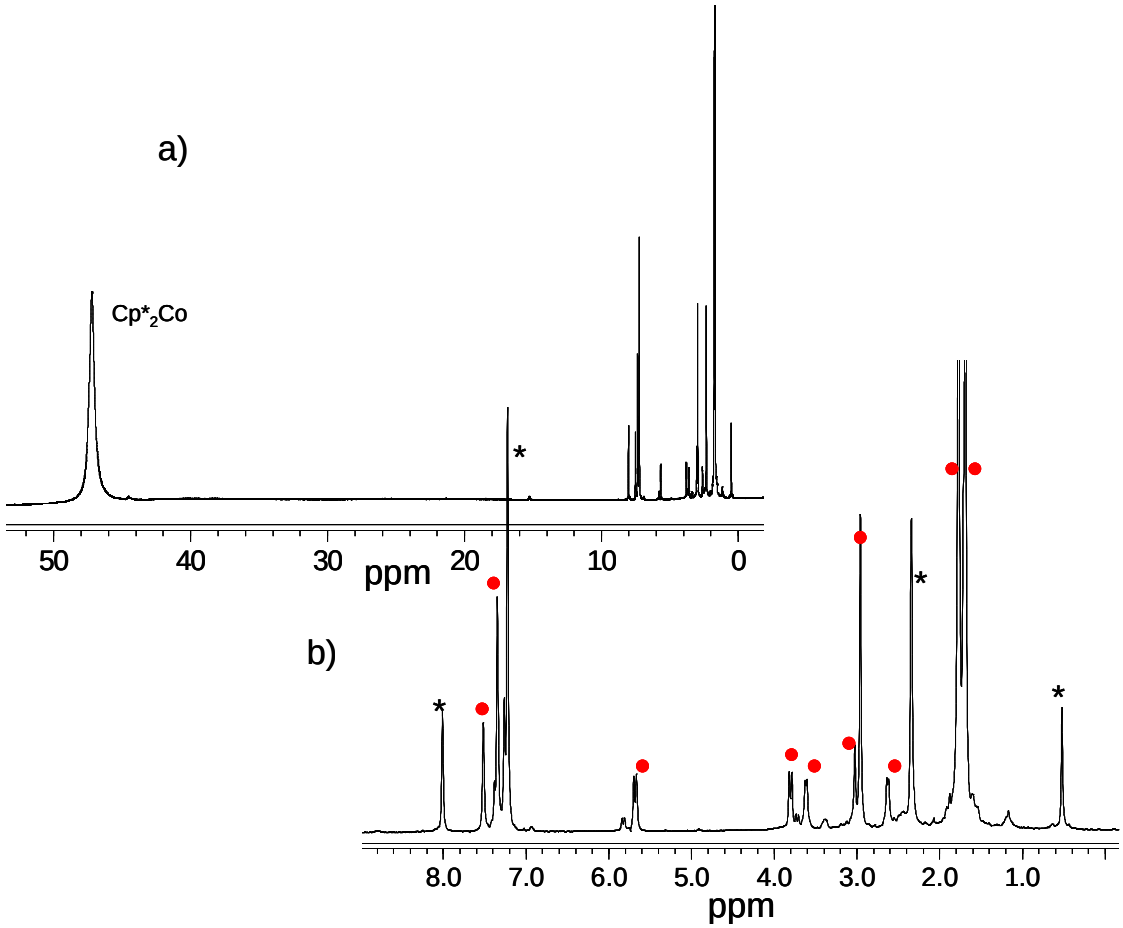
The reduction of 3 with $CoCp^*_2$. A deep red pyridine-d_5 solution (0.5 mL) of [UO_2(salan-^{t}Bu$_2$)] (17.4 mg, 0.020 mmol, 1 equiv.) was added to a pyridine-d_5 suspension (0.2 mL) of Cp^*_2Co (26.4 mg, 0.080 mmol, 4 equiv.). The solution was stirred for 30 min and the color change from deep red to orange. After filtration of unreacted Cp^*_2Co, the filtrated was trasfered to the NMR tube. ^{1}H NMR (Pyridine-d_5; 298 K; 200MHz): -12.81 (br, 2H); -10.17 (br, 2H); -7.08 (s, 3H, -N(CH_3)-); -6.18 (br, 2H, -NCH_2-Ph); -4.56 (s, 18H, -*t*Bu); 0.11 (s, 18H, -*t*Bu); 2.76 (s, 2H, -CH-$_{aromatic}$); 4.55 (s, 2H, -CH-$_{aromatic}$); 9.28 (br, 2H, -NCH_2-Ph). μ_{eff} = 2.2 μ_B (pyridine solution, 298K)

Figure S11. NMR spectra of **3** (Blue dots) reacted with 4 equiv. $CoCp^*_2$ (excess) in pyridine-d_5 (298K, 400MHz) (Only one isomer is pointed in this case)



* solvent signals

Figure S12. ^{1}H NMR spectra of a) **3** (red dots) reacted with 4 equiv. $CoCp^{*}_{2}$ (excess) in deuterated toluene (298K, 400MHz). b) Zoom on the 0-10 ppm region (Complex **3** remains unchanged. Only one isomer is pointed in this case).



