Supplementary Information: **Controlling uranyl oxo group interactions to Group 14 elements using polypyrrolic Schiff-base macrocyclic ligands**

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Contents

1. Experimental

1.1 Attempted synthesis of 2(Sn)

To a solution of $UO_2(H_2L^A)$ (20 mg, 0.17 mmol) in d_5-pyridine (ca. 1 mL) was added $Sn\{N(SiMe_3)_2\}_2$ (7.3 mg, 0.46 mmol) followed by pyridine-N-oxide (6.4 mg, 66 mmol, 4 eq.). The ^{1}H NMR spectrum small resonances which were attributed to the pyridine-N-oxide adduct. ^{1}H NMR (400 MHz, Pyridine-d_5) δ 10.00 (s, 2H), 9.27 (s, 2H), 8.08 (s, 2H), 7.73 (d, *J* = 5.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.91 (s, 2H), 6.68 (s, 2H), 6.37 (s, 2H), 6.14 (s, 2H), 5.84 (d, *J* = 7.0 Hz, 2H), 2.63-2.55 (m, 4H), 2.36-2.33 (m, 2H), 1.78-1.74 (m, 2H), 1.30-1.15 (m, 9H), 0.70 (t, *J* =6.9 Hz, 3H) (NOTE: Some proton signals were covered by large pyridine N-oxide resonances); ^{119}Sn NMR (186 MHz, pyridine-d_5) -481 ppm.

1.2 Attempted synthesis of 2(Ge)

To a solution of $UO_2(H_2L^A)$ (20 mg, 17 µmol) in d_5-pyridine (ca. 1 mL) was added $Ge\{N(SiMe_3)_2\}_2$ $_2$ (6.5 mg, 17 µmol) followed by excess pyridine-N-oxide (16 mg, 166 µmol, 10 eq.). The ^{1}H NMR spectrum showed loss of the starting materials and the formation of multiple minor species.

To a solution of $UO_2H_2L^A$ (20 mg, 0.17 mmol) in d_8-THF (ca. 1 mL) was added $Ge\{N(SiMe_3)_2\}_2$ (6.5 mg, 0.17 mmol) and the solution was heated overnight at 80°C before addition of pyridine-N-oxide (1.6 mg, 66 mmol, 1 eq.). A brown precipitate formed which was redissolved in d_5-pyridine. The ^{1}H NMR spectrum of this precipitate showed it to be a messy mixture of species.

1.3 Attempted synthesis of 3(Sn)

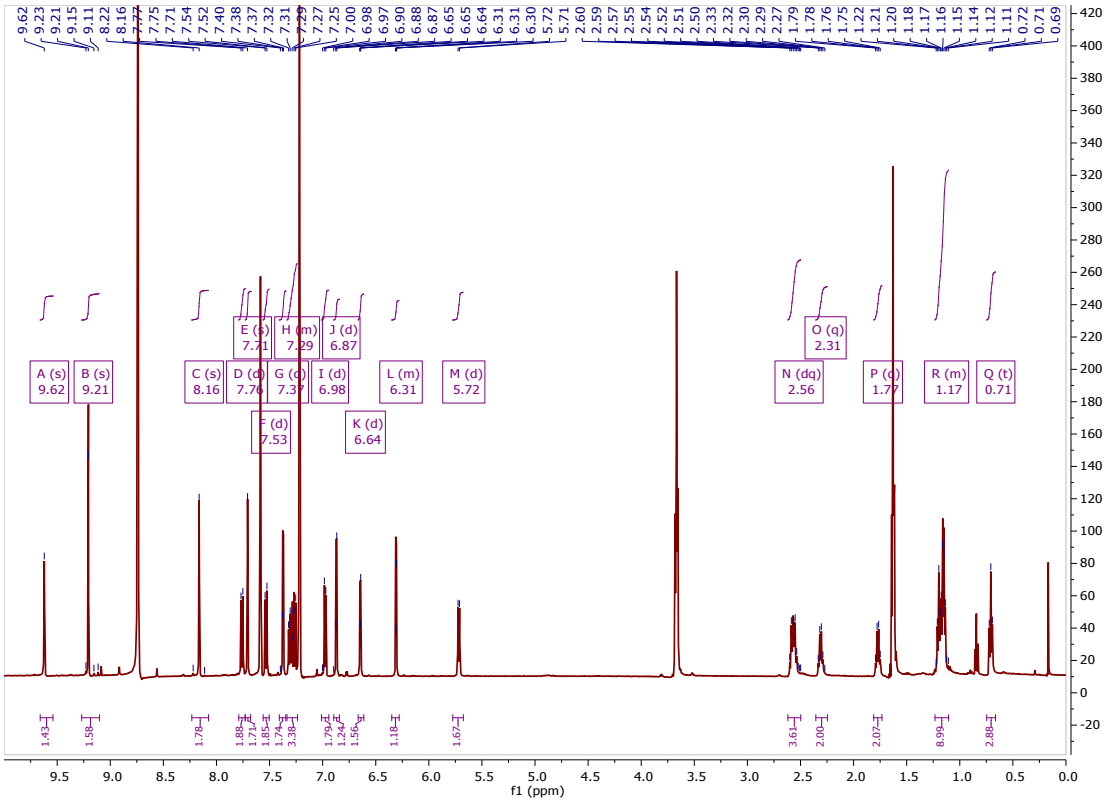
To a solution of $UO_2(H_2L^{Me})$ (10 mg, 0.94 µmol) in d_5-pyridine (ca. 0.5 mL) was added a solution of $Sn\{N(SiMe_3)_2\}_2$ (4.4 mg, 0.94 µmol) in d_5-pyridine (ca. 0.5 mL). ^{1}H NMR immediately showed multiple paramagnetically shifted resonances as well as starting material which did not converge upon one product even after heating for long periods. Repeating the reaction at low temperature, in THF solvent or with two equivalents of $Sn\{N(SiMe_3)_2\}_2$ all resulted in a similar mixture of species by ^{1}H NMR spectroscopy.

1.4 Attempted synthesis of 3(Ge)

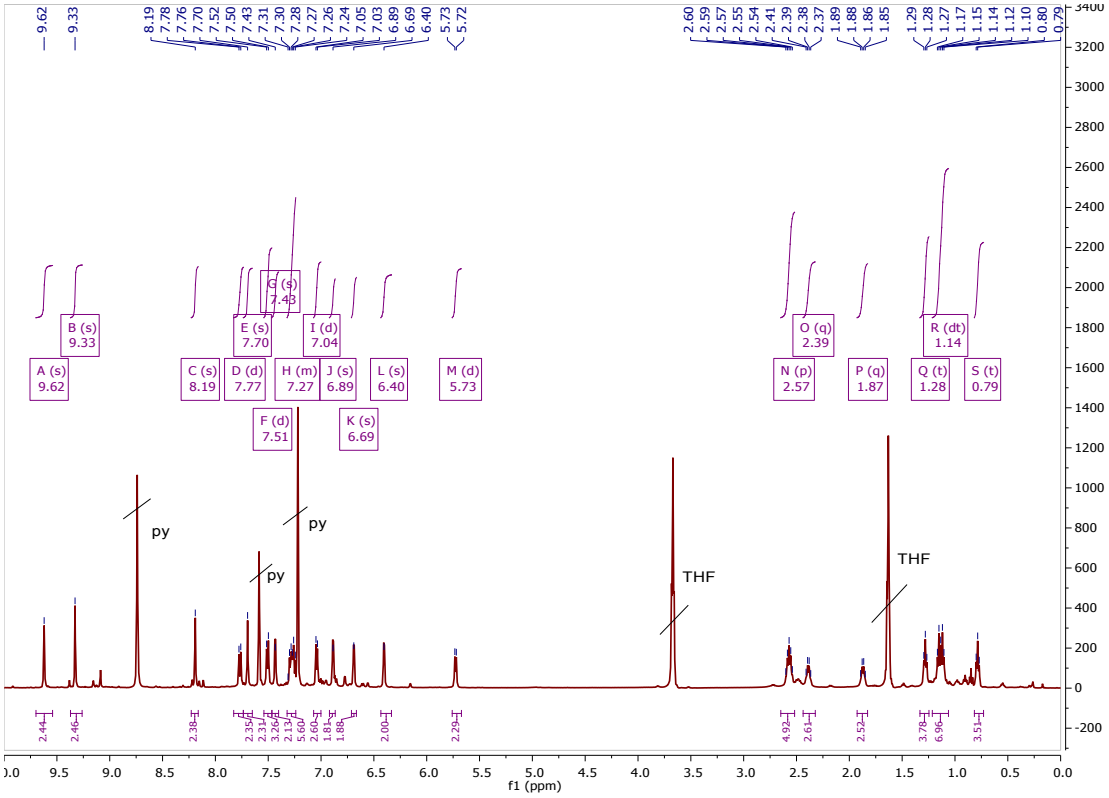
To a solution of $UO_2(H_2L^{Me})$ (10 mg, 9.4 µmol) in d_5-pyridine (ca. 0.5 mL) was added a solution of $Ge\{N(SiMe_3)_2\}_2$ (5.9 mg, 0.94 µmol) in d_5-pyridine (ca. 0.5 mL). ^{1}H NMR showed only starting material at room temperature. Minor paramagnetic resonances appeared after heating to 80°C for long periods however upon heating to 125°C for 24h resonances appeared which were attributed to the previously synthesised $[(Me_3Si)OUOH_2L^{Me}]$.[1]

