Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Structural and Computational Characterization of a Bridging Zwitterionic-Amidoxime Uranyl Complex

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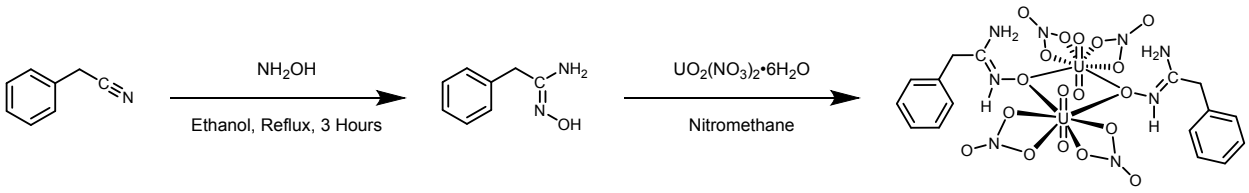
General Experimental:



SchemeS1 Synthetic route to **1**.

Caution! Although the uranyl salt used in this study contains isotopically depleted uranium, precautions for working with radioactive materials should be followed.

Uranyl nitrate hexahydrate (SPI-CHEM) and nitromethane (Acros Organics) were used without purification. Benzylamidoxime (BnAO) was synthesized according to a reported procedure.[1]

Single Crystal X-ray Diffraction

Diffraction quality crystals were grown by slow evaporation of a nitromethane solution of BnAO and uranyl nitrate hexahydrate in a 1:1 molar ratio. The crystal selected was a yellow prism with dimensions of 0.12 mm x 0.09 mm x 0.07 mm.

X-ray diffraction data for **1** were collected at 100 K on a Bruker D8 Venture using MoKα-radiation (λ=0.71073 Å). Data have been corrected for absorption using SADABS[2] area detector absorption correction program. Using Olex2[3], the structure was solved with the SHELXT[4] structure solution program using Direct Methods and refined with the SHELXL[5] refinement package using least squares minimization. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to heteroatoms were found from the residual density maps, placed, and refined with isotropic thermal parameters. All other hydrogen atoms in the investigated structure were located from difference Fourier maps but finally their positions were placed in geometrically calculated positions and refined using a riding model. Isotropic thermal parameters of the placed hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to. Calculations and refinement of structures were carried out using APEX3,[6] SHELXTL,[7] and Olex2 software.

Crystallographic Data for **1** $C_{16}H_{22}N_8O_{19}U_2$ (M =1106.47 g/mol): monoclinic, space group C2/c (no. 15), a = 14.7408(7) Å, b = 9.3327(5) Å, c = 20.6545(10) Å, β = 94.134(2)°, V = 2834.1(2) Å^3, Z = 4, T = 100 K, μ(MoKα) = 11.513 mm^{-1}, *Dcalc* = 2.593 g/cm^3, 76494 reflections measured (6.388° ≤ 2Θ ≤ 55.056°), 3268 unique (R_{int} = 0.0336, R_{sigma} = 0.0102) which were used in all calculations. The final R_1 was 0.0199 (I > 2σ(I)) and wR_2 was 0.0423 (all data).

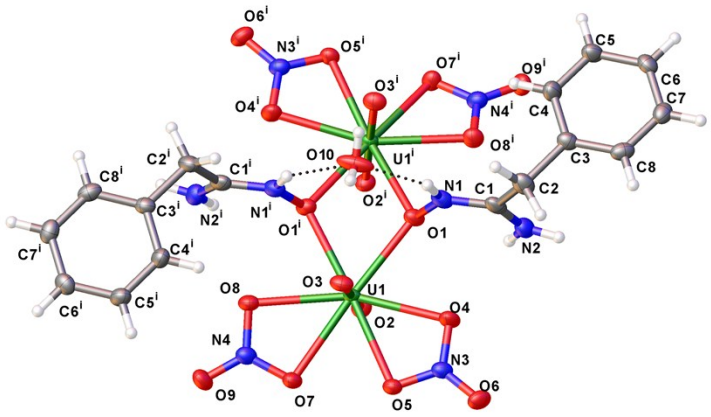


Figure S1 Complex **1** with atom labels. Hydrogen bond depicted as a black dotted line. Thermal ellipsoids drawn at the 50% probability level. Symmetry code(s): (i) −x+1, y, −z+3/2.

