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Synthesis of Uranium-in-Cryptand Complexes

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EXPERIMENTAL DETAILS

All syntheses and manipulations described below were conducted under Ar with rigorous exclusion of air and water using glovebox, Schlenk-line, and high-vacuum-line techniques. UI_3[1] and $LaCl_3$[2] materials were prepared according to previously published literature. 2.2.2-Cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, Aldrich) was placed under vacuum (10^{-3} Torr) for 12 h before use. THF and Et_2O were sparged with UHP Ar and dried over columns containing Q-5 and molecular sieves. DMF, MeCN, and CH_2Cl_2 were dried over 3 Å molecular sieves for 1 week and degassed using three freeze-pump-thaw cycles. IR samples were prepared as KBr pellets on a Jasco FT/IR-4700 spectrometer. Elemental analyses were performed on a PerkinElmer series II 2400 CHNS analyzer.

[U(crypt)I_2]I, 1. In an argon-filled glovebox, a blue solution of UI_3 (100 mg, 0.160 mmol) in THF (2 mL) was added dropwise to a stirred colorless THF (2 mL) solution of 2.2.2-cryptand (60 mg, 0.160 mmol). A green/brown precipitate immediately formed. This mixture was stirred for 30 min. The solvent was removed in vacuo yielding a light green solid (123 mg, 76%). The solid was dissolved in CH_2Cl_2 (2 mL). The green solution was filtered and then layered with Et_2O and placed in a −35 °C freezer. After 1 d, X-ray quality green crystals were isolated. IR: 3243w, 3169w, 2943w, 2926w, 2894w, 2860w, 1611w, 1490w, 1479m, 1468m, 1451m, 1437w, 1361w, 1354w, 1335w, 1311w, 1288w, 1262m, 1240w, 1159w, 1103s, 1085s, 1075s, 1050m, 1029m, 960s, 949m, 911w, 873w, 832m, 823m, 803w, 763w, 757w cm^{-1}. Anal. Calcd. for [U(crypt)I_2]I, $C_{18}H_{36}N_2O_6I_3U$: C, 21.72; H, 3.65; N, 2.81. Found: C, 21.92; H, 3.49; N, 2.52.

[La(crypt)Cl_2]Cl, 2. In an argon-filled box, a suspension of $LaCl_3$ (100 mg, 0.408 mmol) in DMF (2 mL) was added to a solution of 2.2.2-cryptand (153 mg, 0.408 mmol) in DMF (2 mL). The suspension was stirred for 12 h at room temperature. The colorless solution was layered into Et_2O at –35 °C. X-ray quality colorless crystals were isolated (220 mg, 85%). IR: 2968m, 2873m, 2821m, 2744w, 1666m, 1641m, 1482m, 1448m, 1427m, 1411w, 1387w, 1373w, 1354m, 1325w, 1304m, 1291m, 1266w, 1256m, 1233w, 1215w, 1162m, 1116s, 1091s, 1068s, 1022m, 957s, 936m, 829m, 805w, 757m cm^{-1}. Anal. Calcd. for [La(crypt)Cl_2]Cl, $C_{18}H_{36}N_2O_6Cl_3La$: C, 34.77; H, 5.84; N, 4.51. Found: C, 34.52; H, 5.34; N, 4.93.

[U(crypt)I(OH_2)][I]$_2$, 3. In an argon-filled box, a THF (1 mL) solution of 2.2.2-cryptand (11 mg, 0.030 mmol) was added to a blue solution of UI_3 (19 mg, 0.030 mmol) in THF (2 mL).

The solution immediately became a maroon suspension. The mixture was placed in a –15 °C freezer from which green X-ray quality crystals of [U(crypt)(OH_2)(I)][I]$_2$ were obtained (15 mg, 50%).

[U(crypt)I(OH_2)][I][BPh_4], 4. In an argon-filled box, a green MeCN (3 mL) solution of [U(crypt)I_2]I, **1** (30 mg, 0.03 mmol) was added to a MeCN solution of $NaBPh_4$ (10 mg 0.03 mmol). The green mixture was stirred for 2 d and then filtered to remove brown solids. The resulting green solution was filtered and layered with Et_2O and placed in a –35 °C freezer. Brown/green X-ray quality crystals of [U(crypt)I(OH_2)][I][BPh_4] were obtained (10 mg, 28%).