2. ^{1}H NMR spectra

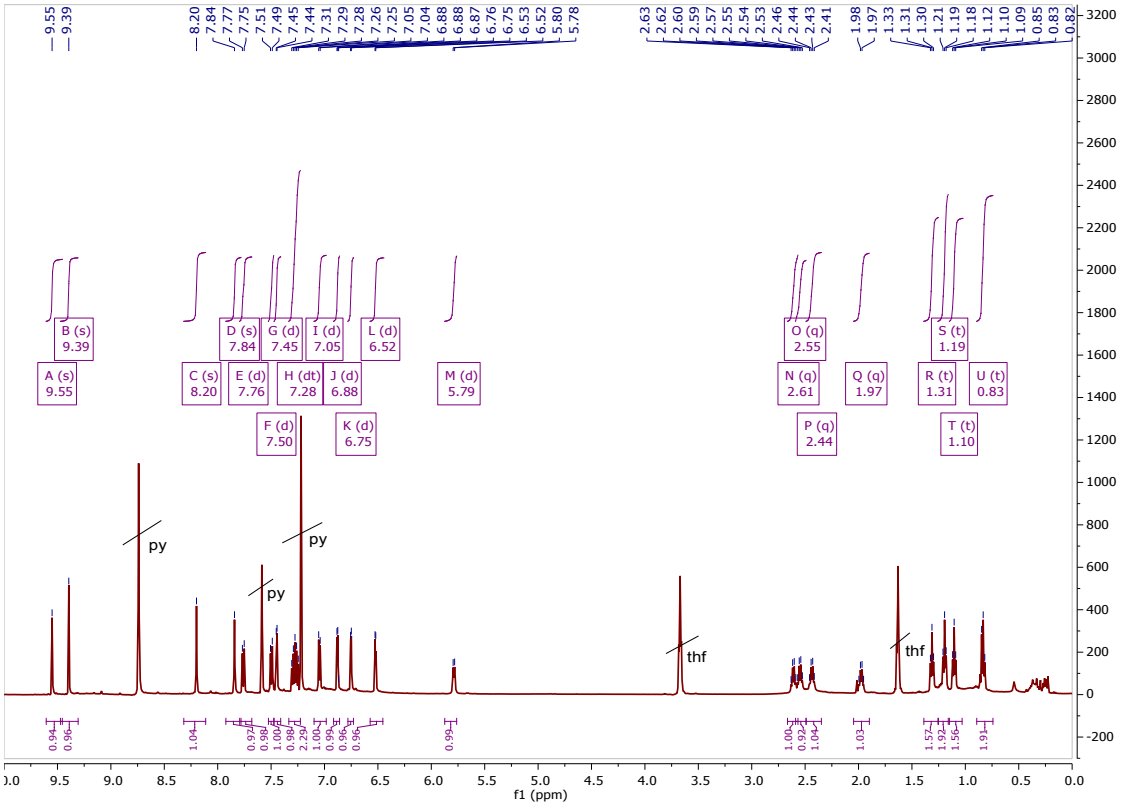
2.1 Spectrum of 1(Ge) in d_5-pyridine



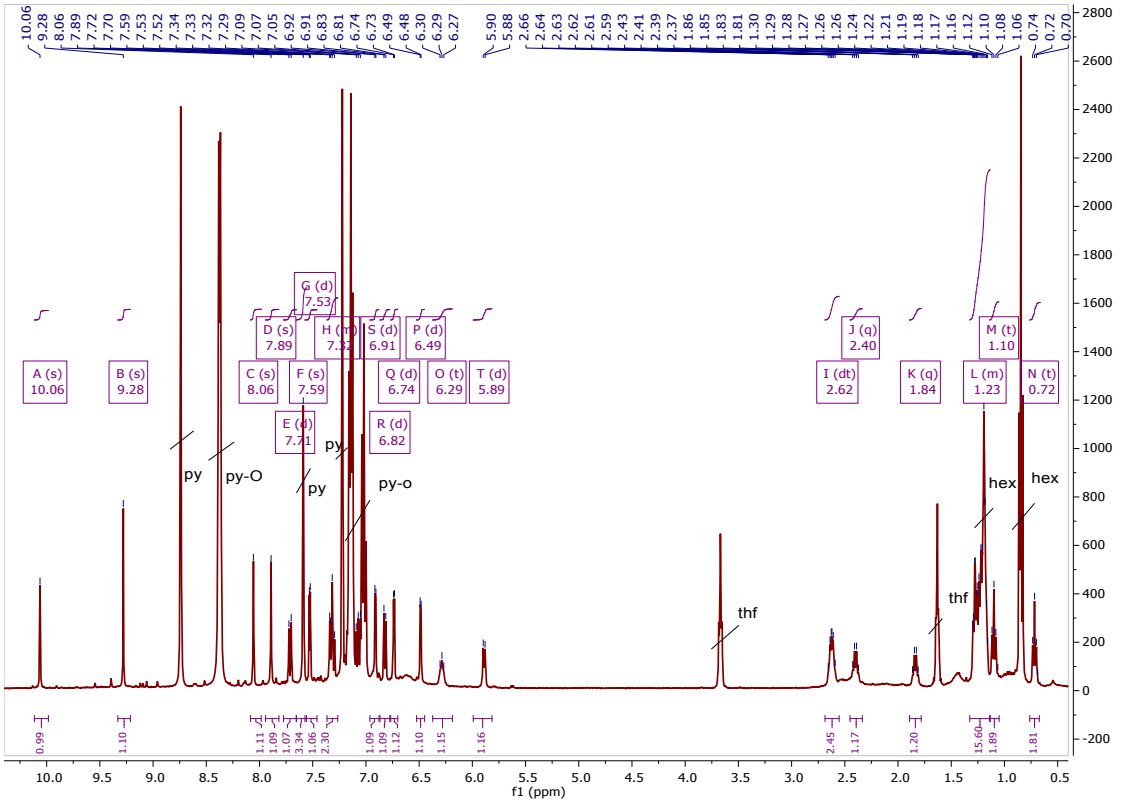
2.2 Spectrum of 1(Sn) in d_5-pyridine



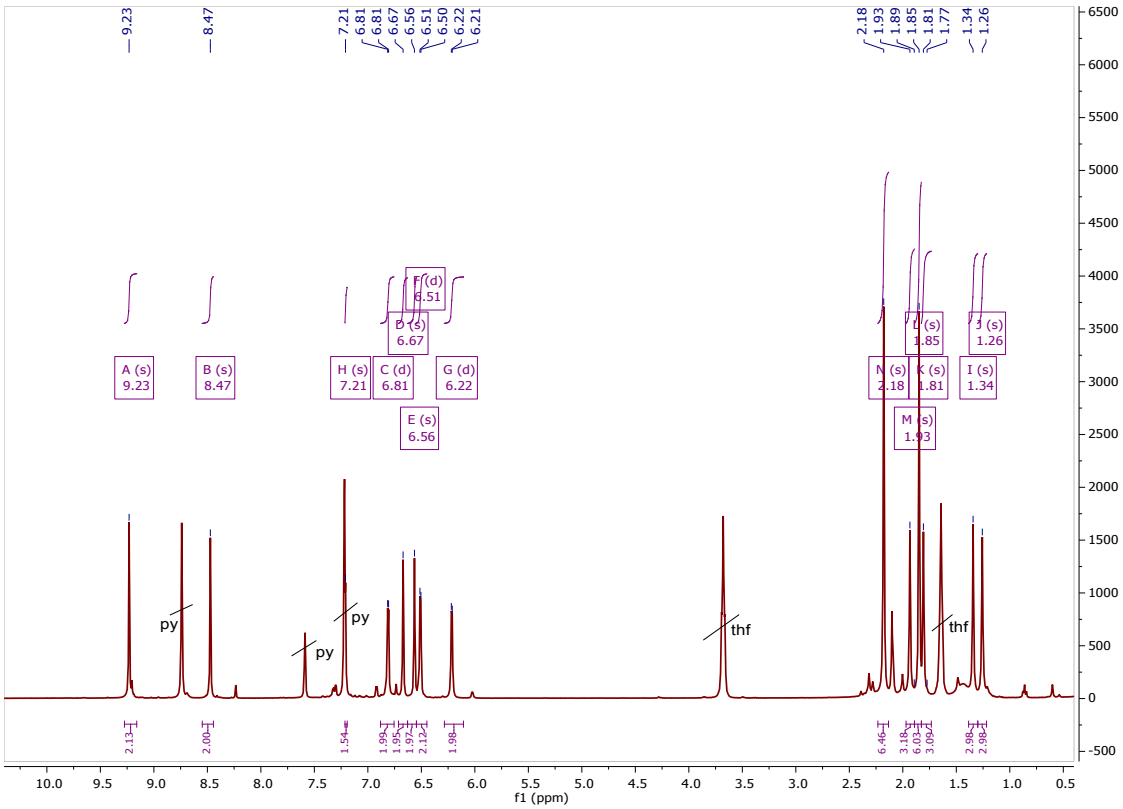
2.3 Spectrum of 1(Pb) in d_5-pyridine



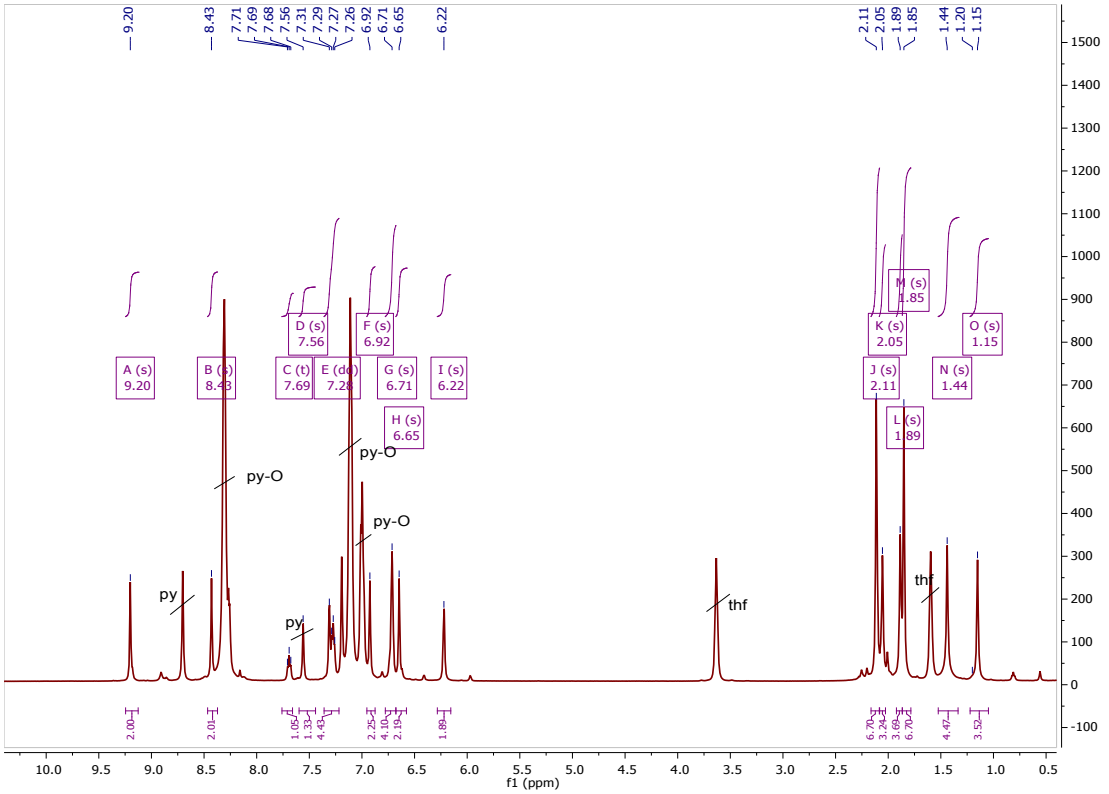
2.4 Spectrum of 2(Pb) in d_5-pyridine



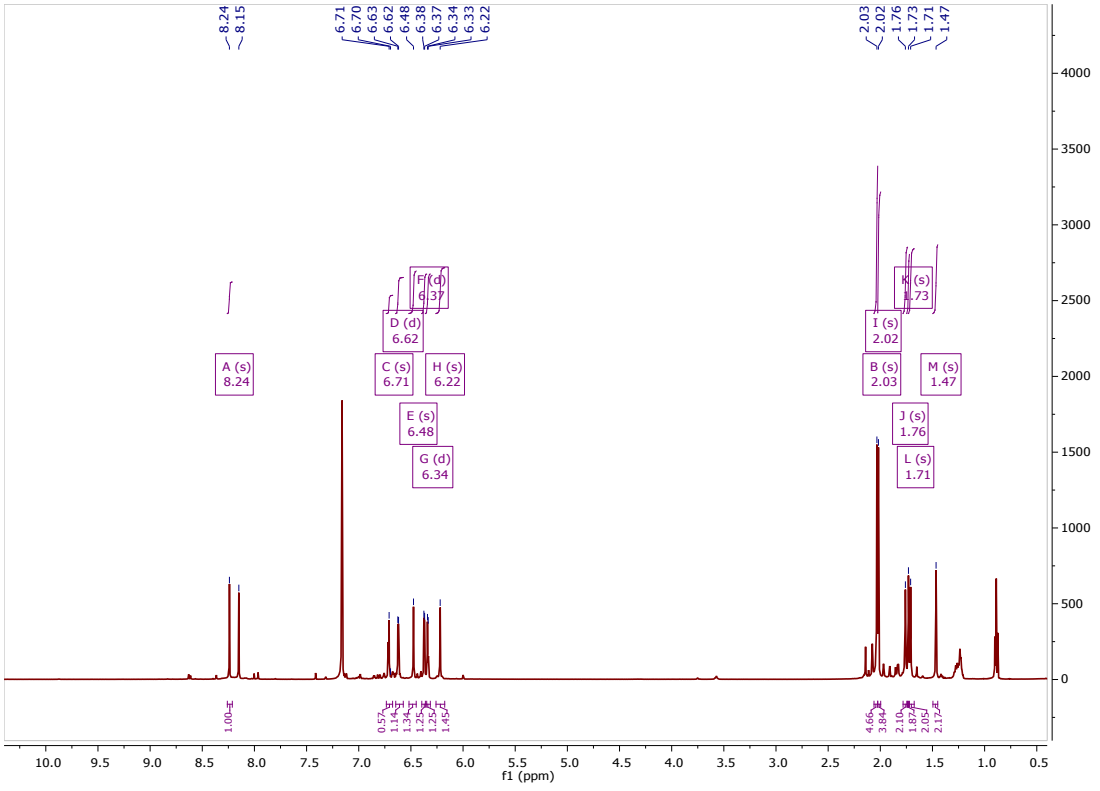
2.5 Spectrum of 3(Pb) in d_5-pyridine



2.6 Spectrum of 4(Pb) in d_5-pyridine



