Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Combining coordination and supramolecular chemistry to explore uranyl assembly in the solid state

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I. Additional Figures

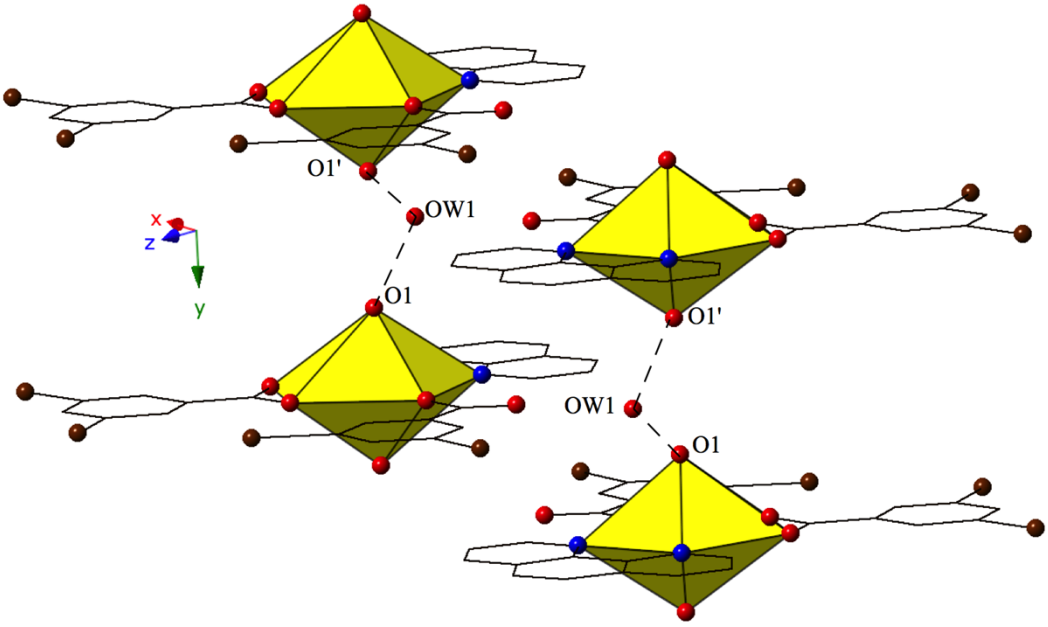

Figure S1: Complex **3** shown down the [010] direction highlighting the hydrogen bonding interactions that decorate the 1D chain of uranyl monomers.

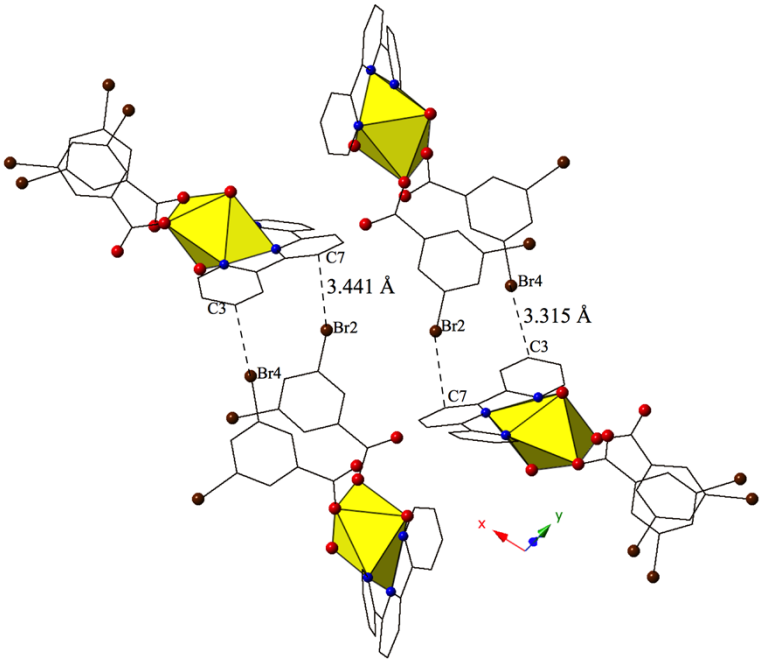

Figure S2: Complex **7** viewed down approximately the [110] direction highlighting the localized Br-π interactions that assemble neighboring uranyl monomers.

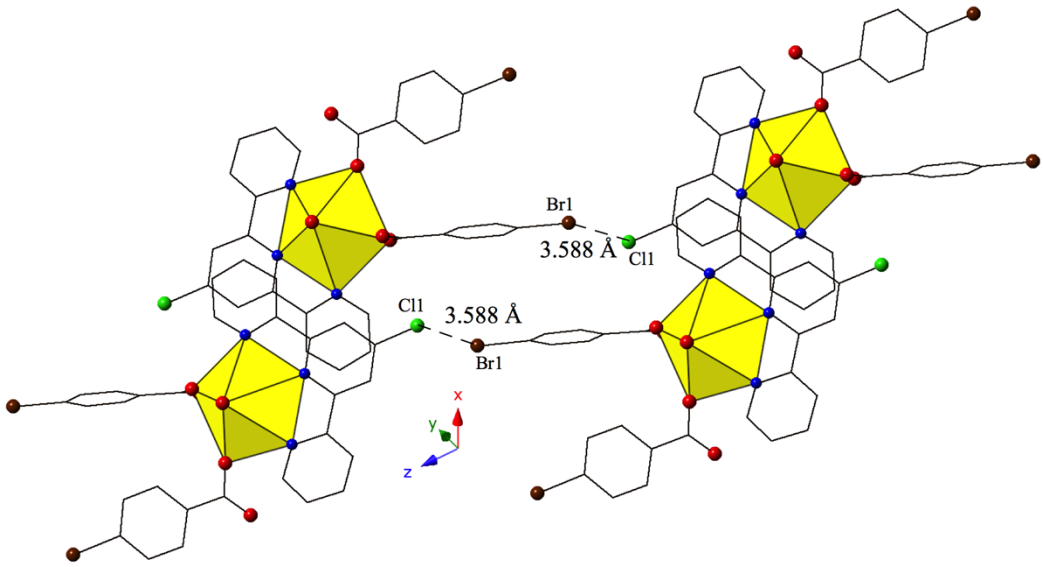

Figure S3: Complex **10** viewed down approximately the [011] direction highlighting the Type I Br-Cl interaction that links neighboring uranyl monomers.

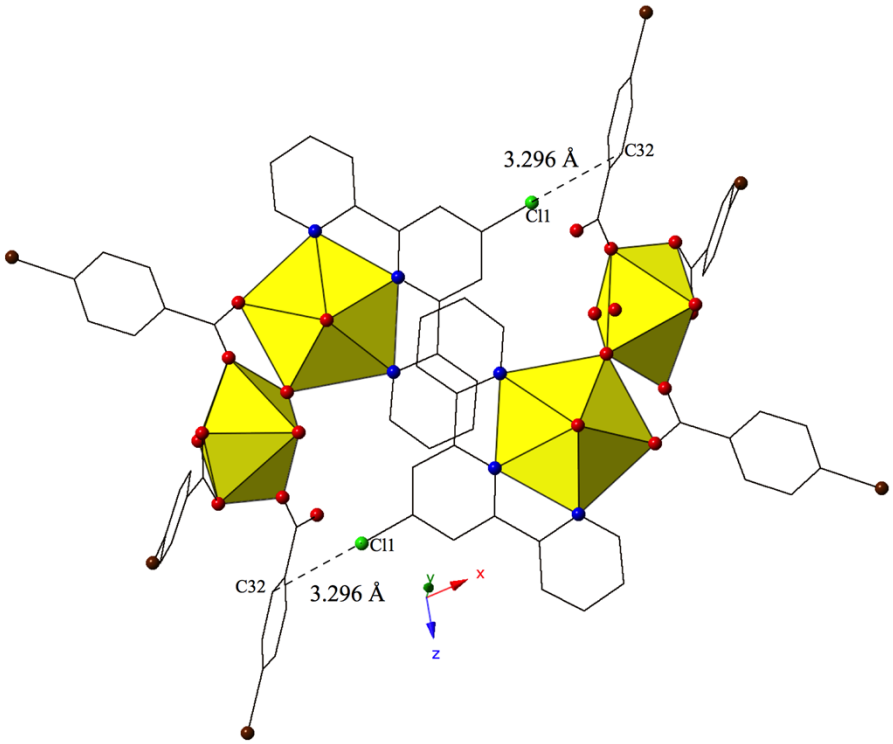

Figure S4: Complex **12** viewed along approximately the [100] direction highlighting the localized Cl-π interaction that links adjacent uranyl dimers.

II. Powder X-ray diffraction data

For the following PXRD spectra it is important to note that calculated patterns are from low temperature (100K) (complexes **1, 3, 7** and **11)** data collections while observed patterns were collected at room temperature (298 K). This difference may result in slight shifts in two-theta values. For complexes **2, 4-6, 8-10** and **12** calculated and observed patterns were both collected a room temperature (298K).