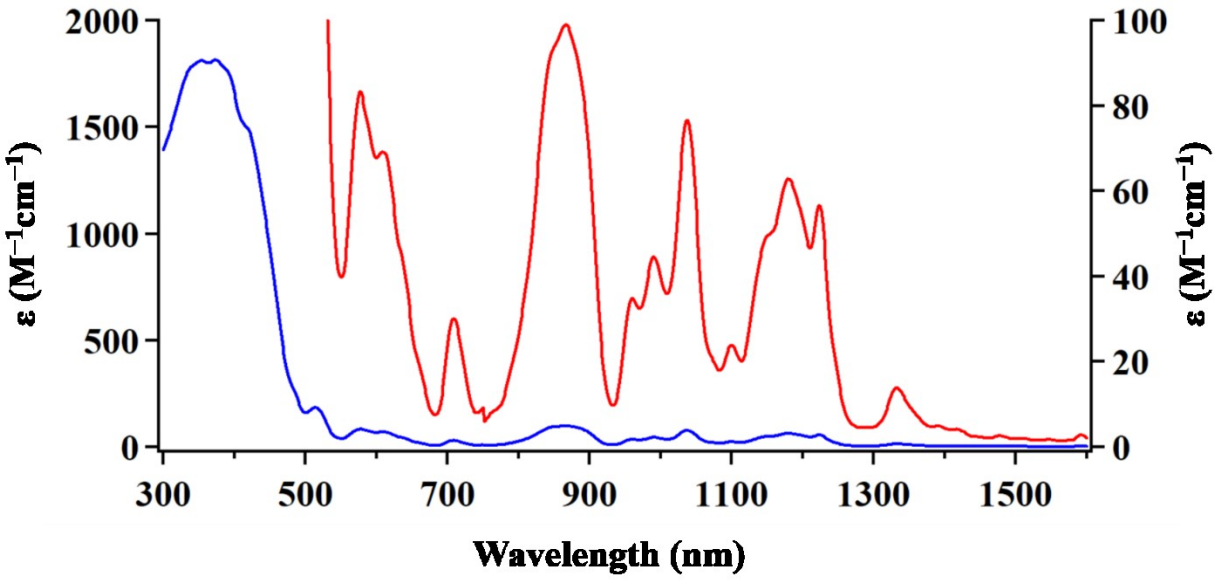

Figure S1. NIR/UV-Vis of 5mM [U(crypt)I_2]I, **1**, in DMF. Full spectrum (blue, left axis) and 20x zoom of full spectrum (red, right axis).

X-ray Data Collection, Structure Solution and Refinement for [U(crypt)I_2]I, 1.

A green crystal of approximate dimensions 0.084 x 0.205 x 0.331 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[3] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[4] and SADABS[5] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[6] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[7] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were three molecules of dichloromethane solvent present.

Least-squares analysis yielded wR2 = 0.0497 and Goof = 1.059 for 352 variables refined against 8749 data (0.76 Å), R1 = 0.0225 for those 7986 data with $I > 2.0\sigma(I)$.

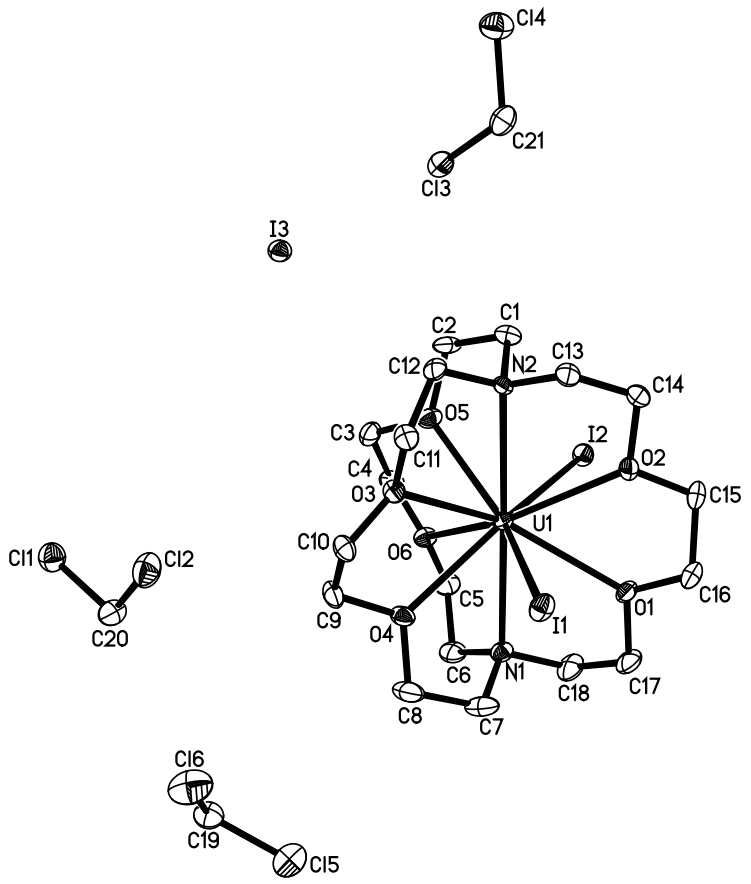

Figure S2. ORTEP representation of [U(crypt)I_2]I, **1.** Thermal ellipsoid plot drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for [U(crypt)I_2]I, **1**.