2.7 Spectrum of 5 in C_6D_6



3. X-ray crystal structures

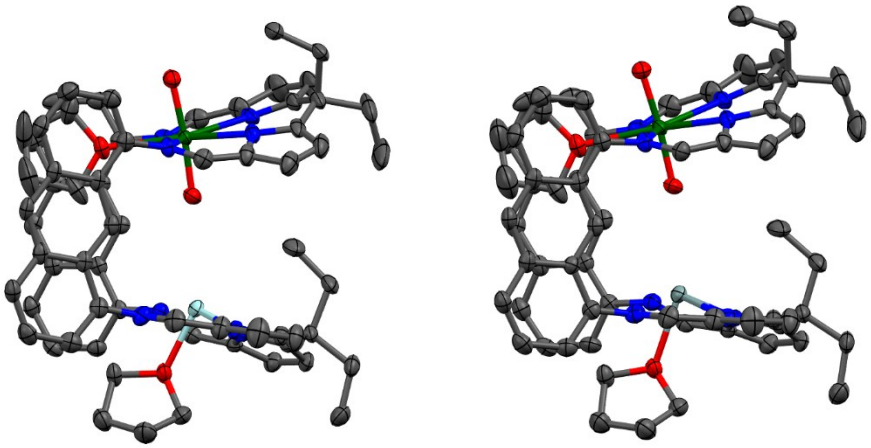


Figure S1: Solid state structure of **1(Ge)-thf** (left) and **1(Sn)-thf** (right). For clarity, hydrogen atoms, disordered carbon atoms and one THF molecule solvent are omitted (displacement ellipsoids are drawn at 50% probability). Atom colours: green = uranium; blue = nitrogen; red = oxygen; light grey = Group 14 element; dark grey = carbon.