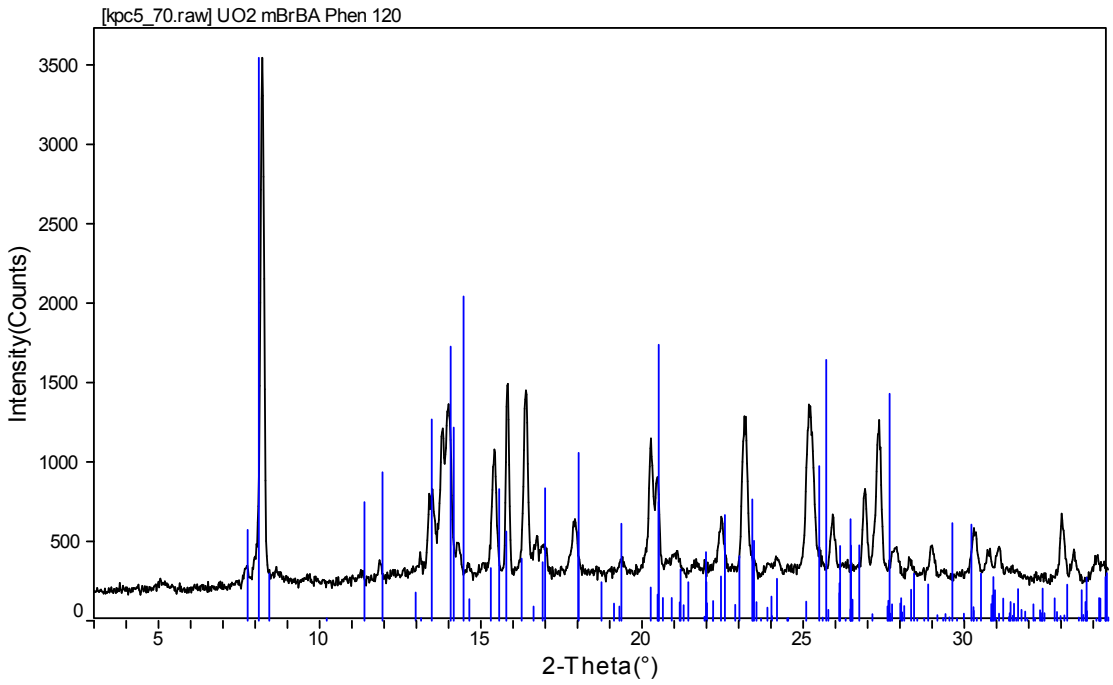

Figure S5: The observed PXRD pattern of structure **1** with calculated pattern overlaid in blue.

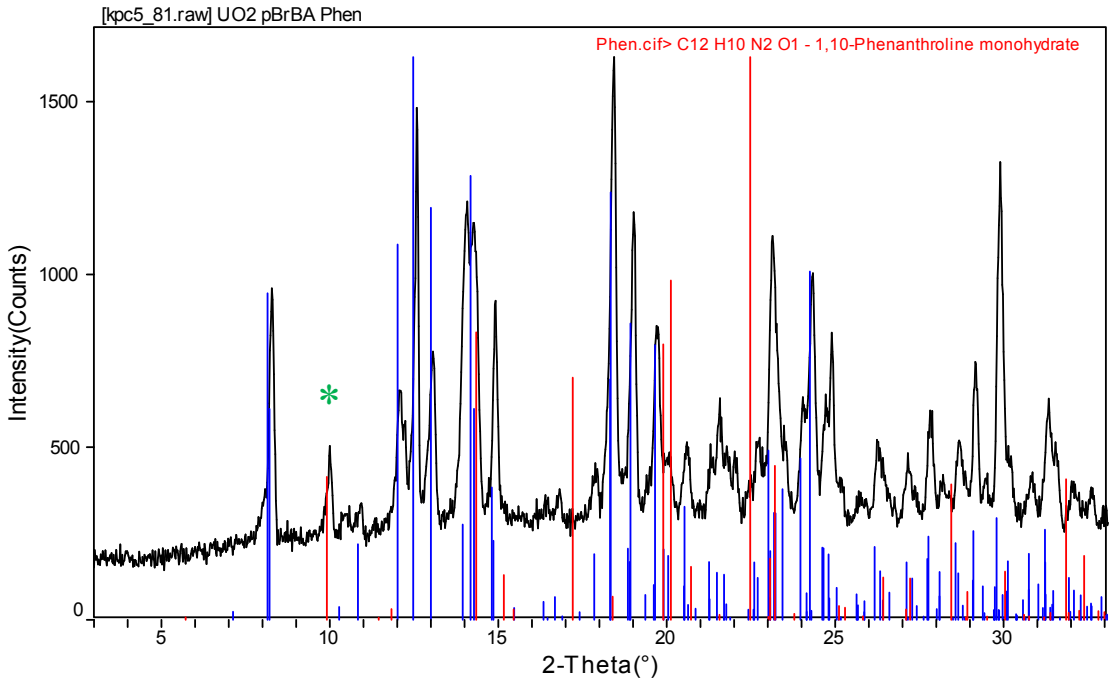

Figure S6: The observed PXRD pattern of structure **2** with calculated pattern overlaid in blue. We acknowledge a minor impurity as indicated with an asterisk and we have identified this impurity as excess 1,10-phenanthroline (calculated CIF overlaid in red).

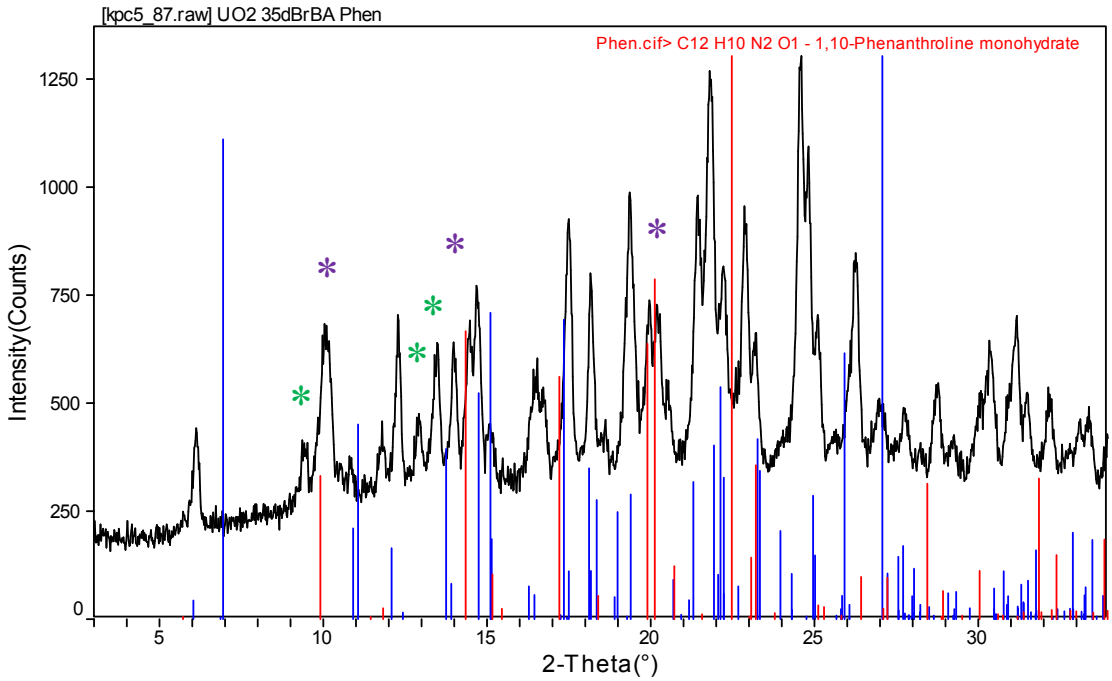

Figure S7: The observed PXRD pattern of structure **3** with calculated pattern overlaid in blue. We acknowledge several impurities in the bulk product. Some of these impurities have been identified as 1,10-phenanthroline (calculated CIF overlaid in red) and these are indicated with purple asterisks. Impurities that could not be identified are indicated with green asterisks.

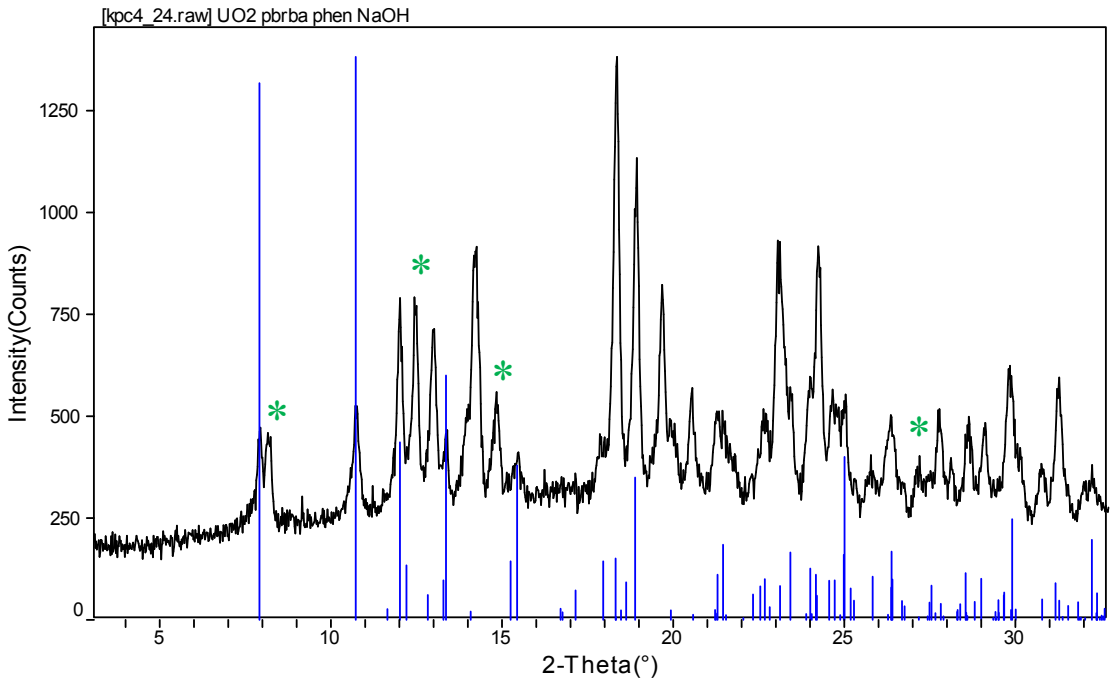

Figure S8: The observed PXRD pattern of structure **4** with calculated pattern overlaid in blue. We acknowledge several impurities as indicated with asterisks.