Identification code	dnh34 (Daniel Huh)
Empirical formula	C_{18} H_{36} I_3 N_2 O_6 U • 3(CH_2Cl_2)
Formula weight	1249.99
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.485(2) Å a= 90°.

	b = 26.766(5) Å	b= 101.244(2)°.
	c = 12.275(2) Å	g = 90°.
Volume	3700.8(12) Å^3	
Z	4	
Density (calculated)	2.243 Mg/m^3	
Absorption coefficient	7.356 mm^{-1}	
F(000)	2332	
Crystal color	green	
Crystal size	0.331 x 0.205 x 0.084 mm^3	
Theta range for data collection	1.522 to 27.874°	
Index ranges	$-14 \leq h \leq 15$, $-35 \leq k \leq 34$, $-16 \leq l \leq 16$	
Reflections collected	43788	
Independent reflections	8749 [R(int) = 0.0457]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4316 and 0.2781	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8749 / 0 / 352	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I) = 7986 data]	R1 = 0.0225, wR2 = 0.0483	
R indices (all data, 0.76 Å)	R1 = 0.0265, wR2 = 0.0497	
Largest diff. peak and hole	0.880 and -0.608 e.Å^{-3}	

Table S2. Bond lengths [Å] for [U(crypt)I_2]I, **1**.

U(1)-O(1)	2.568(2)
U(1)-O(4)	2.623(2)
U(1)-O(2)	2.646(2)
U(1)-O(3)	2.669(2)
U(1)-O(5)	2.676(2)

U(1)-O(6)	2.697(2)
U(1)-N(1)	2.803(3)
U(1)-N(2)	2.853(3)
U(1)-I(2)	3.3106(5)
U(1)-I(1)	3.3292(6)

Table S3. Bond angles [°] for [U(crypt)I_2]I, **1**.

O(1)-U(1)-O(4)	100.13(7)
O(1)-U(1)-O(2)	60.75(7)
O(4)-U(1)-O(2)	68.38(7)
O(1)-U(1)-O(3)	68.81(7)
O(4)-U(1)-O(3)	59.70(7)
O(2)-U(1)-O(3)	95.70(7)
O(1)-U(1)-O(5)	108.29(7)
O(4)-U(1)-O(5)	143.23(7)
O(2)-U(1)-O(5)	146.79(7)
O(3)-U(1)-O(5)	109.68(7)
O(1)-U(1)-O(6)	144.05(7)
O(4)-U(1)-O(6)	107.93(7)
O(2)-U(1)-O(6)	109.52(7)
O(3)-U(1)-O(6)	145.70(7)
O(5)-U(1)-O(6)	59.22(7)
O(1)-U(1)-N(1)	57.76(7)
O(4)-U(1)-N(1)	121.28(7)
O(2)-U(1)-N(1)	118.50(7)
O(3)-U(1)-N(1)	61.58(7)
O(5)-U(1)-N(1)	60.98(7)
O(6)-U(1)-N(1)	120.12(7)
O(1)-U(1)-N(2)	121.54(7)
O(4)-U(1)-N(2)	58.01(7)

O(2)-U(1)-N(2)	60.79(7)
O(3)-U(1)-N(2)	117.70(7)
O(5)-U(1)-N(2)	119.96(7)
O(6)-U(1)-N(2)	60.81(7)
N(1)-U(1)-N(2)	179.06(7)
O(1)-U(1)-I(2)	72.73(5)
O(4)-U(1)-I(2)	137.71(5)
O(2)-U(1)-I(2)	72.25(5)
O(3)-U(1)-I(2)	140.59(5)
O(5)-U(1)-I(2)	74.54(5)
O(6)-U(1)-I(2)	71.41(5)
N(1)-U(1)-I(2)	90.76(5)
N(2)-U(1)-I(2)	89.57(6)
O(1)-U(1)-I(1)	137.89(5)
O(4)-U(1)-I(1)	72.21(5)
O(2)-U(1)-I(1)	139.38(5)
O(3)-U(1)-I(1)	72.07(5)
O(5)-U(1)-I(1)	71.08(5)
O(6)-U(1)-I(1)	73.66(5)
N(1)-U(1)-I(1)	90.15(5)
N(2)-U(1)-I(1)	90.17(6)
I(2)-U(1)-I(1)	139.946(10)

X-ray Data Collection, Structure Solution and Refinement for [La(crypt)Cl_2]Cl, 2.