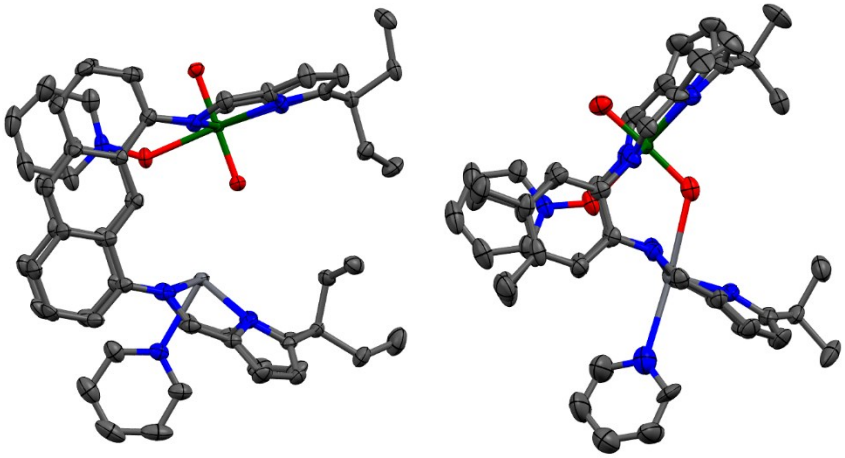


Figure S2: Solid state structure of **2(Pb)-py** (left) and **4(Pb)-py** (right). For clarity, hydrogen atoms and pyridine solvent (for **2(Pb)-py**) are omitted (displacement ellipsoids are drawn at 50% probability). Atom colours: green = uranium; blue = nitrogen; red = oxygen; light grey = lead; dark grey = carbon.

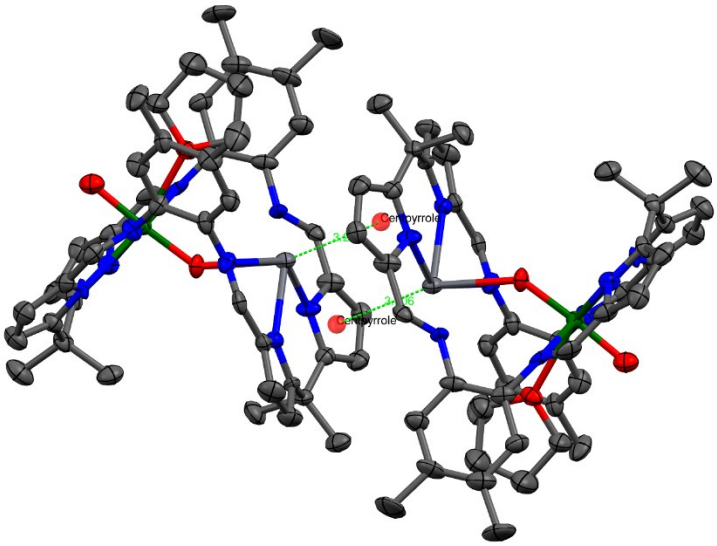


Figure S3: Expanded view of the solid state structure of **3(Pb)-thf** showing an interaction between the lead atom of one molecule and the pyrrole ring of the adjacent ligand. Pb…$Ct_{pyrrole}$ 3.20 Å. Atom colours: green = uranium; blue = nitrogen; red = oxygen; light grey = lead; dark grey = carbon.

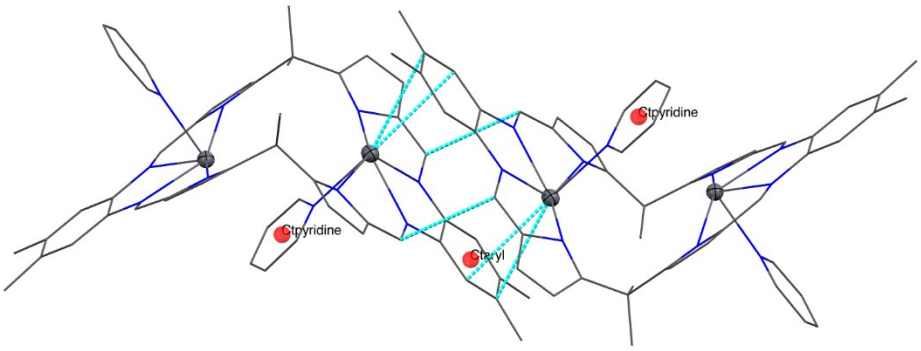


Figure S4: Expanded view of the solid state structure of **5** showing two π-interactions between the lead atoms and either solvent pyridine or the aryl group of an adjacent molecule. Pb…$Ct_{ppyridine}$ 3.42 Å, Pb…Ct_{aryl} 3.23 Å. Atom colours: blue = nitrogen; light grey = lead; dark grey = carbon.

4. Experimental details for X-ray crystallography

X-ray diffraction data were recorded all on an Excalibur Eos diffractometer at 170(2) K using Mo Kα radiation.[2] All structures were solved using SHELXT[3] and least-square refined using SHELX-14[4] in Olex2.[5] All non-hydrogen atoms refined with anisotropic displacement parameters and H parameters were constrained to parent atoms. Structures **2(Ge)-thf** and **2(Sn)-thf** contained disordered ligand ethyl groups which were treated with the PART command and their occupancies refined freely. Structure **2(Pb)-thf** was refined as a two component twin in $P^{-}1$.[6] Structures **2(Pb)-py**, **2(Pb)-thf**, **3(Pb)-py** and **4(Pb)-py** were all treated using the SQUEEZE function of Platon[7] to remove 78 (2 pyridine molecules), 144 (2 benzene and 1.5 thf molecules), 362 (9 pyridine molecules) and 430 electrons respectively (10 pyridine molecules) per unit cell. In **5** one free pyridine solvent molecule (containing N69) was significantly disordered and was heavily restrained.

Table S1: Experimental details for XRD

	1(Ge)-thf	1(Sn)-thf	1(Pb)-thf	2(Pb)-py	2(Pb)-thf
Chemical formula	$C_{66}H_{64}GeN_8O_4U{\cdot}C_4H_8O$	$C_{66}H_{64}N_8O_4SnU{\cdot}C_4H_8O$	$C_{66}H_{64}N_8O_4PbU{\cdot}C_4H_8O$	$C_{68}H_{58}N_{10}O_3PbU{\cdot}4(C_5H_5N)$	$C_{87}H_{89}N_9O_6PbU$
M_r	1415.97	1461.06	1551.08	1824.86	1801.89
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
Temperature (K)	170	170	170	170	170
a, b, c (Å)	11.44279 (12), 22.2890 (2), 24.0677 (2)	11.4369 (2), 22.3418 (4), 24.1875 (4)	22.7520 (2), 22.2812 (2), 24.1927 (3)	13.4766 (2), 14.4442 (2), 23.4695 (3)	22.2550 (3), 16.4556 (3), 23.0701 (4)
α, β, γ (°)	90, 98.0274 (10), 90	90, 97.5479 (16), 90	90, 97.5987 (10), 90	97.652 (1), 97.141 (1), 110.056 (1)	90, 105.360 (2), 90
V (Å^3)	6078.29 (10)	6126.84 (19)	12156.6 (2)	4181.79 (10)	8146.9 (2)
Z	4	4	8	2	4
μ (mm^{-1})	3.22	3.11	5.49	4.00	4.11
Crystal size (mm)	0.3 × 0.19 × 0.11	0.50 × 0.26 × 0.25	0.56 × 0.26 × 0.10	0.38 × 0.32 × 0.18	0.40 × 0.30 × 0.06
T_{min}, T_{max}	0.838, 0.931	0.307, 0.498	0.749, 0.936	0.094, 0.289	0.976, 0.996
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	139112, 13933, 11376	135432, 13495, 11216	332738, 27853, 20316	19171, 19171, 15630	124254, 16651, 12622
R_{int}	0.056	0.068	0.074	0.040	0.072
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.641	0.649	0.649	0.625
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.070, 1.07	0.036, 0.123, 0.91	0.038, 0.142, 0.97	0.029, 0.072, 1.05	0.040, 0.086, 1.06
No. of reflections	13933	13495	27853	19171	16651
No. of parameters	790	790	1539	968	917
No. of restraints	60	120	240	207	34
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.32, -0.59	1.52, -0.59	1.69, -1.87	1.92, -0.72	1.36, -0.72
CCDC	1480061	1480064	1480093	1480062	1480069