Table S1 Selected bond lengths (Å)

U1—U1^{i}	4.0513 (3)	O1—U1^{i}	2.466 (2)
U1—O1^{i}	2.466 (2)	O1—N1	1.408 (4)
U1—O1	2.442 (2)	O4—N3	1.279 (4)
U1—O2	1.757 (3)	O5—N3	1.275 (4)
U1—O3	1.764 (3)	O6—N3	1.209 (4)
U1—O4	2.492 (3)	O7—N4	1.275 (4)
U1—O5	2.519 (2)	O8—N4	1.275 (4)
U1—O7	2.509 (2)	O9—N4	1.216 (4)
U1—O8	2.515 (3)	N1—C1	1.316 (5)
N2—C1	1.310 (5)		

Symmetry code(s): (i) −*x*+1, *y*, −*z*+3/2.

Table S2 Selected hydrogen-bond parameters

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
N1—H1···O10	0.91 (5)	2.05 (4)	2.839 (5)	143 (4)
N2—H2A···O9^{i}	0.87 (5)	2.31 (5)	3.083 (4)	148 (4)
O10—H10···O5^{ii}	0.79 (5)	2.45 (6)	3.112 (3)	143 (6)
O10—H10···O6^{ii}	0.79 (5)	2.30 (6)	3.000 (3)	149 (6)

Symmetry code(s): (i) x, $-y+1$, $z-1/2$; (ii) $x-1/2$, $y+1/2$, z.

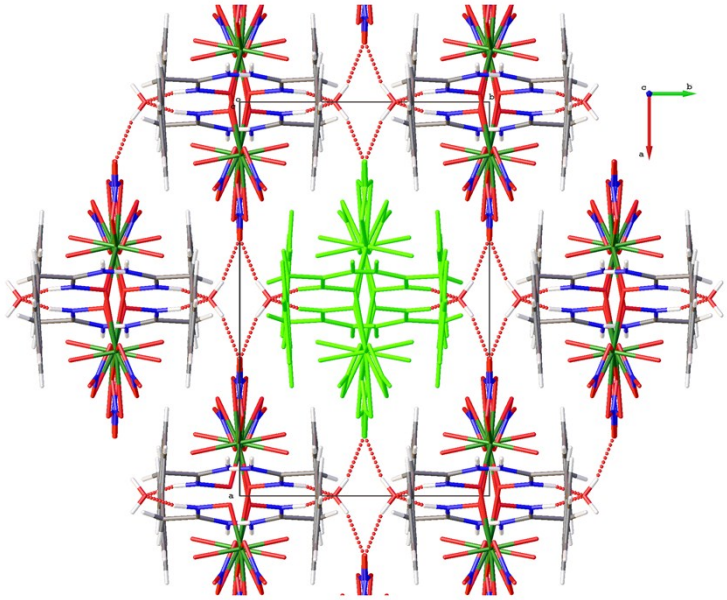


Figure S2 A packing diagram of **1** viewed down the crystallographic *c* axis highlighting the interchain HBing network established by the noncoordinating water. The bright green complexes specify one chain of complexes propagating in the *c* direction. HBs are depicted as red dotted lines.

Structural Database Search Parameters

ConQuest, version 1.22, was used to collect and measure geometric data from the CSD (version 5.39 November 2017, updates through May 2018). The search of organic amidoximes imposed no restrictions to augment the small data set (84 structures returned with 126 unique AOs) and only explored amidoximes where the amide group was -NH_2.

Table S3 Table of selected AO bond lengths.

Binding mode	*CSD refcode*	*C—N_{oxime}*	*C—N_{amide}*	*N—O_{oxime}*	*U—O_{oxime}*	*Equatorial coordination number*
Bridging Tautomer	**Complex 1**	1.316(5)	1.310(5)	1.408(4)	2.442(2), 2.466(2)	6
Monodentate Tautomer	COJGOX*	1.30	1.35	1.38	2.26	4
Monodentate Tautomer	COJGIR*	1.299	1.325	1.374	2.307	4
eta 2	BARYUQ	1.290(4)	1.349(5)	1.409(4)	2.383(2)	6
eta 2	BARYOK	1.292(4)	1.340(4)	1.422(3)	2.3524(19)	6
eta 2	QEBPOE	1.287(4)	1.357(4)	1.390(4)	2.3225(15)	6
eta 2	HORWOC	1.311(11), 1.290(13), 1.296(13), 1.293(11)	1.363(16), 1.344(16), 1.350(18), 1.362(15)	1.386(12), 1.397(12), 1.398(12), 1.392(12)	2.446(8), 2.414(9), 2.443(9), 2.385(8)	6
eta 2	NIFWEH	1.304(6)	1.349(7)	1.412(6)	2.354(3)	6
*CSD free AO***		1.291(0.01)	1.348(0.013)	1.426 (0.015)	n/a	
Bridging (μ_2) Tautomer with Lanthanides	SEYXIG[#]	1.300(4)	1.304(5)	1.367(3)	n/a	
	SEYXOM[#]	1.306(4)	1.317(5)	1.368(3)	n/a	
	SEYXUS[#]	1.305(7)	1.308(7)	1.375(5)	n/a	