A colorless crystal of approximate dimensions 0.089 x 0.117 x 0.283 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[3] program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[4] and SADABS[5] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[6] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group *C*2/*c* was correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[7] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule and chloride ion were located on two-fold rotation axes. There was one molecule of diethylether solvent present. The solvent was located on an inversion center. Both the solvent and chloride ion were disordered and included using multiple components with partial site-occupancy-factors.

Least-squares analysis yielded wR2 = 0.0554 and Goof = 1.069 for 183 variables refined against 3496 data (0.74 Å), R1 = 0.0210 for those 3298 data with $I > 2.0\sigma(I)$.

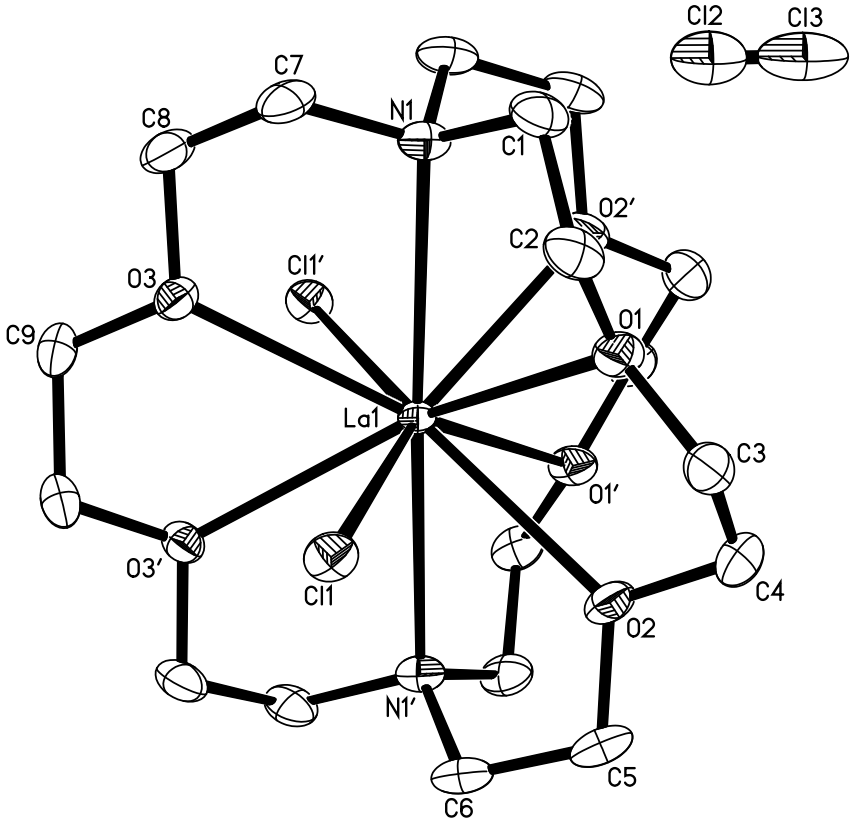

Figure S3. ORTEP representation of [La(crypt)Cl_2]Cl, **2.** Outer sphere chloride is disordered over two locations. Thermal ellipsoid plot drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table S4. Crystal data and structure refinement for [La(crypt)Cl_2]Cl, **2.**

Identification code	dnh40 (Daniel Huh)
Empirical formula	C_{18} H_{36} Cl_3 La N_2 O_6 • $C_4H_{10}O$
Formula weight	695.87
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	a = 13.8322(11) Å a= 90°.

	b = 16.2467(13) Å	b= 106.0577(9)°.
	c = 13.1611(10) Å	g = 90°.
Volume	2842.3(4) Å^3	
Z	4	
Density (calculated)	1.626 Mg/m^3	
Absorption coefficient	1.827 mm^{-1}	
F(000)	1424	
Crystal color	colorless	
Crystal size	0.283 x 0.117 x 0.089 mm^3	
Theta range for data collection	1.980 to 28.770°	
Index ranges	$-18 \leq h \leq 18$, $-21 \leq k \leq 20$, $-17 \leq l \leq 17$	
Reflections collected	16831	
Independent reflections	3496 [R(int) = 0.0321]	
Completeness to theta = 25.500°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6485	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3496 / 0 / 183	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I) = 3298 data]	R1 = 0.0210, wR2 = 0.0541	
R indices (all data, 0.74 Å)	R1 = 0.0232, wR2 = 0.0554	
Largest diff. peak and hole	0.696 and -0.505 e.Å^{-3}	

Table S5. Bond lengths [Å] for [La(crypt)Cl_2]Cl, **2.**

La(1)-O(2)A	2.6725(14)
La(1)-O(2)	2.6726(14)
La(1)-O(1)	2.6942(14)
La(1)-O(1)A	2.6942(14)
La(1)-O(3)A	2.7155(13)