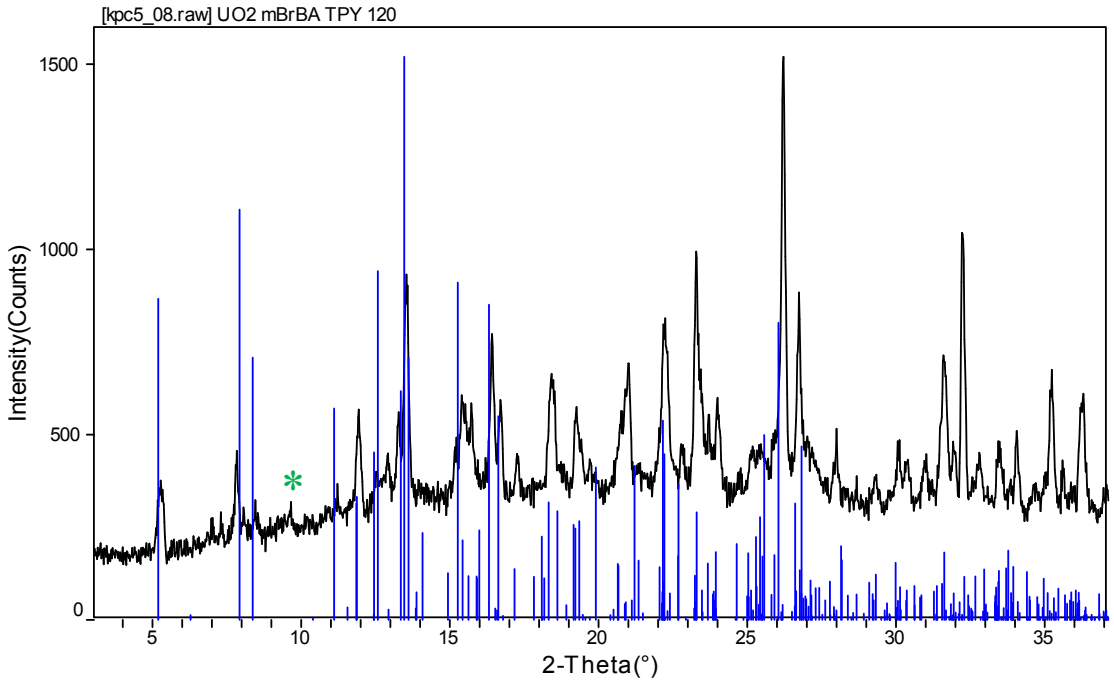

Figure S9: The observed PXRD pattern of structure **5** with calculated pattern overlaid in blue. We acknowledge a minor impurity as indicated with an asterisk.

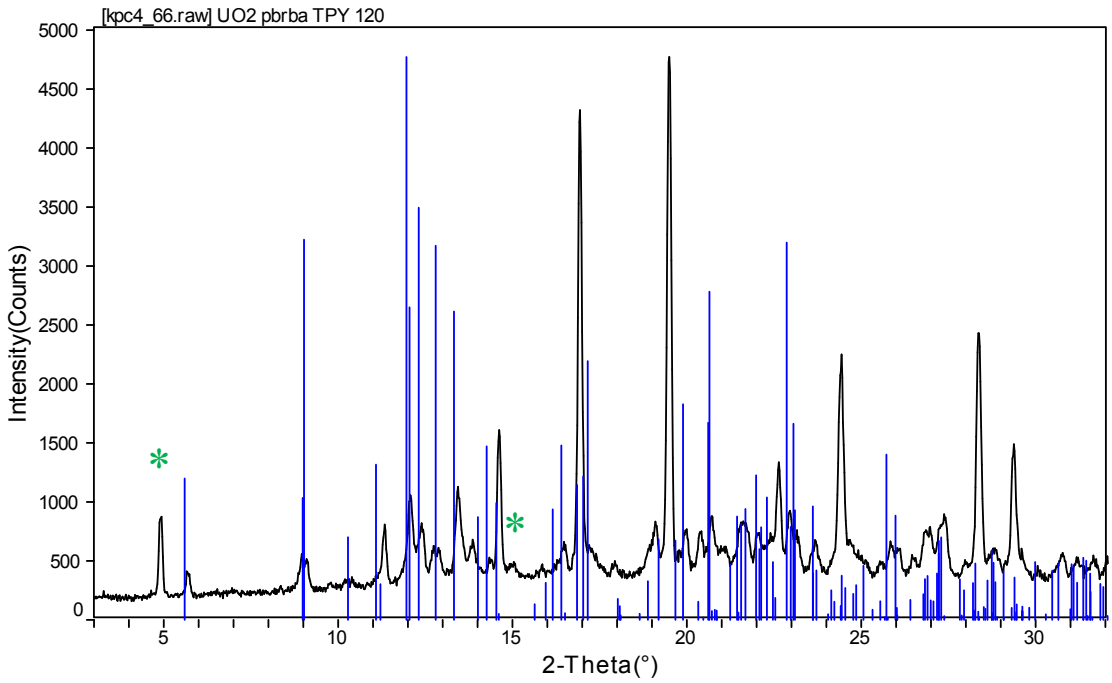

Figure S10: The observed PXRD pattern of structure **6** with calculated pattern overlaid in blue. We acknowledge two minor impurities as indicated with asterisks.

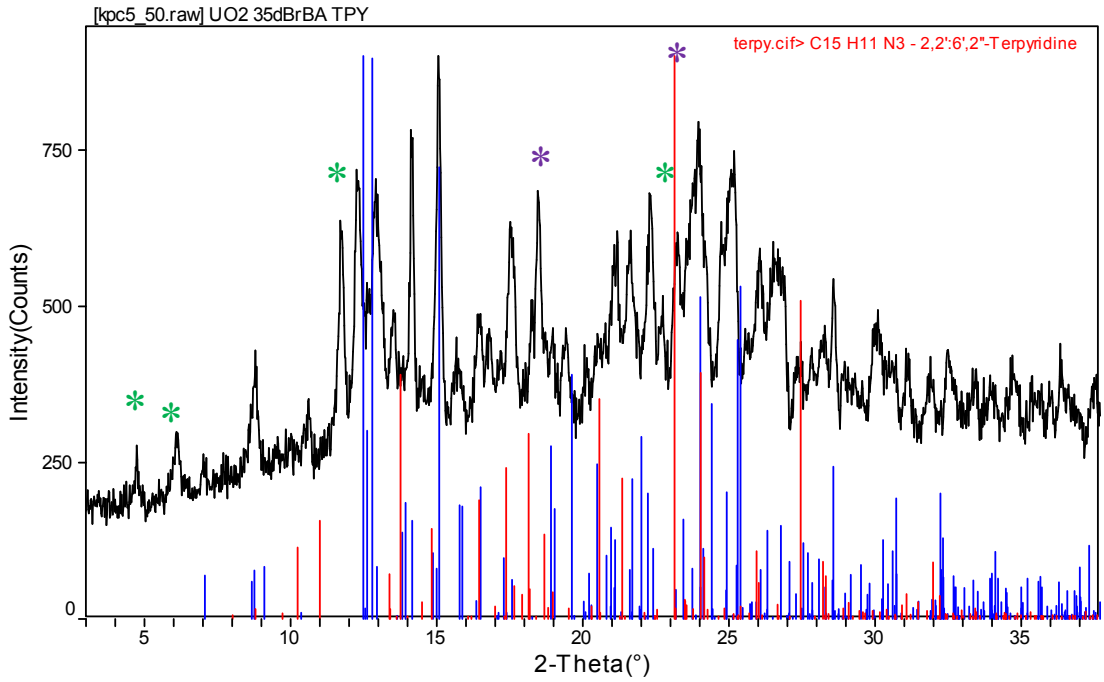

Figure S11: The observed PXRD pattern of structure **7** with calculated pattern overlaid in blue. We acknowledge several impurities in the bulk product. Some of these impurities

have been identified as 2,2':6',2"-terpyridine (calculated CIF overlaid in red) and these are indicated with purple asterisks. Impurities that could not be identified are indicated with green asterisks.