Data in light blue are AO–uranyl structures. *Average values reported **Average values reported, standard deviation in parentheses #only one value provided as the other AOs are generated by symmetry (same values) or disordered.

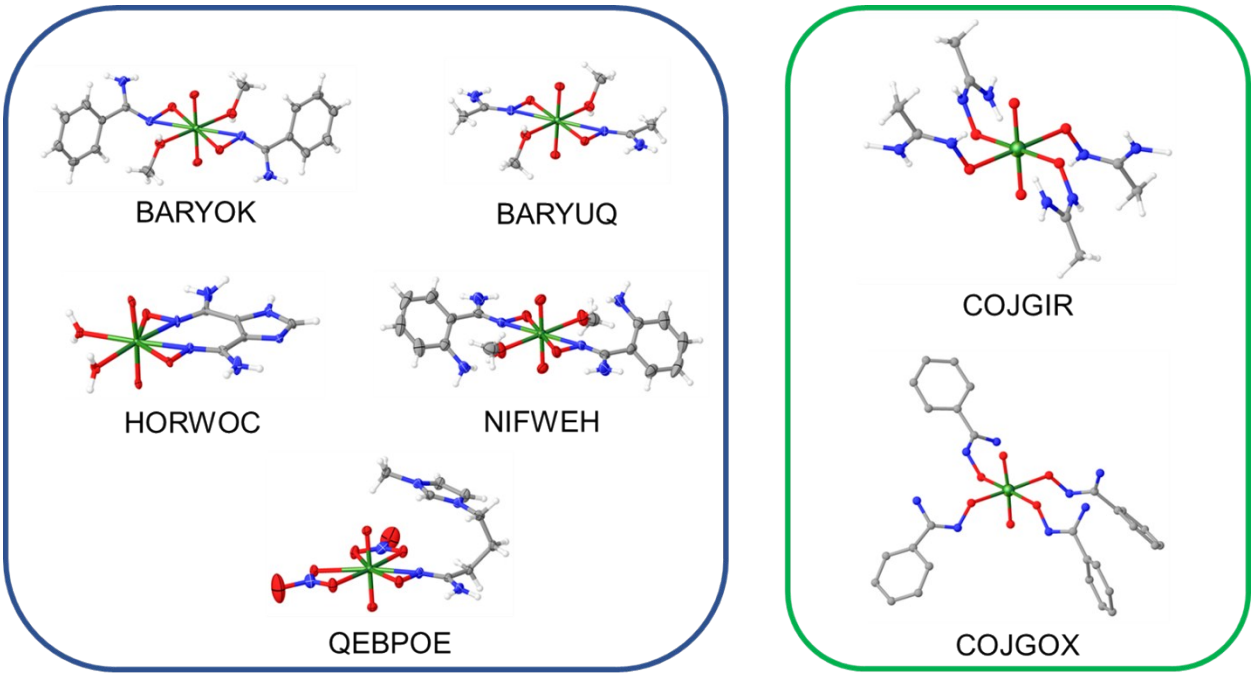


Figure S3 All 7 AO–uranyl structures in the literature with associated CSD ref codes. There are two structures of BARYOK in the database. Structures in the blue rectangle are η^2-AOs while the green rectangle contains the η^1-AOs.