La(1)-O(3)	2.7156(13)
La(1)-Cl(1)A	2.8161(5)
La(1)-Cl(1)	2.8161(5)
La(1)-N(1)	2.8927(17)
La(1)-N(1)A	2.8927(17)

Table S6. Bond angles [°] for [La(crypt)Cl_2]Cl, **2.**

O(2)A-La(1)-O(2)	95.71(7)
O(2)A-La(1)-O(1)	67.50(4)
O(2)-La(1)-O(1)	60.05(4)
O(2)A-La(1)-O(1)A	60.05(4)
O(2)-La(1)-O(1)A	67.50(4)
O(1)-La(1)-O(1)A	97.83(6)
O(2)A-La(1)-O(3)A	145.55(4)
O(2)-La(1)-O(3)A	109.78(4)
O(1)-La(1)-O(3)A	145.66(4)
O(1)A-La(1)-O(3)A	108.27(4)
O(2)A-La(1)-O(3)	109.78(4)
O(2)-La(1)-O(3)	145.55(4)
O(1)-La(1)-O(3)	108.27(4)
O(1)A-La(1)-O(3)	145.66(4)
O(3)A-La(1)-O(3)	59.85(6)
O(2)A-La(1)-Cl(1)A	72.41(4)
O(2)-La(1)-Cl(1)A	139.88(4)
O(1)-La(1)-Cl(1)A	137.31(3)
O(1)A-La(1)-Cl(1)A	73.61(3)
O(3)A-La(1)-Cl(1)A	73.17(3)
O(3)-La(1)-Cl(1)A	72.07(3)
O(2)A-La(1)-Cl(1)	139.88(4)
O(2)-La(1)-Cl(1)	72.41(4)

O(1)-La(1)-Cl(1)	73.61(3)
O(1)A-La(1)-Cl(1)	137.31(3)
O(3)A-La(1)-Cl(1)	72.07(3)
O(3)-La(1)-Cl(1)	73.17(3)
Cl(1)A-La(1)-Cl(1)	139.69(2)
O(2)A-La(1)-N(1)	58.00(5)
O(2)-La(1)-N(1)	120.35(5)
O(1)-La(1)-N(1)	60.42(4)
O(1)A-La(1)-N(1)	118.01(5)
O(3)A-La(1)-N(1)	120.92(4)
O(3)-La(1)-N(1)	61.17(4)
Cl(1)A-La(1)-N(1)	86.31(4)
Cl(1)-La(1)-N(1)	94.41(4)
O(2)A-La(1)-N(1)A	120.35(5)
O(2)-La(1)-N(1)A	58.01(5)
O(1)-La(1)-N(1)A	118.01(5)
O(1)A-La(1)-N(1)A	60.42(4)
O(3)A-La(1)-N(1)A	61.17(4)
O(3)-La(1)-N(1)A	120.92(4)
Cl(1)A-La(1)-N(1)A	94.41(4)
Cl(1)-La(1)-N(1)A	86.31(4)
N(1)-La(1)-N(1)A	177.91(7)

X-ray Data Collection, Structure Solution and Refinement for [U(crypt)I(OH$_2$)][I]$_2$, 3.

A green crystal of approximate dimensions 0.154 x 0.241 x 0.404 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[3] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[4] and SADABS[5] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[6] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[7] for neutral atoms were used throughout the analysis. Hydrogen atoms H(71) and H(72) were located from a difference-map and refined (x,y,z and U_{iso}). The remaining hydrogen atoms were included using a riding model.

At convergence, wR2 = 0.1096 and Goof = 1.257 for 288 variables refined against 6137 data (0.78Å), R1 = 0.0474 for those 5617 data with $I > 2.0\sigma(I)$.