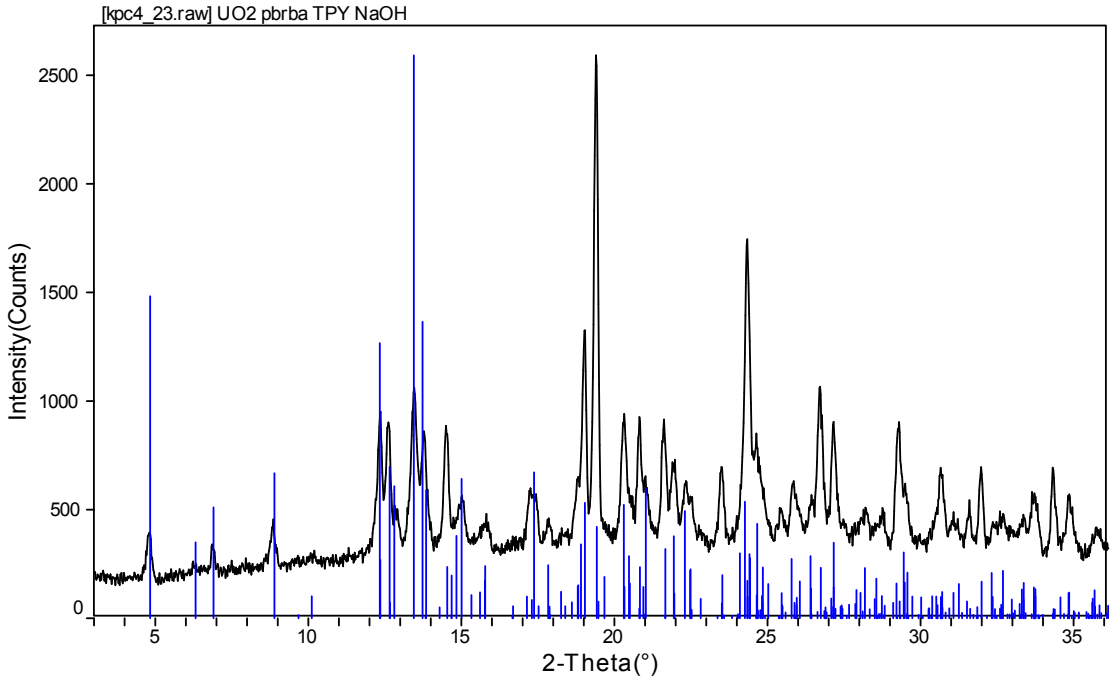

Figure S12: The observed PXRD pattern of structure **8** with calculated pattern overlaid in blue.

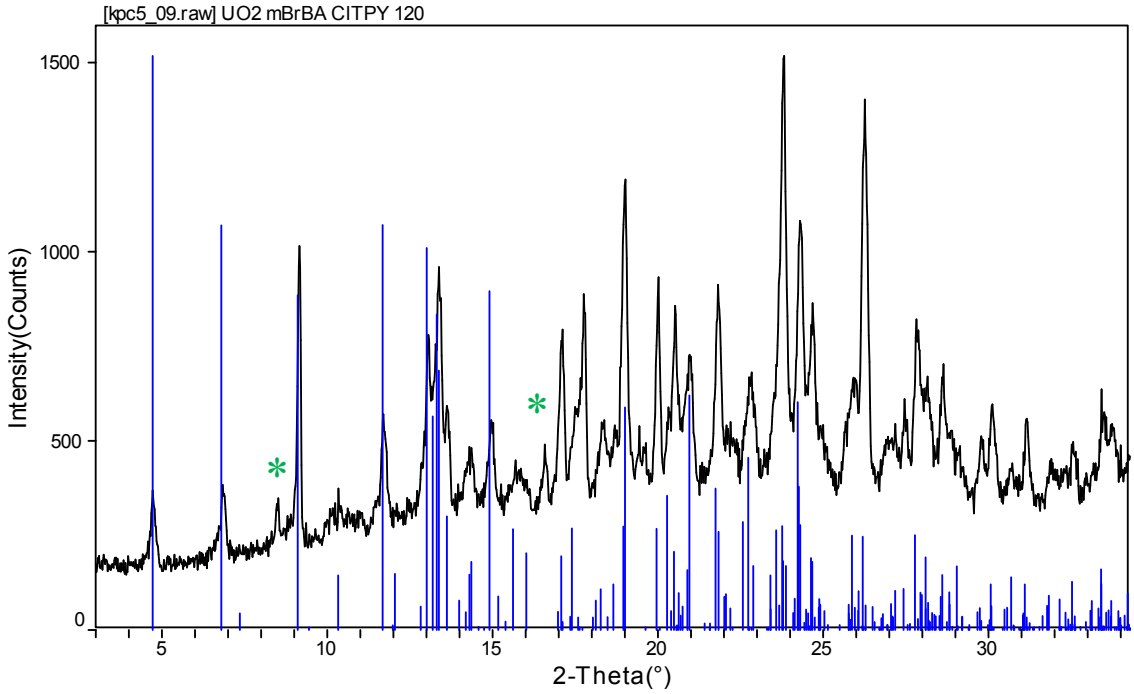

Figure S13: The observed PXRD pattern of structure **9** with calculated pattern overlaid in blue. We acknowledge two minor impurities as indicated with asterisks.

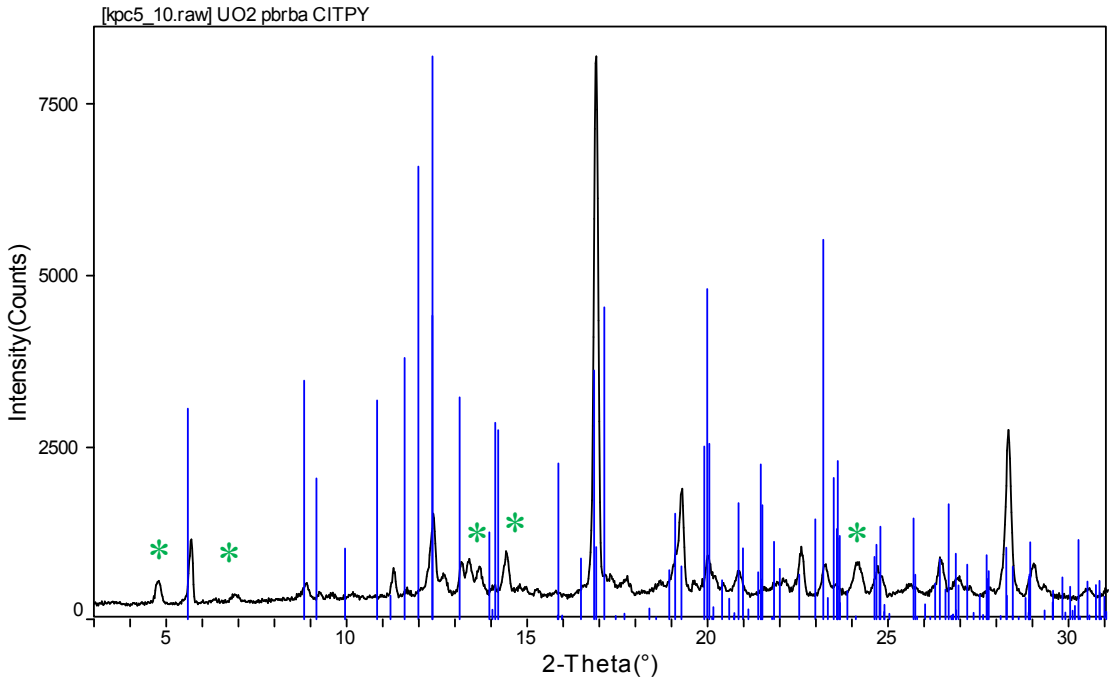

Figure S14: The observed PXRD pattern of structure **10** with calculated pattern overlaid in blue. We acknowledge a number of minor impurities as indicated with asterisks.

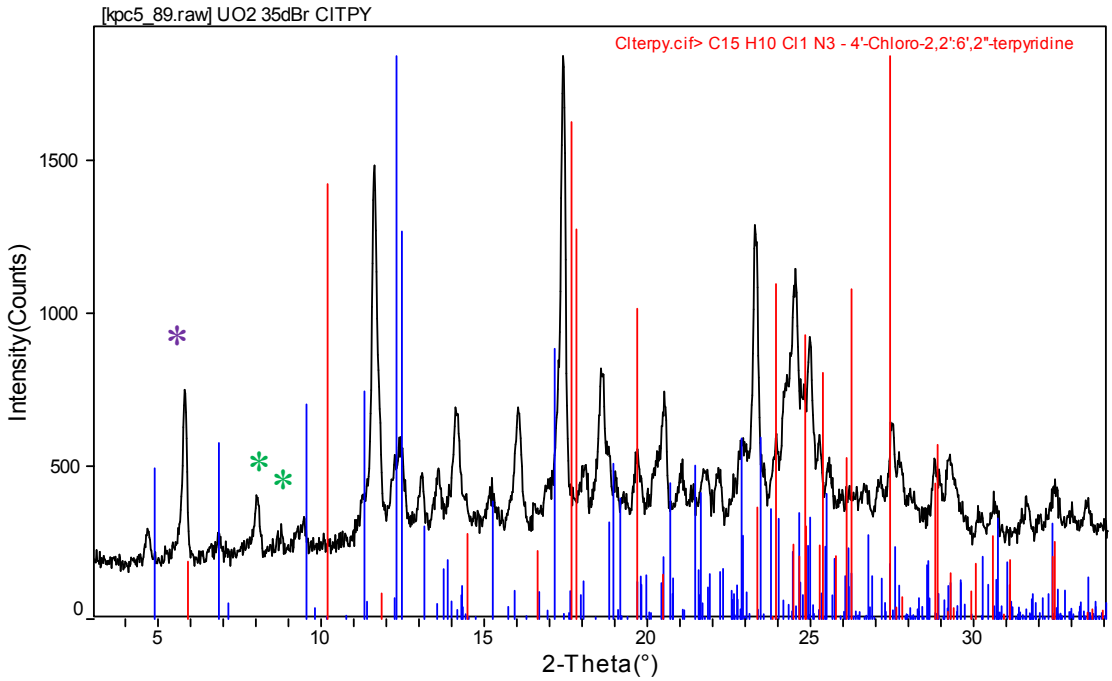

Figure S15: The observed PXRD pattern of structure **11** with calculated pattern overlaid in blue. We acknowledge a couple of minor impurities in the bulk product. One of these impurities was identified as 4'-chloro-2,2':6',2"-terpyridine (calculated CIF overlaid in red) and it is indicated with a purple asterisk. Impurities that could not be identified are indicated with green asterisks.