Computational

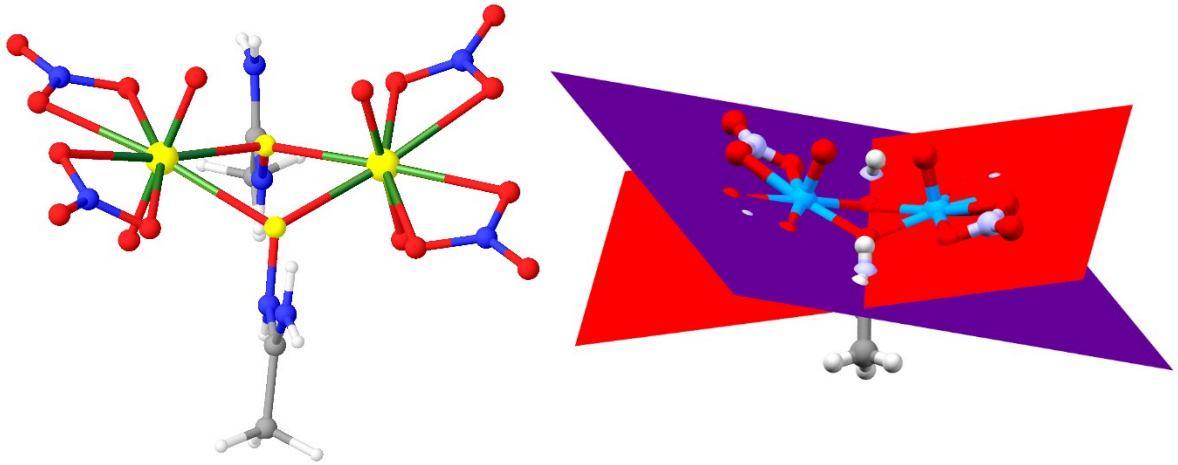


Figure 4S. Highlighting the U···μ2O···μ2O···U dihedral angle scanned. Atoms used to generate the two planes are in yellow (left), and the two planes for measuring the dihedral are represented in purple and red planes (right).

Coordinates for rigid dihedral potential energy scan

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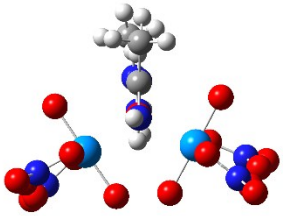

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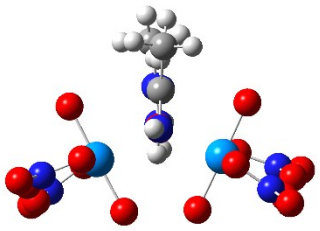

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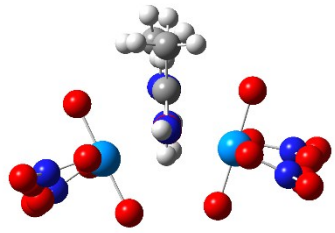

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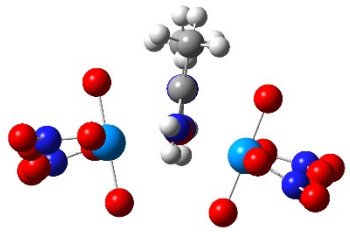

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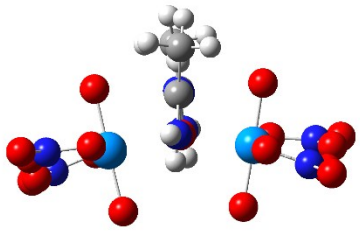

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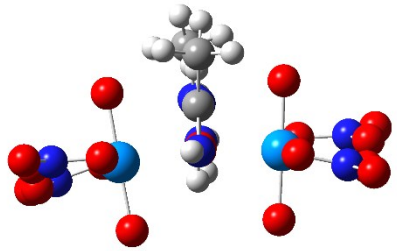
170



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N	-1.14505075	-0.49665235	3.09215454
H	-2.00429151	-0.16874603	3.05808449
N	0.03150025	-2.29840769	3.88344932
H	0.01617258	-3.10665173	4.20346125
H	0.74640978	-2.05405826	3.48102328
N	-0.64466716	-2.92441816	-0.06898583
N	-0.21097823	1.15276584	-2.70271978
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C	-2.33293500	-2.08180130	4.46530124
H	-2.63253868	-3.02948698	4.06903178
H	-3.11280116	-1.36645431	4.30722701
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O	1.64332230	0.49346749	7.01969372
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N	-0.26417164	4.54180598	-0.38247333
H	-0.28423927	5.35235298	-0.69633932
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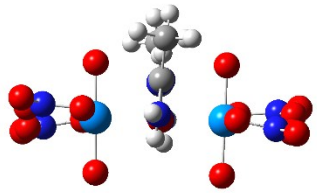

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H	-2.00429151	-0.16874603	3.05808449
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H	0.01617258	-3.10665173	4.20346125
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C	-1.08398451	-1.62177981	3.77172435