* solvent signals

Reduction of **3** with $Cp^{*}_{2}Co$ in toluene after addition of K(18C6) leads to the formation of the pentavalent uranyl complex.

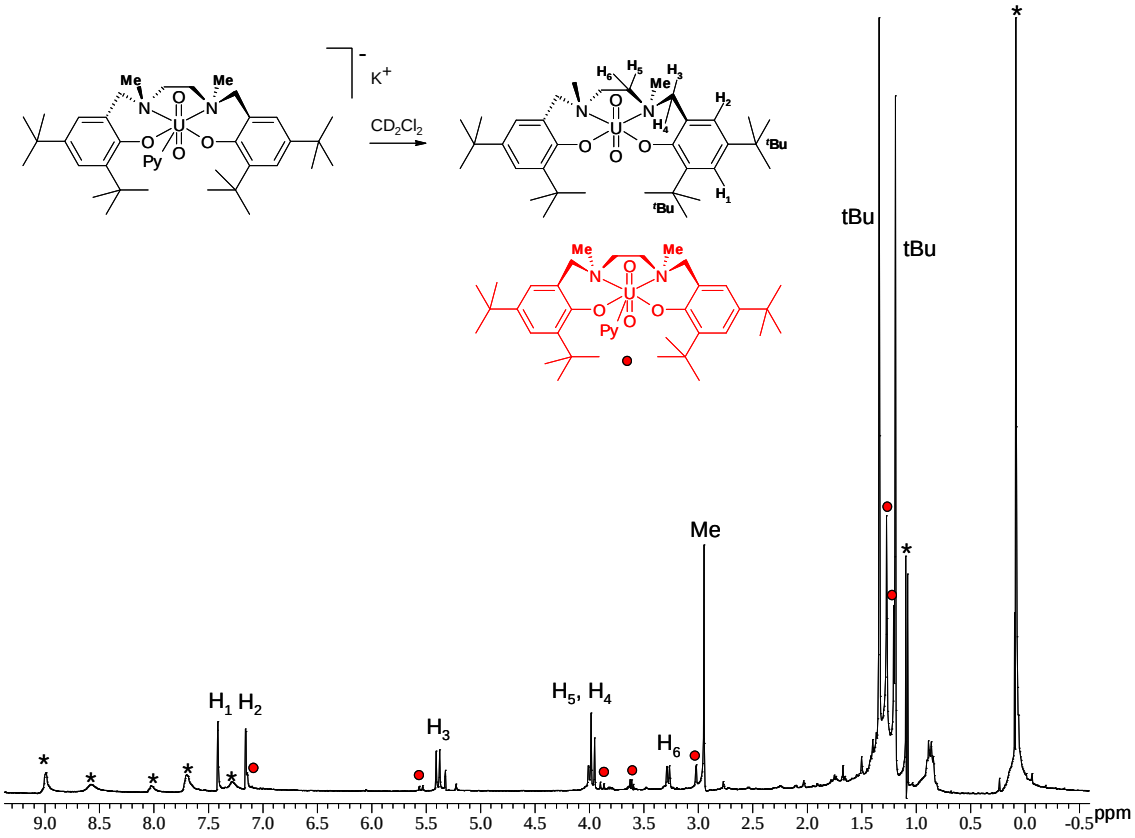
The reaction of 2 with O_2

A solution of **2** (4.5 mg) of in pyridine-d_5 (0.5 mL) was introduced in a NMR tube equipped with a Young valve. The tube was cooled under vacuum to around -30ºC. Dry O_2 (dried over NaOH) was than let diffuse into the tube resulting in the immediate colour change from pink to deep red. The resulting ^{1}H NMR spectrum shows the presence of complex **3** as the major product.

Reactivity of 2 with CD_2Cl_2

Dissolution of **2** in CD_2Cl_2 results in the immediate complete oxidation of the complex and formation of an uranyl(VI) compound.