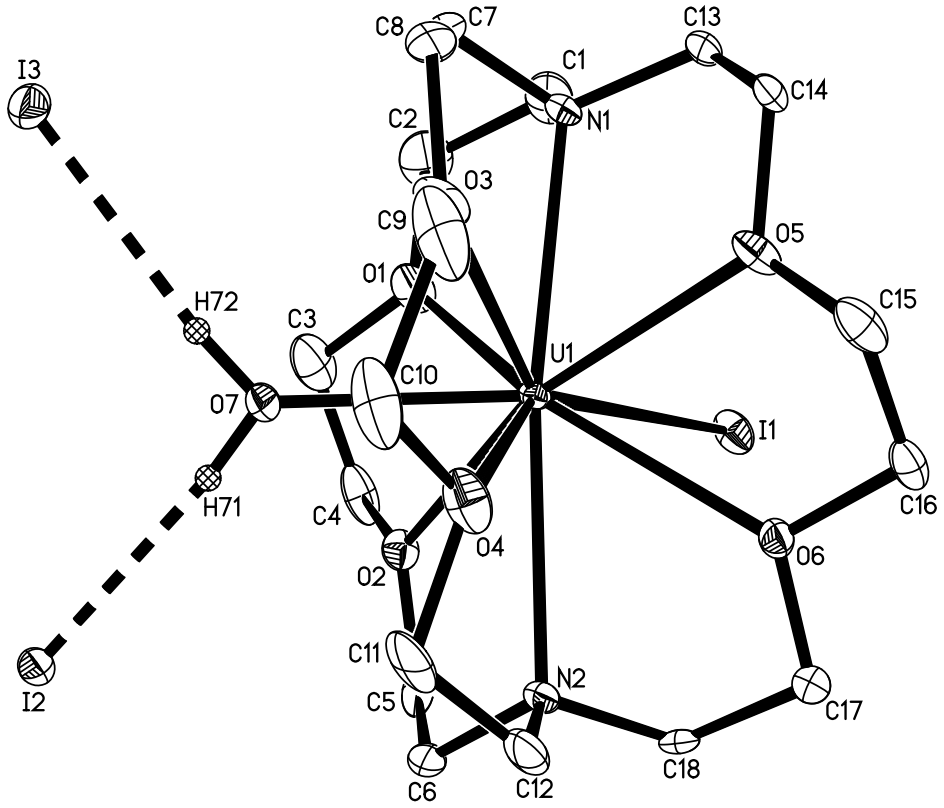

Figure S4. ORTEP representation of [U(crypt)I(OH_2)][I]$_2$, **3.** Thermal ellipsoid plot drawn at 50% probability level. Hydrogen atoms except those of H_2O are omitted for clarity.

Table S7. Crystal data and structure refinement for [U(crypt)I(OH_2)][I]$_2$, **3.**

Identification code	cjw56 (Cory Windorff)	
Empirical formula	C_{18} H_{38} I_3 N_2 O_7 U	
Formula weight	1013.23	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.8943(11) Å	a= 90°.
	b = 19.313(2) Å	b= 96.0099(13)°.

	c = 13.3229(14) Å g = 90°.
Volume	2787.8(5) $Å^3$
Z	4
Density (calculated)	2.414 Mg/m^3
Absorption coefficient	9.181 mm^{-1}
F(000)	1868
Crystal color	green
Crystal size	0.404 x 0.241 x 0.154 mm^3
Theta range for data collection	1.864 to 27.103°
Index ranges	$-13 \leq h \leq 13$, $-24 \leq k \leq 24$, $-17 \leq l \leq 17$
Reflections collected	31414
Independent reflections	6137 [R(int) = 0.0494]
Completeness to theta = 25.500°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4316 and 0.3056
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6137 / 0 / 288
Goodness-of-fit on F^2	1.257
Final R indices [I>2sigma(I) = 5617 data]	R1 = 0.0474, wR2 = 0.1077
R indices (all data, 0.78 Å)	R1 = 0.0523, wR2 = 0.1096
Largest diff. peak and hole	2.792 and -1.209 $e.Å^{-3}$

Table S8. Bond lengths [Å] for [U(crypt)I(OH_2)][I]$_2$, **3.**

U(1)-O(7)	2.549(7)
U(1)-O(3)	2.602(7)
U(1)-O(5)	2.612(7)
U(1)-O(4)	2.632(7)

U(1)-O(1)	2.635(7)
U(1)-O(2)	2.665(6)
U(1)-O(6)	2.683(6)
U(1)-N(1)	2.796(8)
U(1)-N(2)	2.814(8)
U(1)-I(1)	3.2564(7)
I(2)-H(71)	2.55(18)
I(3)-H(72)	2.66(16)

Table S9. Bond angles [°] for [U(crypt)I(OH_2)][$I]_2$, **3.**

O(7)-U(1)-O(3)	66.3(2)
O(7)-U(1)-O(5)	134.4(2)
O(3)-U(1)-O(5)	68.3(2)
O(7)-U(1)-O(4)	68.4(2)
O(3)-U(1)-O(4)	61.5(3)
O(5)-U(1)-O(4)	87.1(2)
O(7)-U(1)-O(1)	70.9(2)
O(3)-U(1)-O(1)	97.4(3)
O(5)-U(1)-O(1)	119.0(2)
O(4)-U(1)-O(1)	139.0(2)
O(7)-U(1)-O(2)	65.7(2)
O(3)-U(1)-O(2)	131.5(2)
O(5)-U(1)-O(2)	159.7(2)
O(4)-U(1)-O(2)	106.2(2)
O(1)-U(1)-O(2)	60.0(2)
O(7)-U(1)-O(6)	138.0(2)
O(3)-U(1)-O(6)	110.5(3)
O(5)-U(1)-O(6)	58.7(2)
O(4)-U(1)-O(6)	73.8(2)
O(1)-U(1)-O(6)	145.9(2)