C	-2.33293500	-2.08180130	4.46530124
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H	-3.11280116	-1.36645431	4.30722701
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O	1.08871577	2.29402556	5.82886433
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H	-0.28423927	5.35235298	-0.69633932
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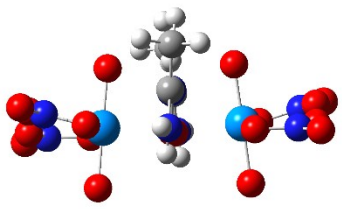

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O	0.64307492	2.30145262	5.95697929
O	0.99640650	0.55725221	7.21313003
O	-0.05070729	4.40799547	4.66811254
O	0.05486737	4.51998678	2.52020987
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H	-2.00429151	-0.16874603	3.05808449
N	0.03150025	-2.29840769	3.88344932
H	0.01617258	-3.10665173	4.20346125
H	0.74640978	-2.05405826	3.48102328
N	0.72785371	1.04210262	6.13839076
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C	-1.08398451	-1.62177981	3.77172435
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H	-3.11280116	-1.36645431	4.30722701
U	-0.59499411	0.05742624	0.04999727
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O	-1.44787253	-2.08145035	-0.94668444
O	-0.64221613	-2.25248925	1.04397639
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N	-0.26417164	4.54180598	-0.38247333
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H	0.50773467	4.20150060	-0.23757019
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C	-2.69401321	4.63713361	-0.13186097
H	-2.72213673	5.60622343	0.32087956
H	-3.45836872	4.02181526	0.29480516
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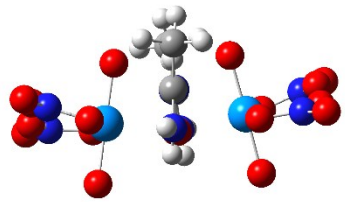
200



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N	0.03150025	-2.29840769	3.88344932
H	0.01617258	-3.10665173	4.20346125
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N	-0.39329457	5.12734836	3.62667240
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O	-0.84718359	-2.22234421	1.10628009
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H	-2.15537391	2.66905827	1.12462187
N	-0.26417164	4.54180598	-0.38247333
H	-0.28423927	5.35235298	-0.69633932
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C	-2.69401321	4.63713361	-0.13186097
H	-2.72213673	5.60622343	0.32087956
H	-3.45836872	4.02181526	0.29480516
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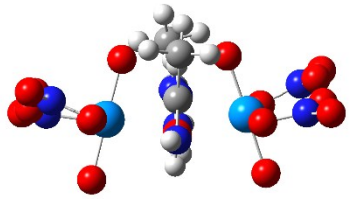
210



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N	0.03150025	-2.29840769	3.88344932
H	0.01617258	-3.10665173	4.20346125
H	0.74640978	-2.05405826	3.48102328
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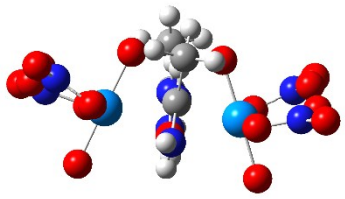
220



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H	-2.00429151	-0.16874603	3.05808449
N	0.03150025	-2.29840769	3.88344932
H	0.01617258	-3.10665173	4.20346125
H	0.74640978	-2.05405826	3.48102328
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N	-0.26417164	4.54180598	-0.38247333
H	-0.28423927	5.35235298	-0.69633932
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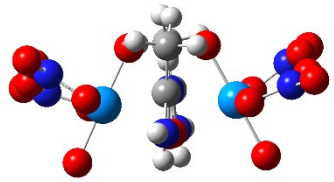

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H	-2.00429151	-0.16874603	3.05808449
N	0.03150025	-2.29840769	3.88344932
H	0.01617258	-3.10665173	4.20346125
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N	-1.32350779	2.88552603	0.79705438
H	-2.15537391	2.66905827	1.12462187
N	-0.26417164	4.54180598	-0.38247333
H	-0.28423927	5.35235298	-0.69633932
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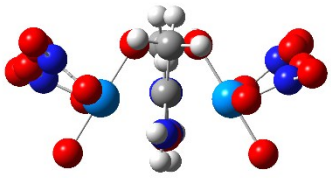
H	-2.72213673	5.60622343	0.32087956
H	-3.45836872	4.02181526	0.29480516
H	-2.14387954	-2.17742577	5.51411676
H	-2.85790384	4.73062211	-1.18509397