	3(Pb)-thf	**3(Pb)-py**	**4-py**	**5**
Chemical formula	$C_{46}H_{48}N_8O_3PbU$	$C_{52}H_{50}N_{10}O_2PbU$	$C_{52}H_{50}N_{10}O_3PbU$	$C_{52}H_{50}N_{10}Pb_2{\cdot}2(C_5H_5N)$
M_r	1206.14	1292.24	1308.24	1387.60
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Triclinic, $P\bar{1}$
Temperature (K)	170	170	170	170
a, *b*, *c* (Å)	12.9064 (4), 14.3173 (3), 17.8924 (5)	10.8424 (3), 15.8907 (3), 33.2881 (8)	13.4429 (2), 19.5975 (3), 21.9112 (4)	11.5029 (3), 13.3149 (3), 17.9962 (6)
α, β, γ (°)	106.269 (2), 97.424 (2), 101.336 (2)	90, 90, 90	90, 90, 90	90.548 (2), 90.690 (2), 99.117 (2)
V (Å^3)	3051.71 (15)	5735.3 (2)	5772.42 (16)	2721.10 (13)
Z	2	4	4	2
μ (mm^{-1})	5.44	5.80	5.76	6.23
Crystal size (mm)	0.40 × 0.27 × 0.03	0.12 × 0.12 × 0.05	0.47 × 0.18 × 0.10	0.46 × 0.21 × 0.05
T_{min}, T_{max}	0.678, 1.000	0.522, 0.772	0.502, 1.000	0.564, 0.891
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	29521, 29521, 20366	11715, 11715, 8552	68331, 13223, 11200	23523, 11982, 9191
R_{int}	0.074	0.181	0.061	0.035
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.707	0.625	0.649	0.649
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.074, 0.204, 1.12	0.083, 0.158, 1.07	0.039, 0.085, 1.05	0.047, 0.154, 1.02
No. of reflections	29521	11715	13223	11982
No. of parameters	541	591	612	693
No. of restraints	83	507	132	122
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	4.38, -2.92	2.59, -1.26	3.43, -2.33	2.70, -1.31
Absolute structure	–	Flack x determined using 2540 quotients [(I+)-(I-)]/[(I+)+(I-)]	Flack x determined using 4427 quotients [(I+)-(I-)]/[(I+)+(I-)]	–
Absolute structure parameter	–	-0.013 (7)	-0.001 (4)	–
CCDC	1480065	1480068	1480066	1480063

5. IR Spectra

All IR spectra were run as either a Nujol mull with a subtracted air background or as solutions in C_6H_6 with a subtracted solvent background. The UO_2 asymmetric stretch was assigned (and bolded) where possible.