Figure S13. ^{1}H NMR spectra of **2** after dissolution in CD_2Cl_2 (298 K; 400MHz) (Minor isomer is marked with red dots)



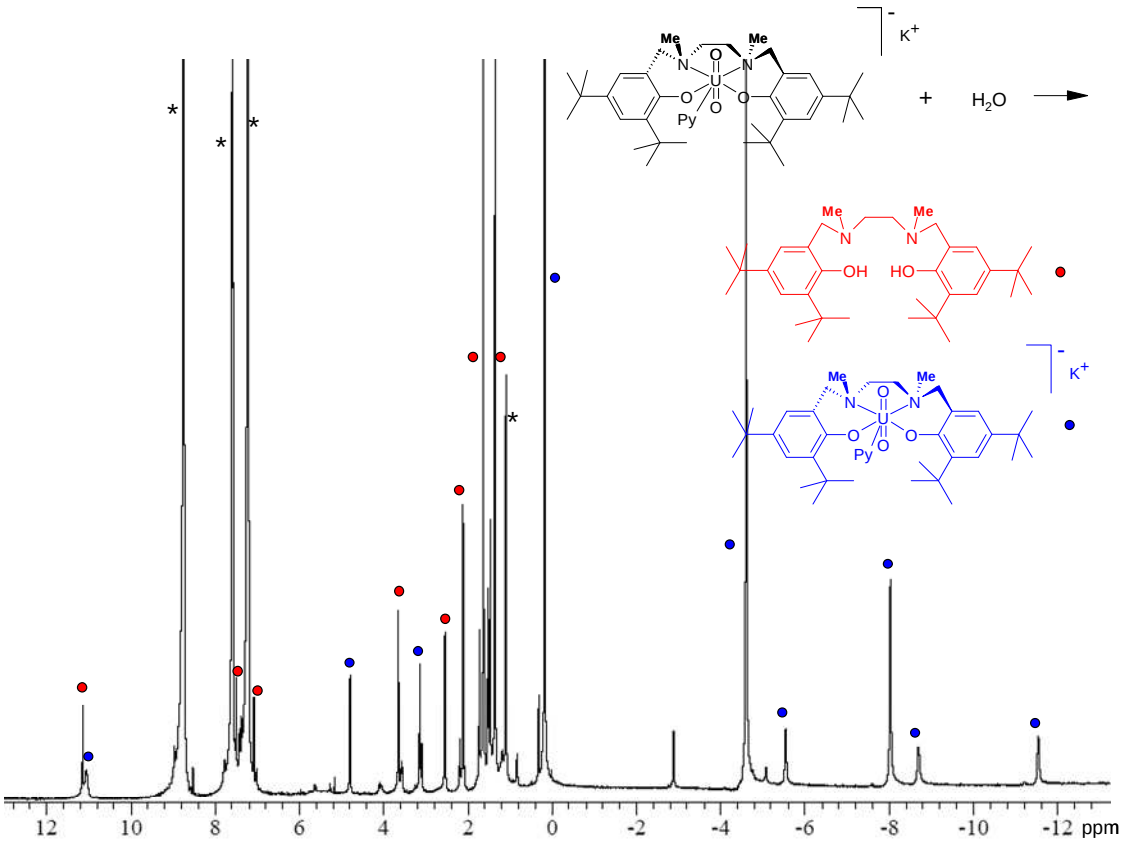
* solvent signals

Reaction of 2 with H_2O

10 µL a 0.5M solution of H_2O in pyridine (~1.25 equiv.) was added to the solution of **2** in pyridine-d_5 (0.6 mL). The reaction was monitored by ^{1}H NMR spectroscopy for 20 days with spectra registered after 24 hours, 6 days, 15 days and 20 days. During the monitoring time, the growth of minor set of signals in the diamagnetic region was observed, while the main set of signals corresponding to complex **2** remained essentially unchanged. The minor set of signals was further assigned to H_2salan-^{t}Bu$_2$ (**2**: H_2salan-^{t}Bu$_2$ = 1.75:1, after 20 days).

After 20 days 80 µL of a 0.5M solution of H_2O in pyridine (~10 equiv) was added to the solution. A rapid colour change was observed. After 24 hours the solution was clear and brownish precipitate was found at the bottom of NMR tube. The ^{1}H NMR revealed the presence of H_2salan-^{t}Bu$_2$ in solution as the only product.

Figure S14. ^{1}H NMR spectra of the reaction mixture of **2** + 1 equiv. H_2O after 20 days (Pyridine-d_5; 298 K; 400MHz)



* solvent signals

References

1. Tshuva, E. Y.; Goldberg, I.; Kol, M., *J. Am. Chem. Soc.* **2000,** 122, 10706-10707.
2. Natrajan, L.; Burdet, F.; Pecaut, J.; Mazzanti, M., *J. Am. Chem. Soc.* **2006,** 128, 7152-7153.
3. Evans, D. F., *J. Am. Chem. Soc.* **1959**, 2003-2005.
4. Mizuoka, K.; Tsushima, S.; Hasegawa, M.; Hoshi, T.; Ikeda, Y., *Inorg. Chem.* **2005,** 44, 6211-6218.