240



U	-0.74559632	2.11412220	3.41222584
O	0.00000000	0.00000000	2.44249831
O	-2.37119835	1.61744903	2.96959313

O	0.89610370	2.61269805	3.82332705
O	-0.55696682	0.28330356	5.09251510
O	-1.19123831	2.17907457	5.89132295
O	-0.92016586	0.48699194	7.23607910
O	-1.84184530	4.15016868	4.38416250
O	-1.00790853	4.40712158	2.41548309
O	-2.05665883	6.06765852	3.35590046
N	-1.14505075	-0.49665235	3.09215454
H	-2.00429151	-0.16874603	3.05808449
N	0.03150025	-2.29840769	3.88344932
H	0.01617258	-3.10665173	4.20346125
H	0.74640978	-2.05405826	3.48102328
N	-0.89191935	0.96160921	6.12423125
N	-1.65381387	4.92121191	3.38760315
C	-1.08398451	-1.62177981	3.77172435
C	-2.33293500	-2.08180130	4.46530124
H	-2.63253868	-3.02948698	4.06903178
H	-3.11280116	-1.36645431	4.30722701
U	-1.38623357	0.25458777	0.41890781
O	-0.09879375	2.23546969	1.03587502
O	-2.69221082	0.94221860	1.37151699
O	-0.05406716	-0.43822452	-0.50737117
O	-1.54406537	2.08243944	-1.26647893
O	-2.64284667	0.29942749	-1.76436451
O	-2.62840344	1.97293336	-3.15869678
O	-2.99216892	-1.60660742	-0.08357927
O	-1.58458570	-2.00918428	1.49683473
O	-3.08824077	-3.50365197	0.99960957
N	-1.32350779	2.88552603	0.79705438
H	-2.15537391	2.66905827	1.12462187
N	-0.26417164	4.54180598	-0.38247333
H	-0.28423927	5.35235298	-0.69633932
H	0.50773467	4.20150060	-0.23757019
N	-2.28799518	1.47454786	-2.10991551

N	-2.57906123	-2.41676304	0.80860003
C	-1.35304534	4.01001077	0.11186858
C	-2.69401321	4.63713361	-0.13186097
H	-2.72213673	5.60622343	0.32087956
H	-3.45836872	4.02181526	0.29480516
H	-2.14387954	-2.17742577	5.51411676
H	-2.85790384	4.73062211	-1.18509397

Dihedral (degrees)	Energy (kcal/mol)	
240	159.77	
230	79.98	
220	44.69	
210	25.47	
200	13.72	
190	6.62	
180	2.20	
170	0.09	
160	0.00	
156.73	0.38	Crystal structure value
150	1.84	
140	6.79	
130	21.12	
120	70.15	

Table S5. single point energies from the rigid dihedral energy scan of a dinuclear AAO-Uranyl complex.

Species	Relative energy (kcal/mol)
AAO-H2O-1 (without water)	0
AAO-1	-5.175687957

Table S5. Relative single point energy computations of dinuclear AAO-Uranyl complexes.