Chart S1: Solid state IR spectrum of **1(Ge)-thf** as a Nujol mull

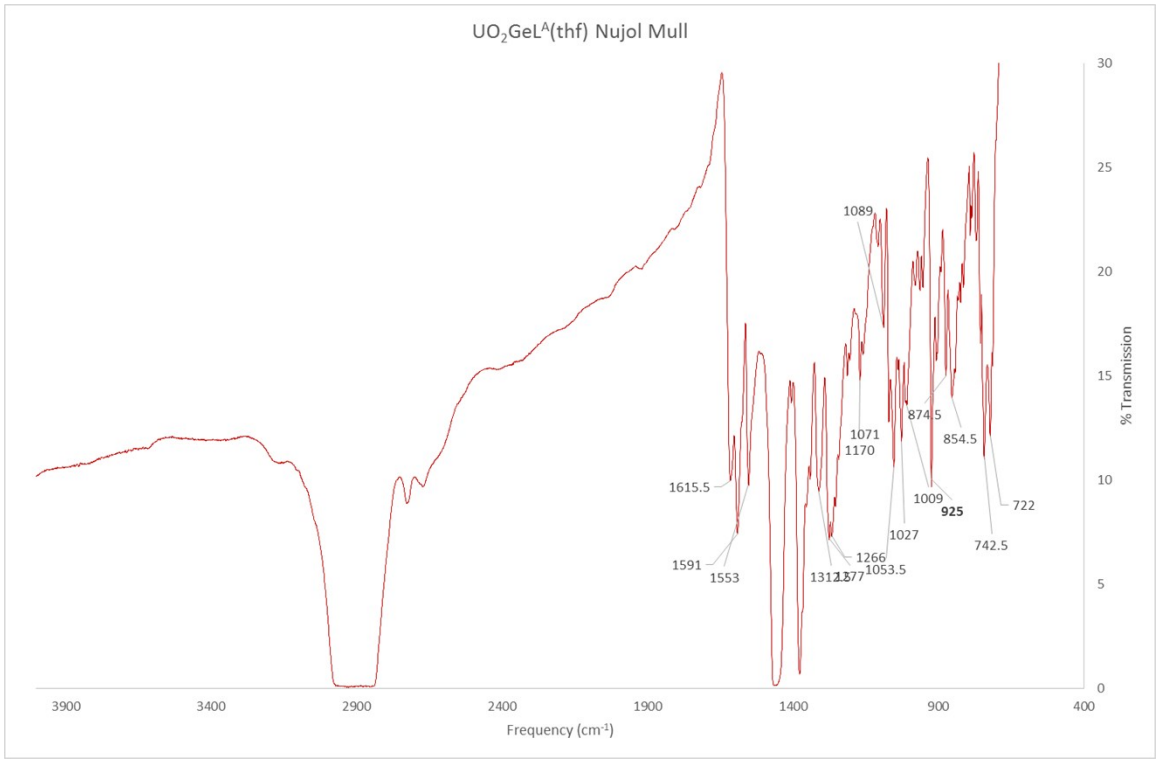


Chart S2: Solution state IR spectrum of 1(Ge)-thf in C_6H_6

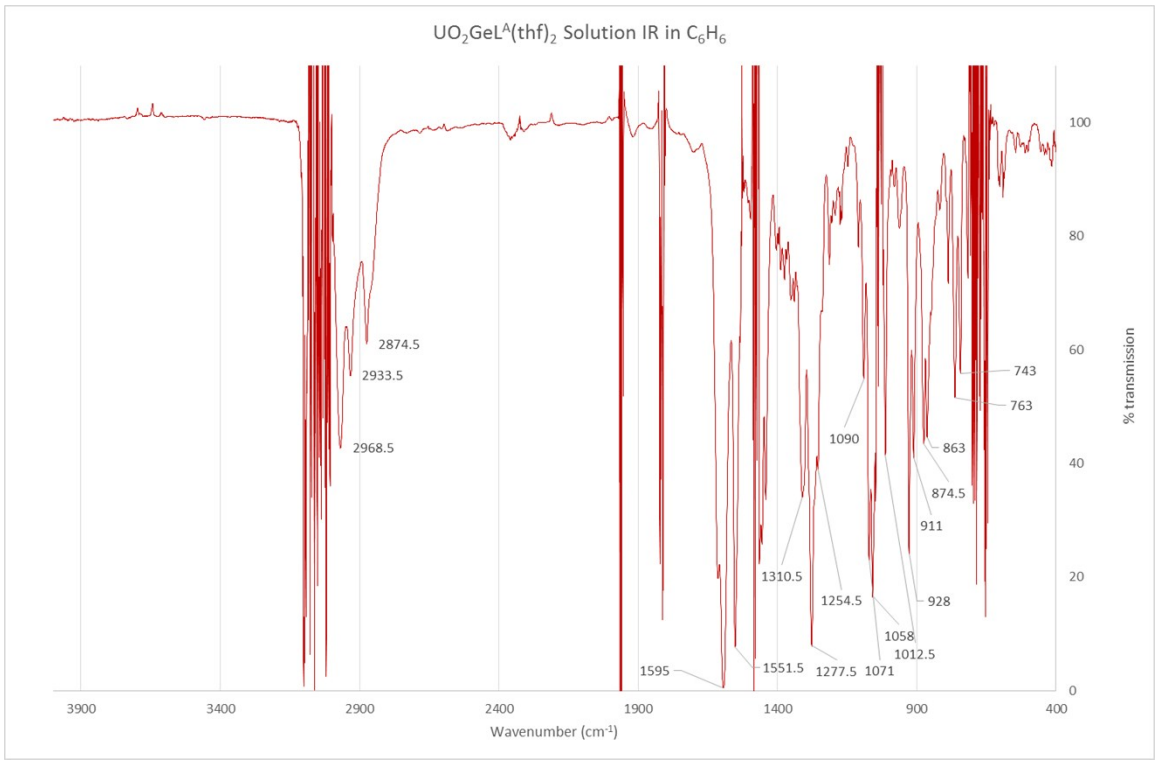


Chart S3: Solid state IR spectrum of **1(Sn)-thf** as a Nujol mull

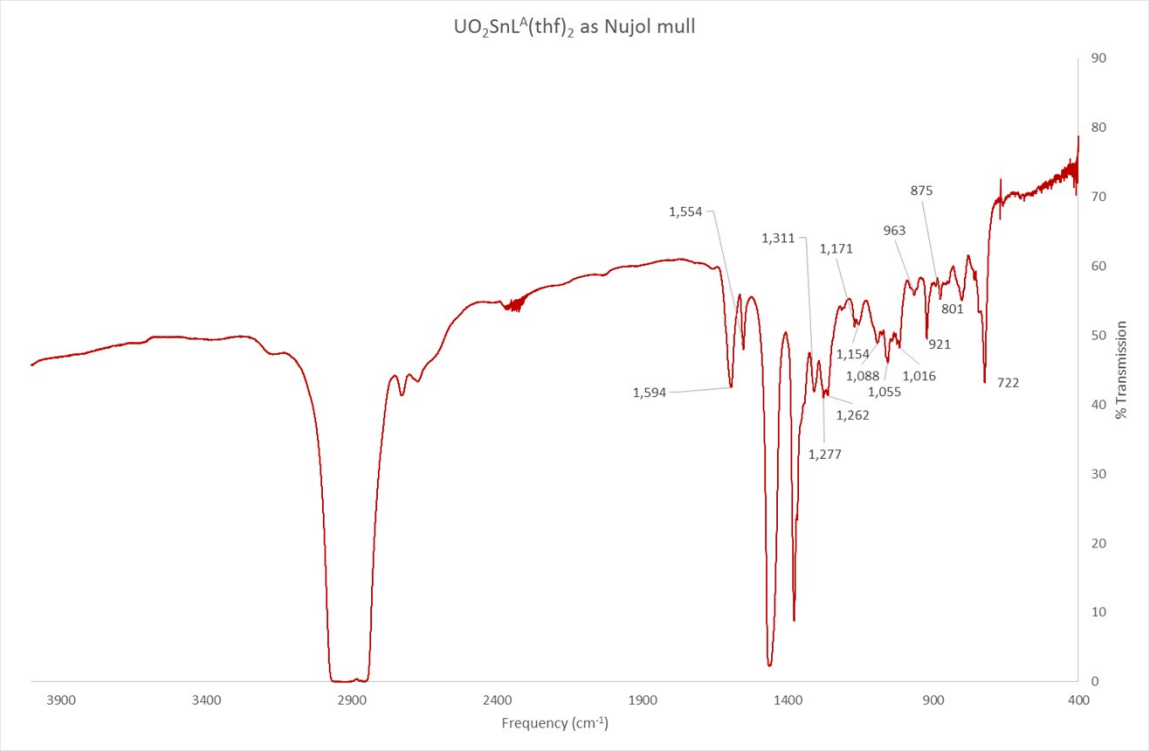


Chart S4: Solution state IR spectrum of **1(Sn)-thf** in C_6H_6

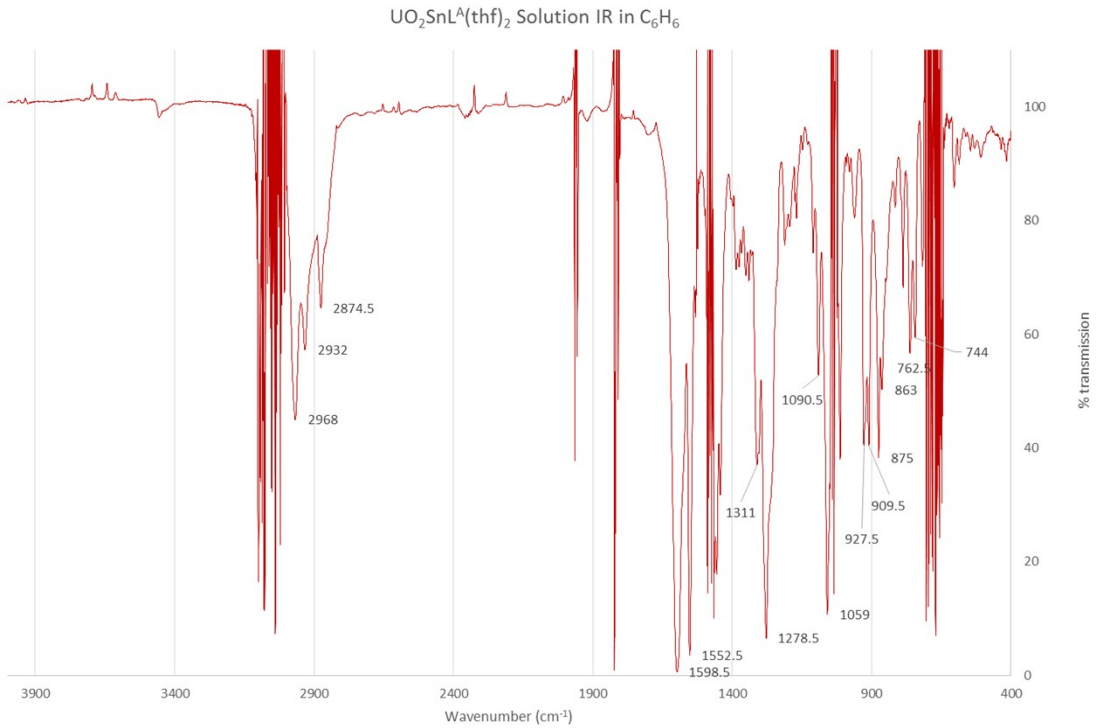