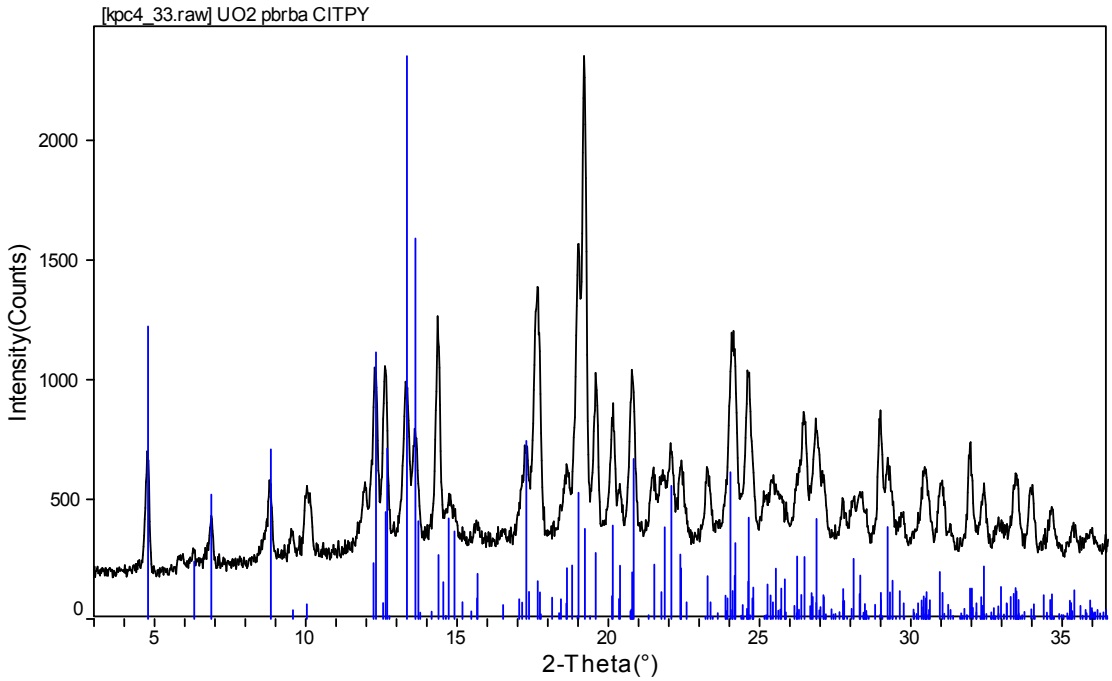

Figure S16: The observed PXRD pattern of structure **12** with calculated pattern overlaid in blue.

III. Thermal Ellipsoid Plots

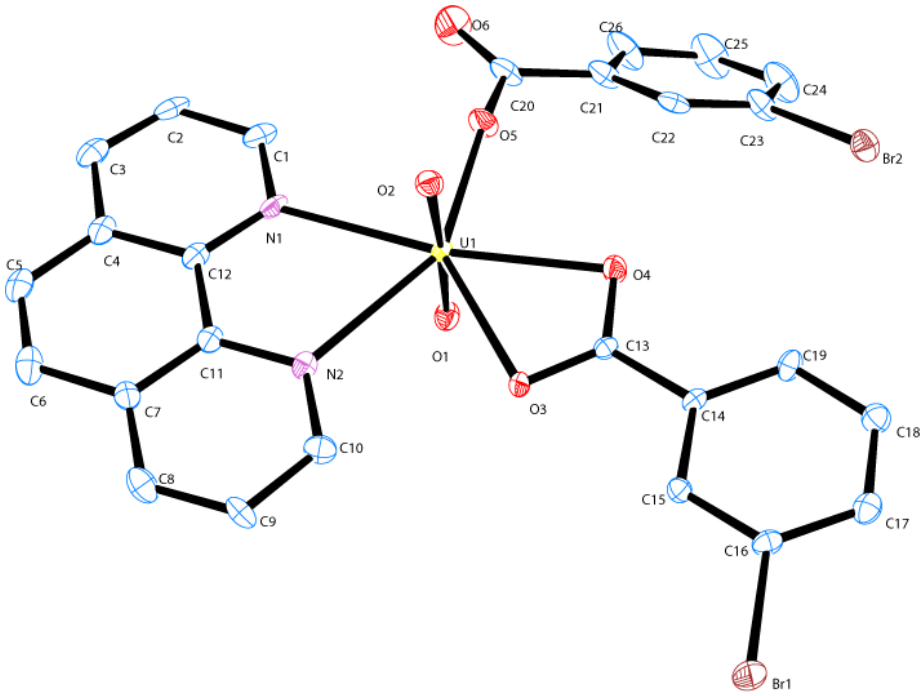

Figure S17: ORTEP illustration of complex **1**. Ellipsoids are shown at 50% probability level.

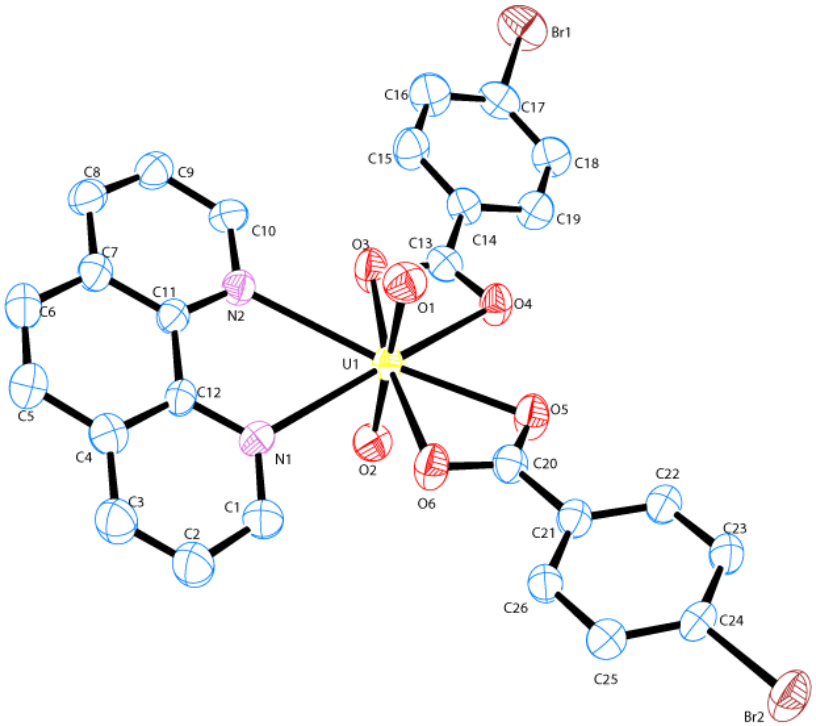

Figure S18: ORTEP illustration of structure **2**. Ellipsoids are shown at 50% probability level.

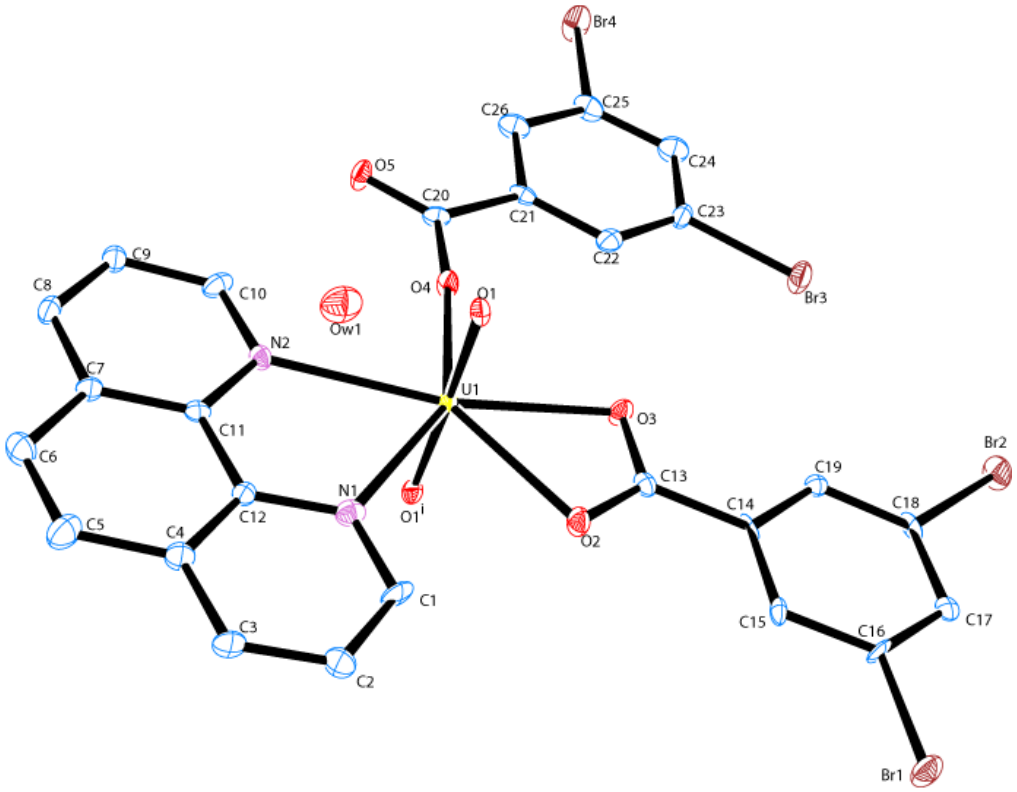

Figure S19: ORTEP illustration of structure **3**. Ellipsoids are shown at 50% probability level. Atoms labelled with an "i" are reproduced through symmetry.