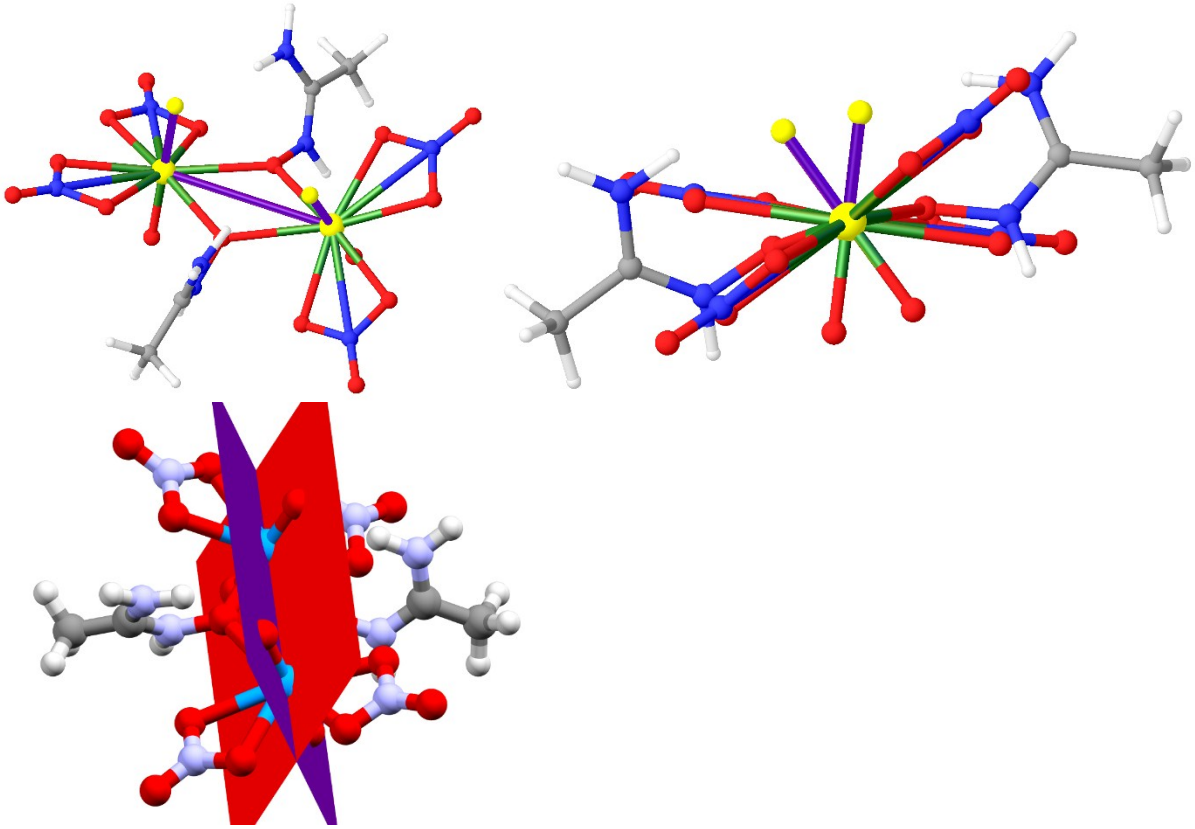


Figure S5. Highlighting the O=U···U=O dihedral angle measured. Atoms used to generate the two planes are in yellow (above), and the two planes for measuring the dihedral are represented in purple and red planes (below).

Coordinates for dinuclear AAO-Uranyl complexes for single point energy calculations

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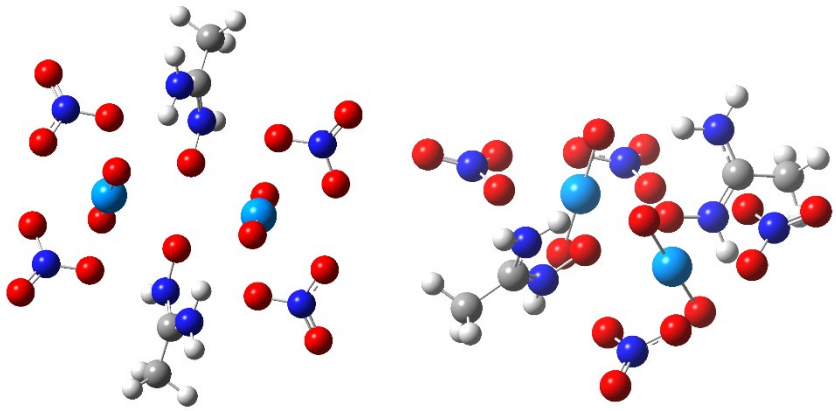
AAO- 1

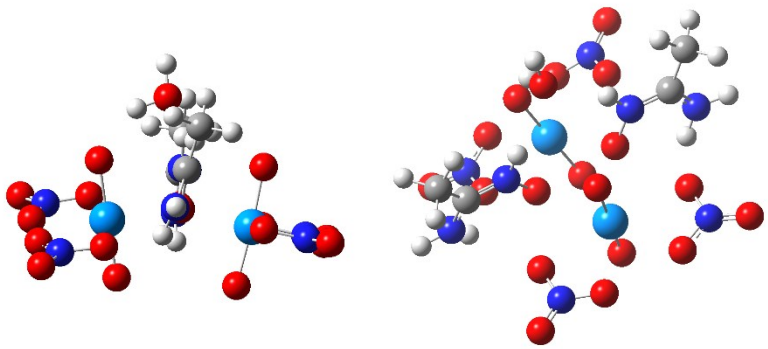


U	-2.19893000	-0.07799000	-0.05131000
O	-0.00575000	1.26682000	-0.15560000
O	-2.10684000	0.56823000	1.60608000
O	-2.28325000	-0.73576000	-1.69929000
O	-2.57378000	2.19460000	-0.99391000
O	-4.35448000	1.12991000	-0.40095000
O	-4.53374000	3.15669000	-1.22706000
O	-4.24532000	-1.34701000	0.57275000
O	-2.37632000	-2.36764000	0.91364000
O	-4.26086000	-3.36567000	1.43854000
N	0.09736000	2.53787000	-0.61984000
H	0.49969000	2.64383000	-1.54561000
N	-0.72512000	3.37434000	1.34105000
H	-1.00677000	4.15979000	1.90569000
H	-0.90862000	2.43411000	1.67887000
N	-3.86503000	2.20408000	-0.89120000
N	-3.66638000	-2.40633000	0.99883000
C	-0.23552000	3.56779000	0.12068000
C	-0.06856000	4.94871000	-0.43022000
U	2.19893000	0.07799000	-0.05130000