O(2)-U(1)-O(6)	109.6(2)
O(7)-U(1)-N(1)	98.7(2)
O(3)-U(1)-N(1)	62.0(3)
O(5)-U(1)-N(1)	62.0(3)
O(4)-U(1)-N(1)	122.3(3)
O(1)-U(1)-N(1)	59.5(3)
O(2)-U(1)-N(1)	119.2(3)
O(6)-U(1)-N(1)	117.0(2)
O(7)-U(1)-N(2)	88.8(2)
O(3)-U(1)-N(2)	124.8(3)
O(5)-U(1)-N(2)	114.7(2)
O(4)-U(1)-N(2)	63.6(3)
O(1)-U(1)-N(2)	120.9(3)
O(2)-U(1)-N(2)	61.0(2)
O(6)-U(1)-N(2)	57.5(2)
N(1)-U(1)-N(2)	171.8(3)
O(7)-U(1)-I(1)	137.27(17)
O(3)-U(1)-I(1)	143.59(18)
O(5)-U(1)-I(1)	84.56(16)
O(4)-U(1)-I(1)	143.42(18)
O(1)-U(1)-I(1)	74.46(19)
O(2)-U(1)-I(1)	75.61(14)
O(6)-U(1)-I(1)	71.42(14)
N(1)-U(1)-I(1)	84.3(2)
N(2)-U(1)-I(1)	87.96(19)

X-ray Data Collection, Structure Solution and Refinement for [U(crypt)I(OH_2)][I][BPh_4], 4.

A green crystal of approximate dimensions 0.121 x 0.136 x 207 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[3] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[4] and SADABS[5] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[6] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[7] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There was one molecule of acetonitrile solvent present.

Least-squares analysis yielded wR2 = 0.0766 and Goof = 1.019 for 525 variables refined against 12099 data (0.75 Å), R1 = 0.0346 for those 9551 data with $I > 2.0\sigma(I)$.

There were several high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals although it was probable that either acetonitrile or diethylether solvent was present. The SQUEEZE[8a] routine in the PLATON[8b] program package was used to account for the electrons in the solvent accessible voids.

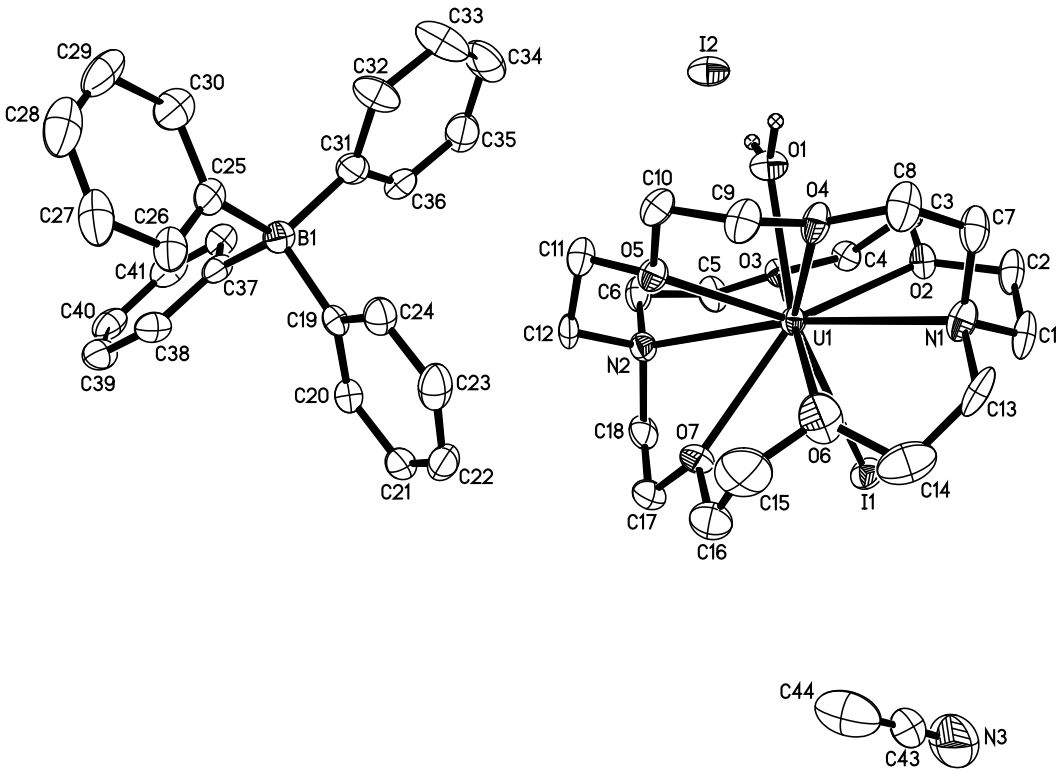

Figure S5. ORTEP representation of [U(crypt)I(OH_2)][I][BPh_4], **4.** Thermal ellipsoid plot drawn at 50% probability level. Hydrogen atoms except those of H_2O are omitted for clarity.