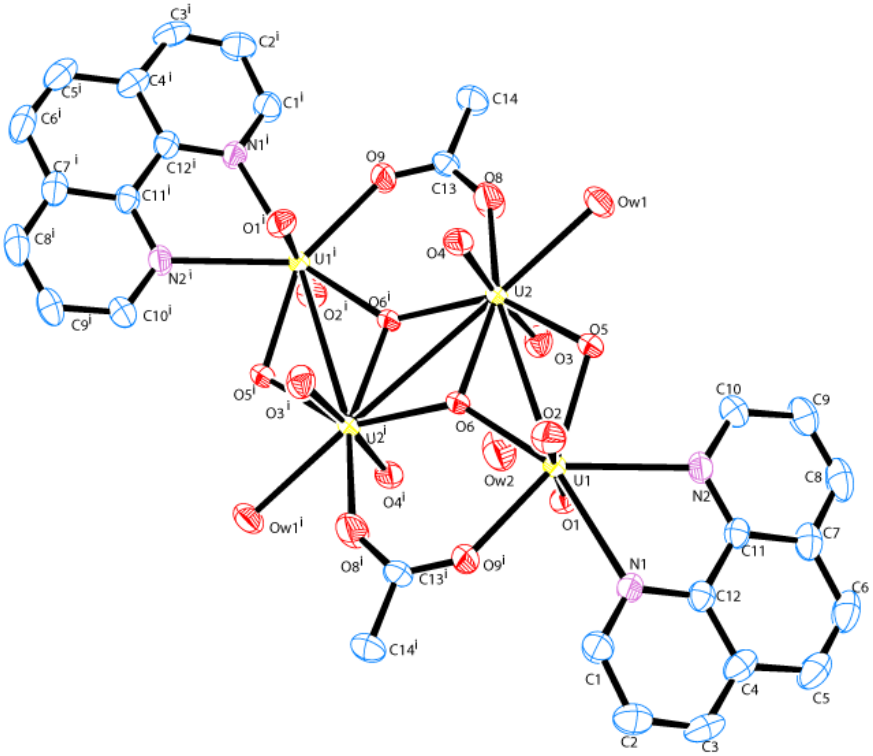

Figure S20: ORTEP illustration of structure **4**. Ellipsoids are shown at 50% probability level. Atoms labelled with an "i" are reproduced through symmetry.

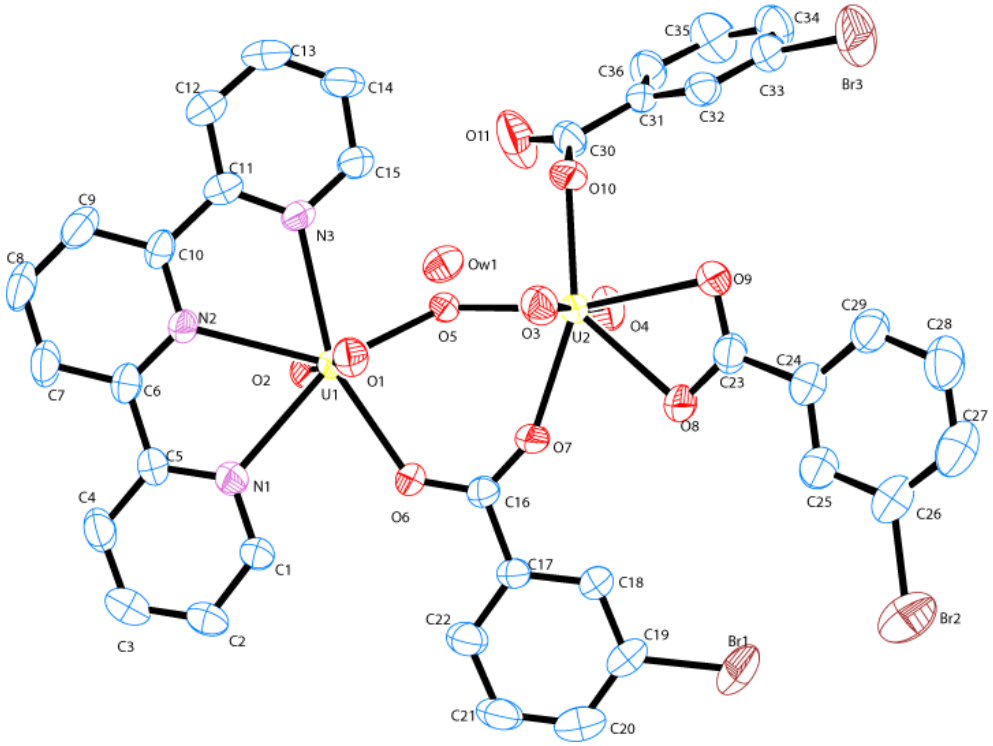

Figure S21: ORTEP illustration of complex **5**. Ellipsoids are shown at 50% probability level.

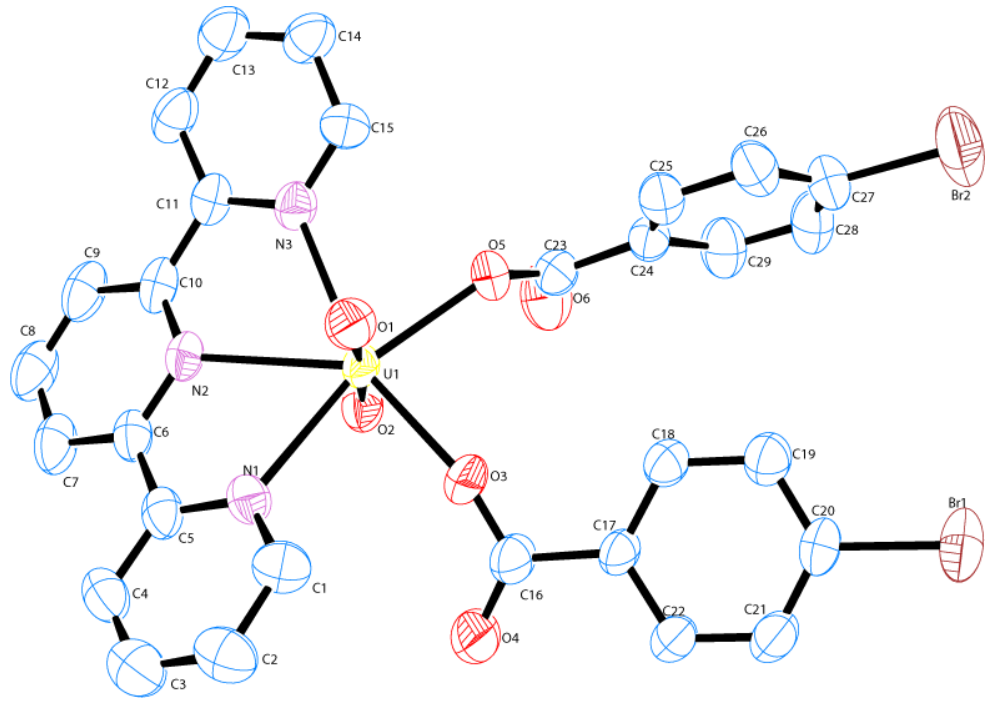

Figure S22: ORTEP illustration of structure **6**. Ellipsoids are shown at 50% probability level.

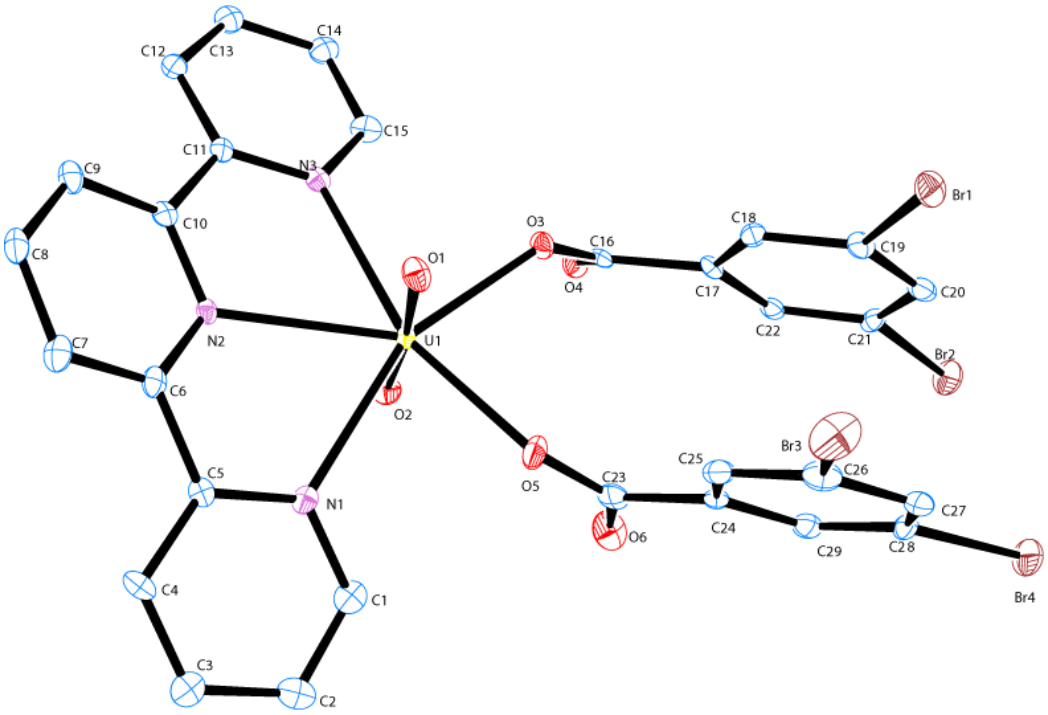

Figure S23: ORTEP illustration of structure **7**. Ellipsoids are shown at 50% probability level.