Chart S5: Solution state IR spectrum of **1(Pb)-thf** in C_6H_6

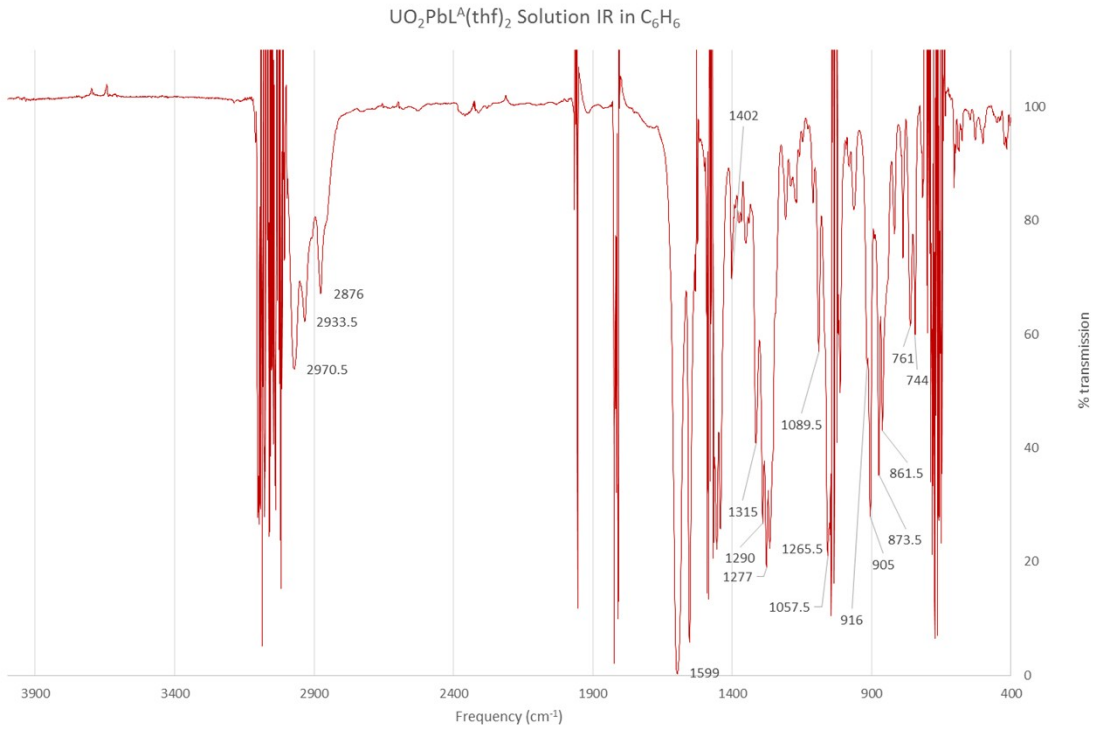


Chart S6: Overlay of the solution state IR spectra of **1(M)-thf** complexes and (thf)$UO_2(H_2L^A)$ showing UO_2 stretching region.

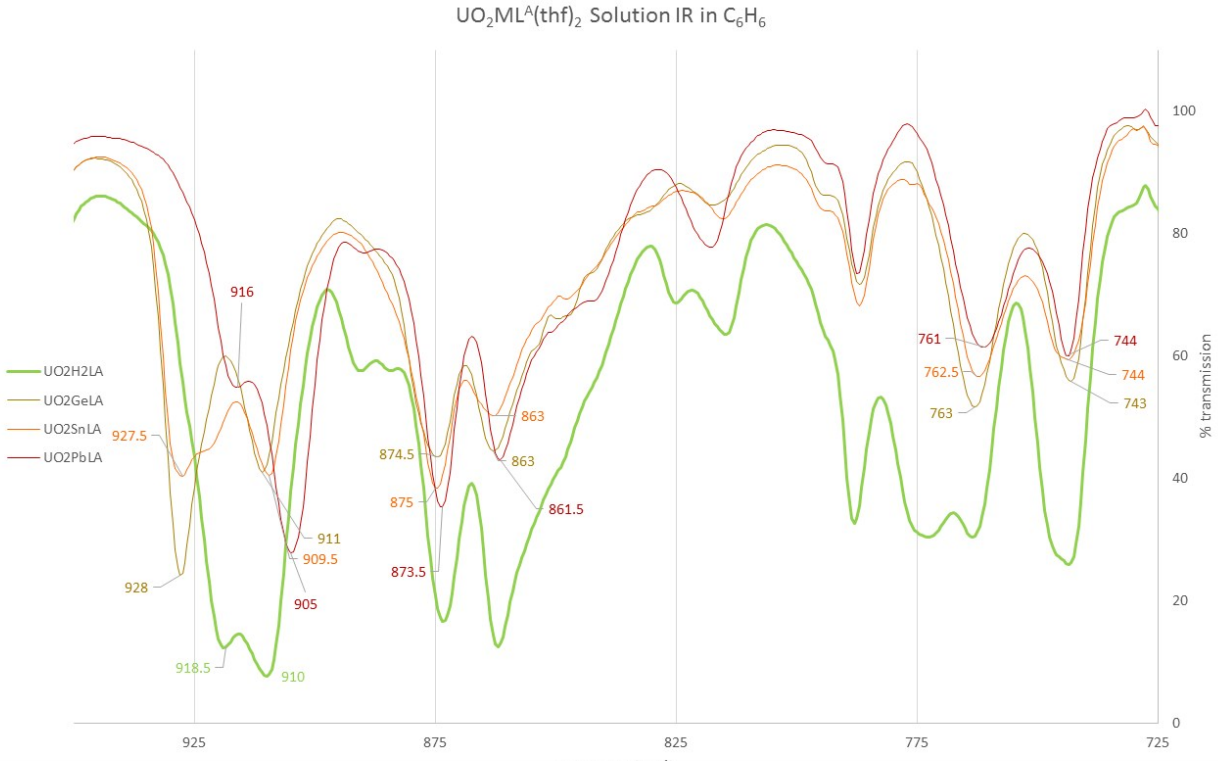


Chart S7: IR spectrum of **2(Pb)-py** as a Nujol mull

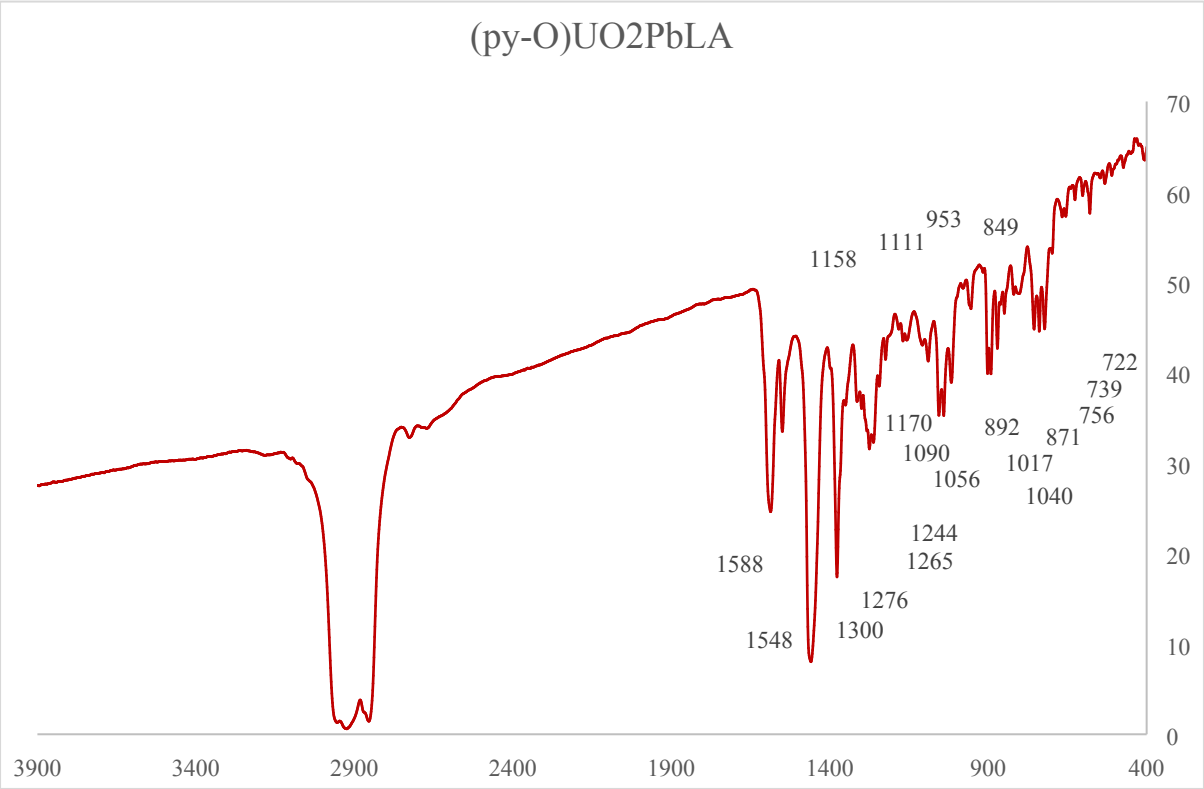


Chart S8: IR spectrum of **3(Pb)-py** as a Nujol mull.