Table S10. Crystal data and structure refinement for [U(crypt)I(OH_2)][I][BPh_4], **4.**

Identification code	dnh54 (Daniel Huh)	
Empirical formula	$C_{42}H_{58}$ B I_2 N_2 O_7 U • CH_3CN	
Formula weight	1246.59	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 20.142(3) Å	a= 90°.
	b = 9.6317(16) Å	b= 107.307(2)°.
	c = 26.979(5) Å	g = 90°.

Volume	4996.9(15) $Å^3$
Z	4
Density (calculated)	1.657 Mg/m^3
Absorption coefficient	4.531 mm^{-1}
F(000)	2420
Crystal color	green
Crystal size	0.207 x 0.136 x 0.121 mm^3
Theta range for data collection	1.498 to 28.343°
Index ranges	$-25 \leq h \leq 25$, $-12 \leq k \leq 12$, $-35 \leq l \leq 35$
Reflections collected	58739
Independent reflections	12099 [R(int) = 0.0588]
Completeness to theta = 25.500°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4311 and 0.3498
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12099 / 0 / 525
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I) = 9551 data]	R1 = 0.0346, wR2 = 0.0709
R indices (all data, 0.75 Å)	R1 = 0.0528, wR2 = 0.0766
Largest diff. peak and hole	1.717 and -1.217 $e.Å^{-3}$

Table S11. Bond lengths [Å] for [U(crypt)I(OH_2)][I][BPh_4], **4**.

U(1)-O(1)	2.503(3)
U(1)-O(4)	2.606(3)
U(1)-O(6)	2.612(3)
U(1)-O(5)	2.615(3)
U(1)-O(2)	2.623(3)
U(1)-O(3)	2.649(3)
U(1)-O(7)	2.659(3)

U(1)-N(2)	2.780(3)
U(1)-N(1)	2.822(4)
U(1)-I(1)	3.2844(5)

Table S12. Bond angles [°] for [U(crypt)I(OH_2)][I][BPh_4], **4**.

O(1)-U(1)-O(4)	64.71(9)
O(1)-U(1)-O(6)	131.57(11)
O(4)-U(1)-O(6)	67.29(11)
O(1)-U(1)-O(5)	70.68(9)
O(4)-U(1)-O(5)	62.13(9)
O(6)-U(1)-O(5)	81.90(11)
O(1)-U(1)-O(2)	73.04(9)
O(4)-U(1)-O(2)	95.51(9)
O(6)-U(1)-O(2)	118.24(10)
O(5)-U(1)-O(2)	142.94(9)
O(1)-U(1)-O(3)	65.12(8)
O(4)-U(1)-O(3)	128.78(9)
O(6)-U(1)-O(3)	163.19(11)
O(5)-U(1)-O(3)	109.21(8)
O(2)-U(1)-O(3)	60.28(8)
O(1)-U(1)-O(7)	136.70(9)
O(4)-U(1)-O(7)	112.43(9)
O(6)-U(1)-O(7)	60.14(10)
O(5)-U(1)-O(7)	71.02(9)
O(2)-U(1)-O(7)	145.43(9)
O(3)-U(1)-O(7)	110.56(9)
O(1)-U(1)-N(2)	87.65(10)
O(4)-U(1)-N(2)	124.81(9)
O(6)-U(1)-N(2)	115.34(11)
O(5)-U(1)-N(2)	63.90(9)

O(2)-U(1)-N(2)	122.04(9)
O(3)-U(1)-N(2)	61.98(9)
O(7)-U(1)-N(2)	57.48(10)
O(1)-U(1)-N(1)	100.88(10)
O(4)-U(1)-N(1)	61.89(10)
O(6)-U(1)-N(1)	60.34(11)
O(5)-U(1)-N(1)	120.88(9)
O(2)-U(1)-N(1)	59.49(10)
O(3)-U(1)-N(1)	119.60(9)
O(7)-U(1)-N(1)	115.76(10)
N(2)-U(1)-N(1)	171.19(10)
O(1)-U(1)-I(1)	137.93(6)
O(4)-U(1)-I(1)	144.46(6)
O(6)-U(1)-I(1)	87.43(9)
O(5)-U(1)-I(1)	141.11(6)
O(2)-U(1)-I(1)	74.20(6)
O(3)-U(1)-I(1)	76.01(6)
O(7)-U(1)-I(1)	71.24(7)
N(2)-U(1)-I(1)	87.94(7)
N(1)-U(1)-I(1)	84.24(7)

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