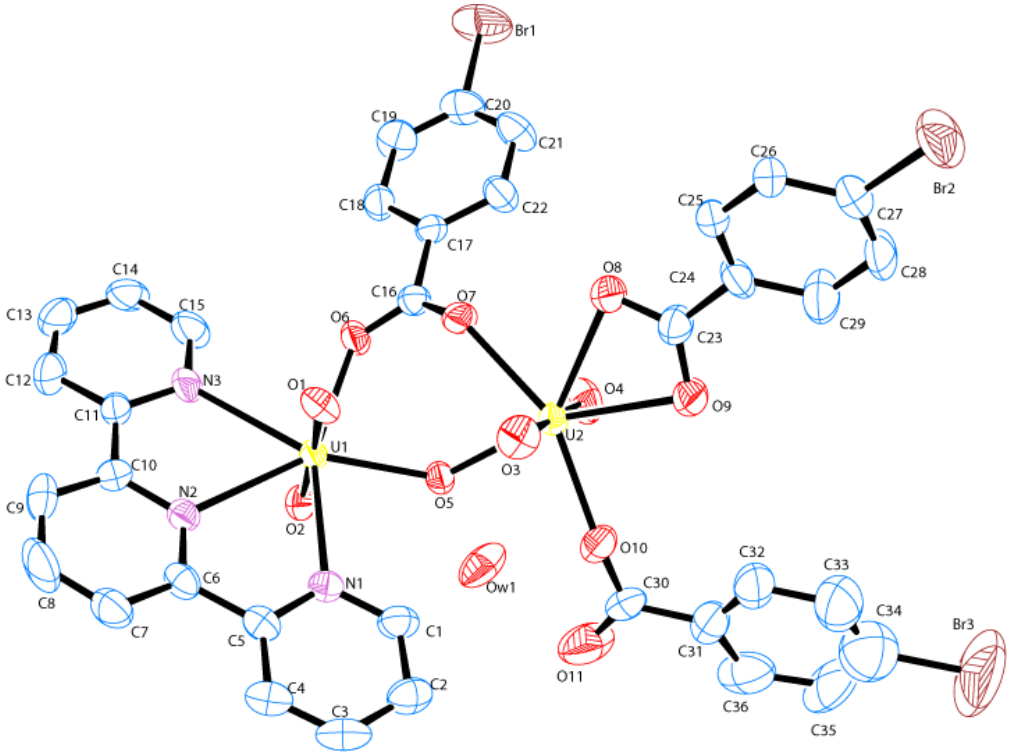

Figure S24: ORTEP illustration of structure **8**. Ellipsoids are shown at 50% probability level.

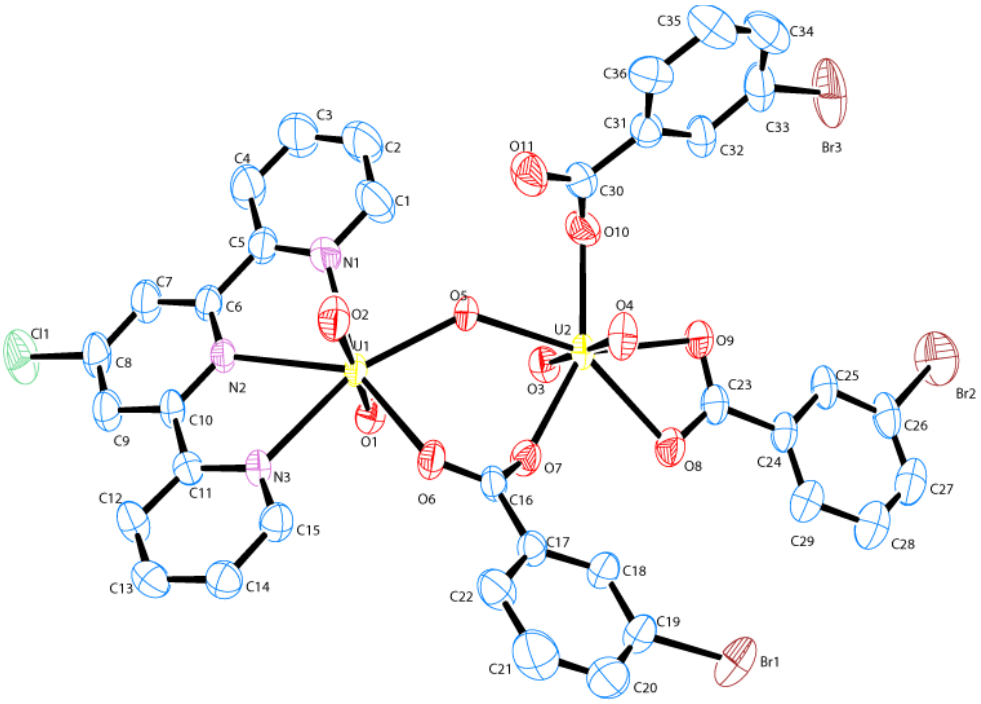

Figure S25: ORTEP illustration of structure **9**. Ellipsoids are shown at 50% probability level.

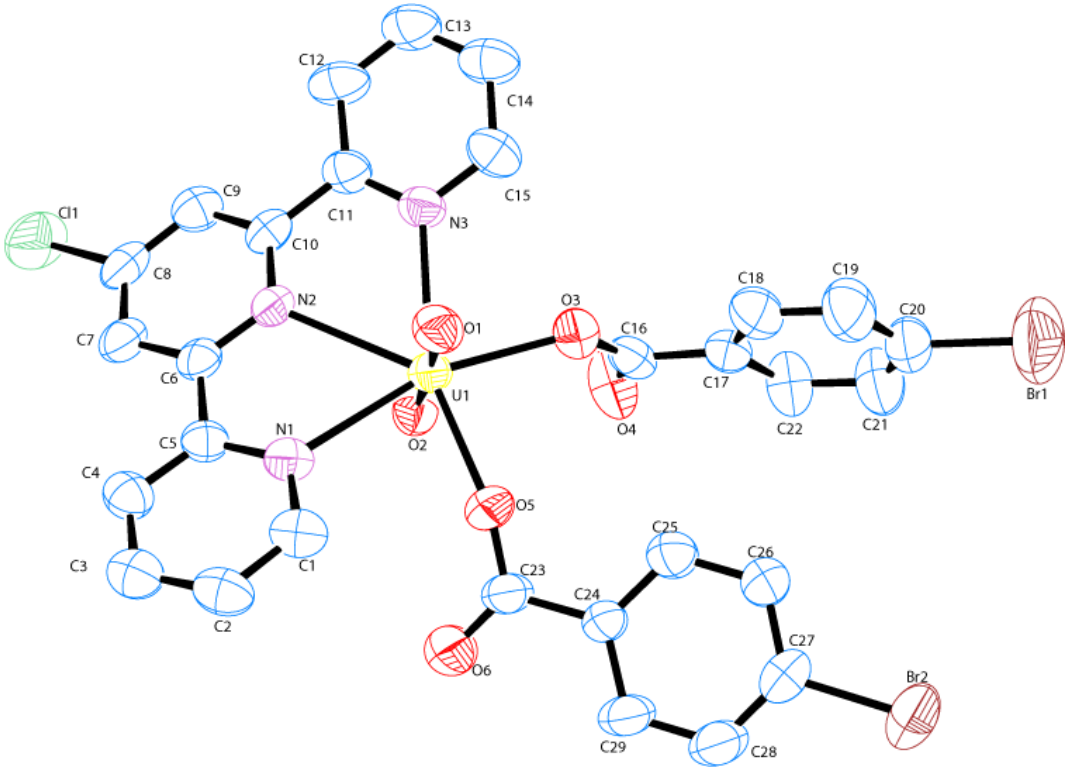

Figure S26: ORTEP illustration of structure **10**. Ellipsoids are shown at 50% probability level.