O	0.00575000	-1.26682000	-0.15558000
O	2.10683000	-0.56821000	1.60610000
O	2.28326000	0.73574000	-1.69929000
O	2.57378000	-2.19460000	-0.99388000
O	4.35448000	-1.12992000	-0.40092000
O	4.53374000	-3.15671000	-1.22701000
O	4.24532000	1.34702000	0.57275000
O	2.37631000	2.36765000	0.91363000
O	4.26086000	3.36569000	1.43853000
N	-0.09736000	-2.53788000	-0.61982000
H	-0.49969000	-2.64385000	-1.54558000
N	0.72511000	-3.37433000	1.34108000
H	1.00677000	-4.15978000	1.90573000
H	0.90861000	-2.43409000	1.67890000
N	3.86503000	-2.20409000	-0.89116000
N	3.66637000	2.40634000	0.99882000
C	0.23552000	-3.56779000	0.12071000
C	0.06857000	-4.94871000	-0.43018000
H	-0.39486000	-4.92624000	-1.41817000
H	1.04554000	-5.43421000	-0.51643000
H	-0.56707000	-5.53893000	0.23662000
H	-1.04552000	5.43422000	-0.51646000
H	0.56710000	5.53892000	0.23656000
H	0.39485000	4.92623000	-1.41823000

AAO-H2O-1

- Starting coordinates for the water were identical to that of the crystal structure.



U	2.11305500	0.02794300	-0.26985000
O	-0.05278000	1.34614600	0.11478500
O	1.75171100	-0.07895900	-1.99615500
O	2.36833200	0.13615100	1.48844600
O	2.39554100	2.50513100	-0.45214500
O	4.19646700	1.34890300	-0.70569500
O	4.29719400	3.54009400	-0.81800400
O	4.23558000	-1.26130100	-0.53479700
O	2.48225900	-2.44257800	-0.11645300
O	4.43088700	-3.43733000	-0.30729200
N	-0.02152700	2.24035900	1.14515300
H	-0.01428900	1.83712100	2.08618400
N	-0.15426800	3.98362000	-0.33208700
H	-0.09105700	4.97009400	-0.52500100
H	-0.08195700	3.32594900	-1.09783800
N	3.67017500	2.51265700	-0.66866400
N	3.75691900	-2.42907000	-0.32197900
C	-0.07494100	3.53110800	0.91296100
C	-0.06258800	4.47969800	2.07111000
H	0.79304200	5.15717700	1.98967600
H	0.01024500	3.94253300	3.01831600
U	-2.10109500	-0.07563200	-0.25944400
O	0.02830100	-1.30852900	0.26849000
O	-1.74320200	0.22539900	-1.96113500
O	-2.42428900	-0.35426500	1.48527500

O	-2.14488700	-2.50140100	-0.84155700
O	-4.05554900	-1.51198800	-0.88727200
O	-3.93737300	-3.64596600	-1.39751000
O	-4.30544100	1.07374500	-0.46595700
O	-2.66800000	2.31021100	0.19458300
O	-4.67472400	3.18415000	0.01859400
N	0.16234700	-1.93312400	1.47568600
H	0.33024300	-1.32260200	2.27611000
N	-0.12698700	-4.01919300	0.55325900
H	-0.09407300	-5.02195900	0.64309800
H	-0.44969400	-3.61238500	-0.31919900
N	-3.41710500	-2.60517000	-1.06291300
N	-3.92840500	2.23480100	-0.08235500
C	0.15278500	-3.24217600	1.59011800
C	0.48063500	-3.84266500	2.92427900
H	-0.30872400	-4.53169600	3.23808900
H	0.59921800	-3.07048200	3.68646600
O	-0.52634500	0.36823400	3.35530700
H	-1.41011200	0.14553600	3.00035600
H	-0.61494300	0.47672600	4.31052600
H	1.42209600	-4.39674200	2.84922700
H	-0.98310400	5.07140700	2.07349000

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