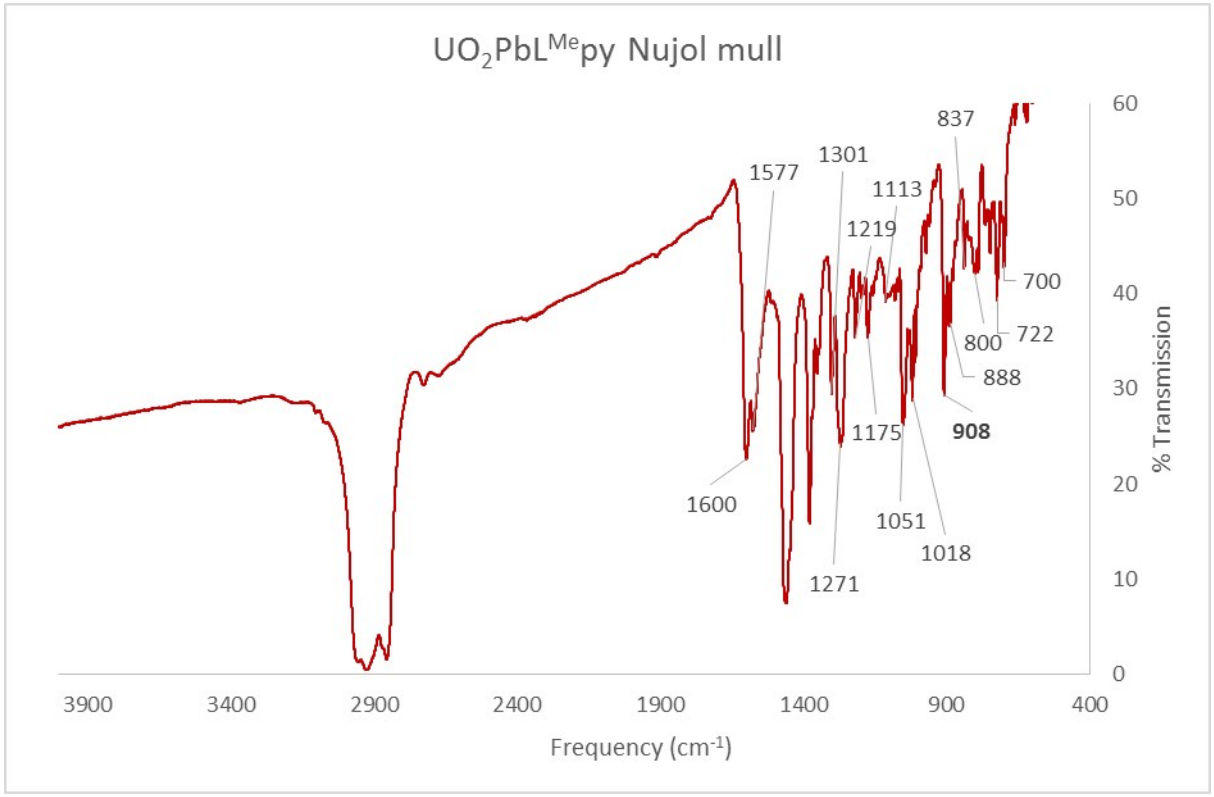


Chart S9: IR spectrum of **3(Pb)-thf** as a Nujol mull.

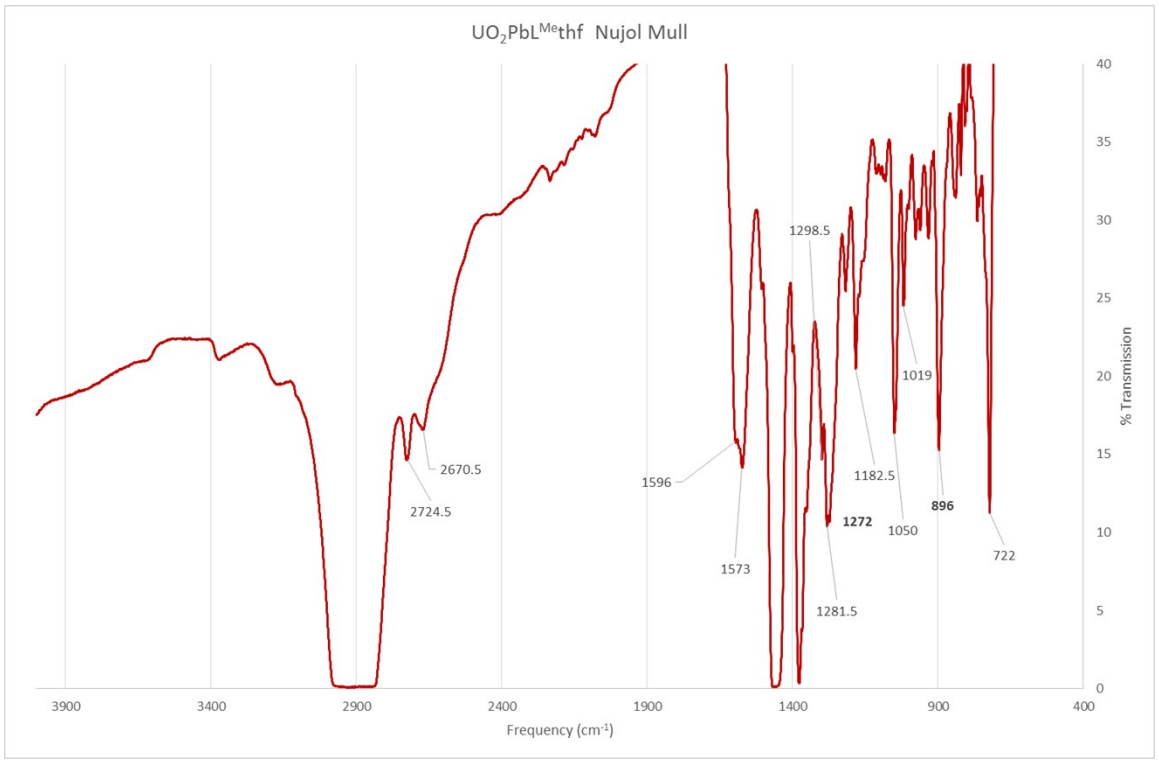
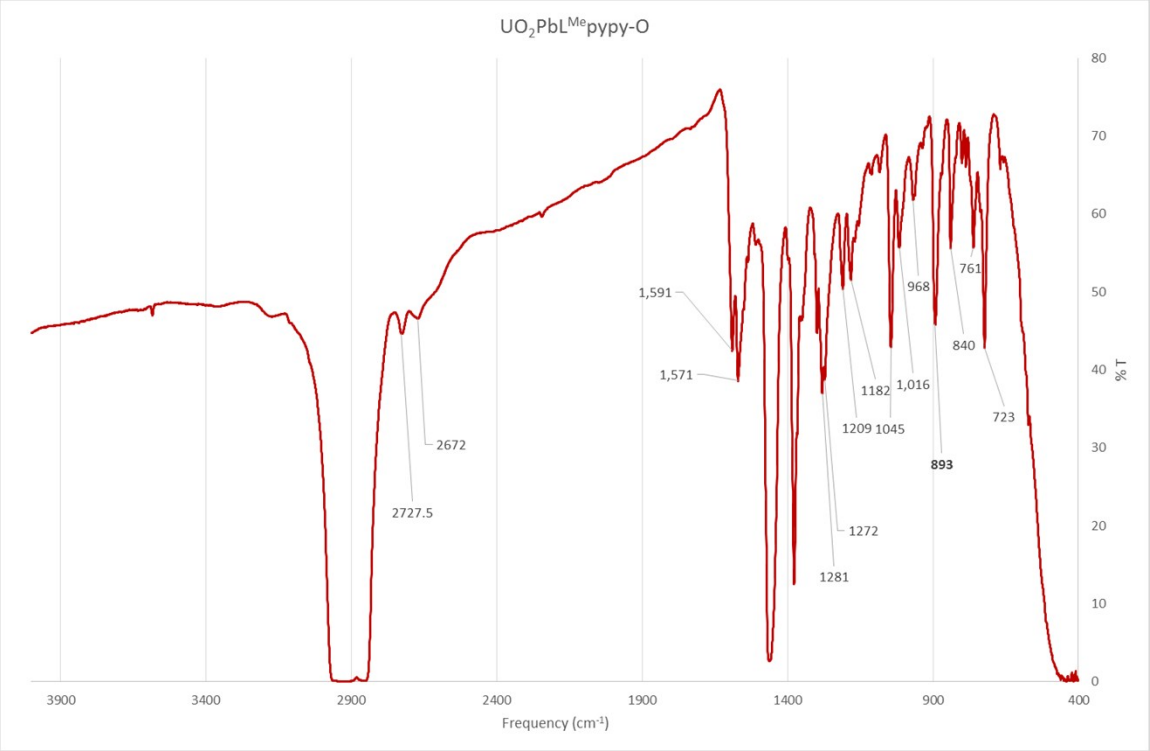


Chart S10: IR spectrum of **4(Pb)-py** as a Nujol mull.



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