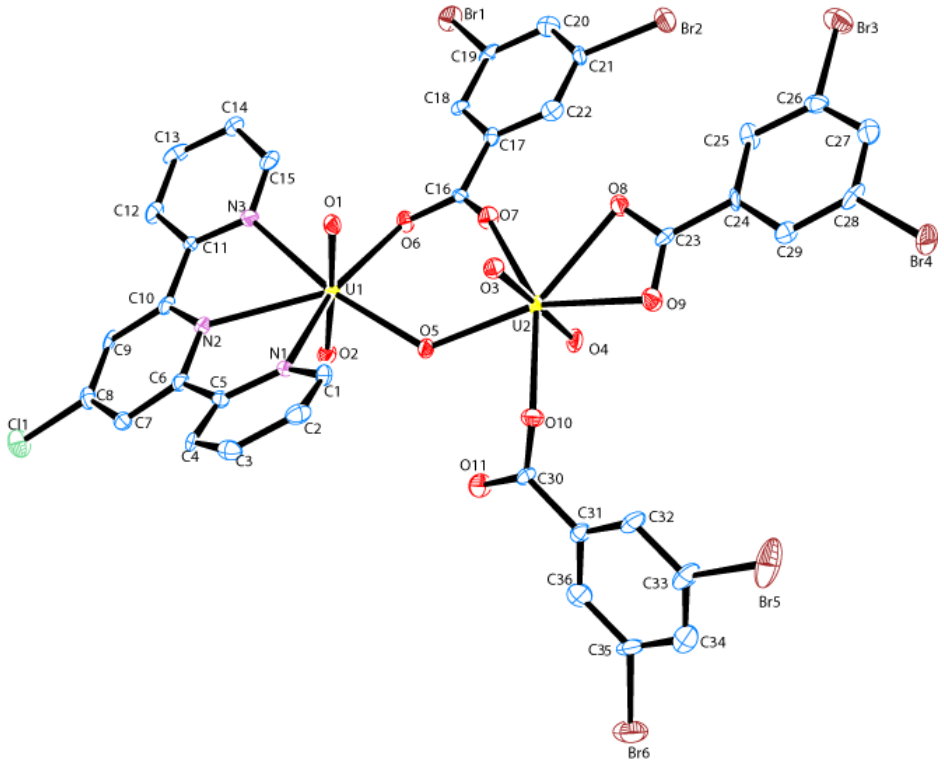

Figure S27: ORTEP illustration of structure **11**. Ellipsoids are shown at 50% probability level.

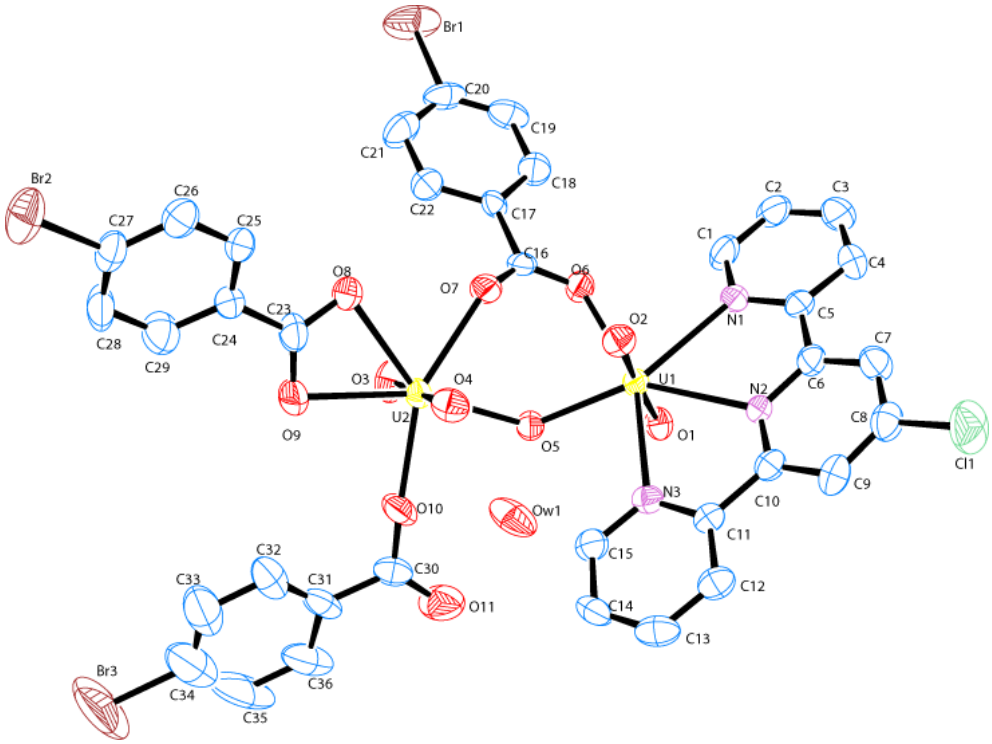

Figure S28: ORTEP illustration of structure **12**. Ellipsoids are shown at 50% probability level.

IV. Tables of Bond Distances

Table S1: U-O Axial Bond Lengths in UO_2^{2+} complexes (**1-12**).

Complex	d_{U1-O1} [Å]	d_{U1-O2} [Å]	d_{U2-O3} [Å]	d_{U2-O4} [Å]
1	1.780(3)	1.769(2)		
2	1.764(3)	1.755(3)		
3	1.773(3)			
4	1.776(3)	1.799(3)	1.794(3)	1.794(3)
5	1.765(3)	1.758(3)	1.760(4)	1.758(4)
6	1.760(3)	1.773(3)		
7	1.776(3)	1.772(3)		
8	1.774(7)	1.759(7)	1.749(7)	1.766(7)
9	1.763(3)	1.757(4)	1.764(4)	1.755(4)
10	1.755(4)	1.754(4)		
11	1.758(4)	1.760(4)	1.778(5)	1.769(5)
12	1.766(4)	1.756(4)	1.767(5)	1.765(4)

Table S2: U-O Equatorial Bond Lengths in UO_2^{2+} complexes (**1-12**).

Complex	d_{U1-O3} [Å]	d_{U1-O4} [Å]	d_{U1-O5} [Å]	d_{U1-O6} [Å]	d_{U2-O5} [Å]	d_{U2-O6} [Å]	d_{U2-O7} [Å]	d_{U2-O8} [Å]	d_{U2-O9} [Å]	d_{U2-O10} [Å]
1	2.405(2)	2.442(2)	2.225(3)							
2	2.404(3)	2.533(3)	2.488(3)	2.439(3)						
3	2.438(4)	2.438(4)	2.235(4)							
4			2.320(3)	2.233(3)	2.355(3)	2.322(3)		2.376(3)		
5			2.255(3)	2.398(3)	2.374(3)		2.314(4)	2.453(4)	2.548(3)	2.276(3)
6	2.230(3)		2.285(3)							
7	2.265(3)		2.268(3)							
8			2.241(6)	2.388(6)	2.361(6)		2.383(6)	2.435(7)	2.451(7)	2.263(7)
9			2.260(3)	2.409(3)	2.406(3)		2.346(3)	2.438(4)	2.436(3)	2.310(4)
10	2.290(4)		2.240(4)							
11			2.264(4)	2.402(5)	2.390(4)		2.336(4)	2.451(4)	2.428(4)	2.293(4)
12			2.226(4)	2.398(4)	2.390(4)		2.391(4)	2.440(4)	2.445(5)	2.244(5)

Table S3: U-N Bond Lengths in UO_2^{2+} complexes (**1-12**).

Complex	d_{U-N1} [Å]	d_{U-N2} [Å]	d_{U-N3} [Å]
1	2.552(3)	2.600(3)	
2	2.664(4)	2.705(4)	
3	2.561(5)	2.540(5)	

4	2.673(4)	2.663(4)	
5	2.592(4)	2.590(4)	2.580(4)
6	2.558(4)	2.600(3)	2.587(3)
7	2.576(3)	2.595(4)	2.560(3)
8	2.561(8)	2.583(8)	2.575(8)
9	2.581(5)	2.603(4)	2.574(4)
10	2.568(5)	2.604(4)	2.589(5)
11	2.568(6)	2.587(5)	2.560(5)
12	2.580(5)	2.585(5)	2.564(5)

V. Bond Valence Summations

Table S4: Bond Valence Summations for oxygen atoms in Compound **4**

O5	Distance (Å)	Bond Valence Sum	**O6**	Distance (Å)	Bond Valence Sum
Bound atoms			Bound atoms		
U1	2.320	0.5886	U1	2.233	0.6961
U2	2.355	0.5502	U2	2.322	0.5864
	Sum	1.138	U2’	2.236	0.6921
				Sum	1.974
OW1					
Bound atoms					
U2	2.595	0.3465			
	Sum	0.3465			

Bond valence summations for selected oxygen atoms in **4**. The values indicated that O5 is a hydroxyl group while O6 is an oxide group. [1, 2]

Table S5: Bond Valence Summations for hydroxide oxygen atom in Compound **5**

O5	Distance (Å)	Bond Valence Sum
Bound atoms		
U1	2.225	0.7069
U2	2.374	0.5305
	Sum	1.237

Table S6: Bond Valence Summations for hydroxide oxygen atom in Compound **8**

O5	Distance (Å)	Bond Valence Sum
Bound atoms		
U1	2.241	0.6854
U2	2.361	0.5439
	Sum	1.229

Table S7: Bond Valence Summations for hydroxide oxygen atom in Compound **9**

O5	Distance (Å)	Bond Valence Sum
Bound atoms		
U1	2.260	0.6608
U2	2.406	0.4987
	Sum	1.159

Table S8: Bond Valence Summations for oxygen atoms in Compound **11**

O5	Distance (Å)	Bond Valence Sum
Bound atoms		
U1	2.264	0.6557
U2	2.390	0.5144
	Sum	1.170

Table S9: Bond Valence Summations for oxygen atoms in Compound **12**

O5	Distance (Å)	Bond Valence Sum
Bound atoms		
U1	2.264	0.7055
U2	2.390	0.5144
	Sum	1.219

VI. References

1. N. E. Brese and M. O'Keeffe, *Acta Crystallographica Section B*, 1991, 47, 192-197.
2. P. C. Burns, R. C. Ewing and F. C. Hawthorne, *The Canadian Mineralogist*, 1997, 35, 1551-1570.