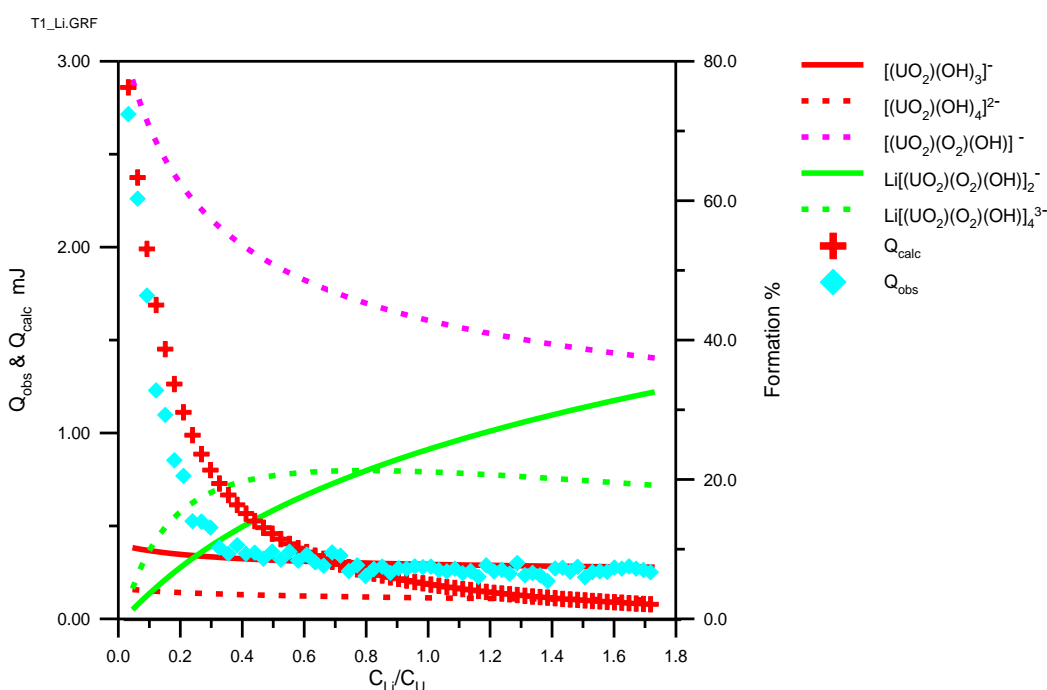


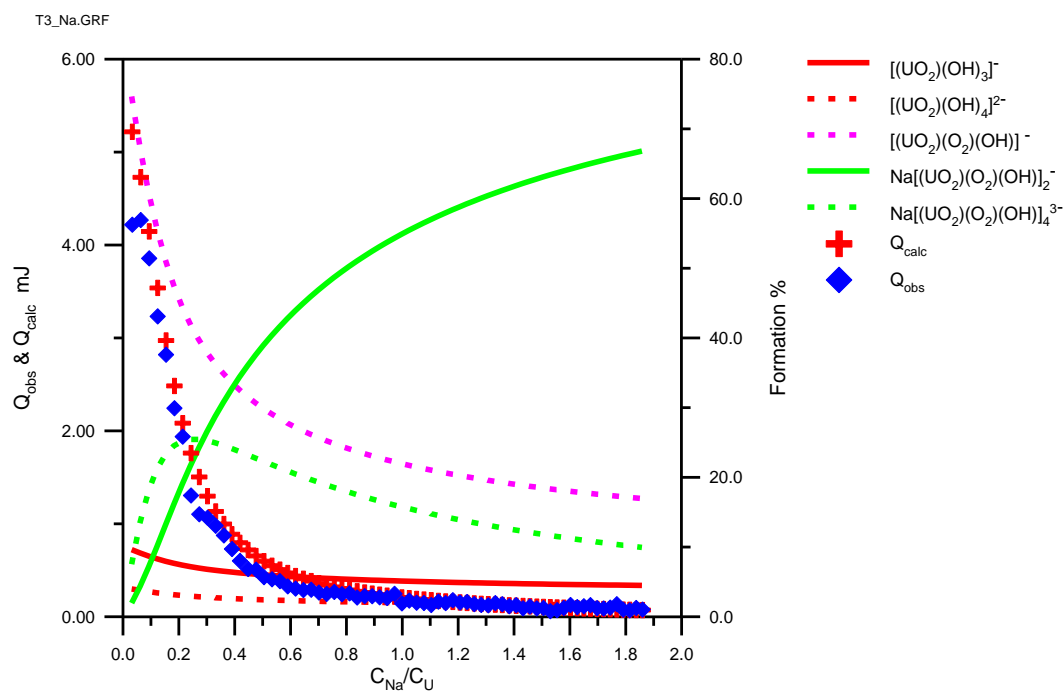
## Electronic Supporting Information to

# Alkali - Metal Ion Coordination in Uranyl(VI) Poly-Peroxide Complexes in Solution. Part 1, The $\text{Li}^+$ , $\text{Na}^+$ and $\text{K}^+$ - Peroxide – Hydroxide Systems.

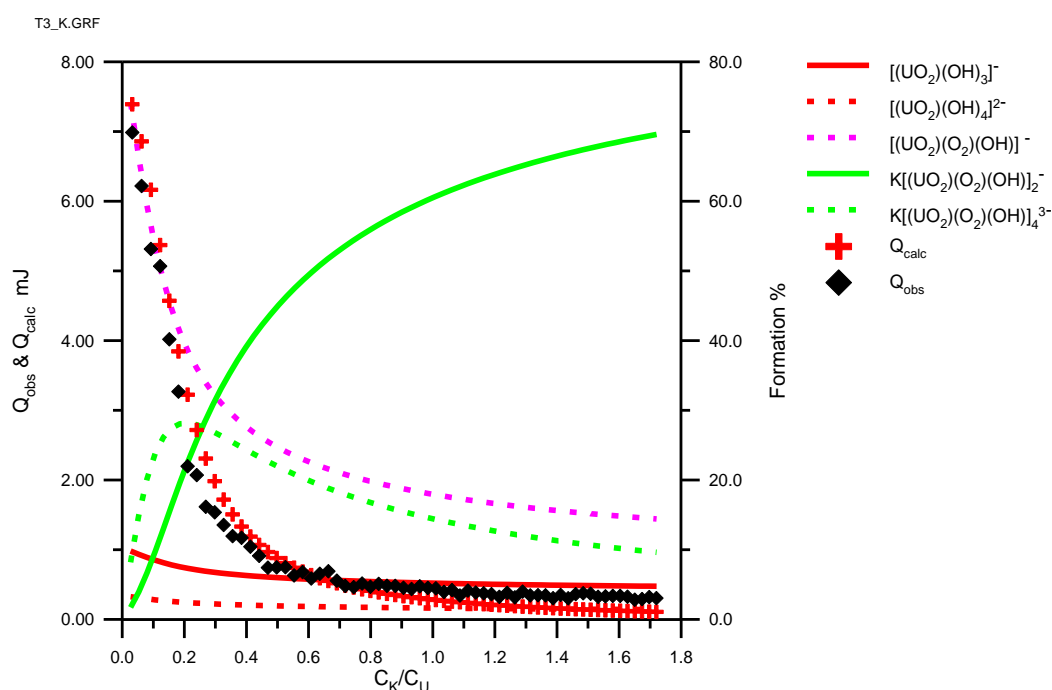
Pier Luigi Zanonato, Plinio Di Bernardo, Valerie Vallet, Zoltán Szabó and Ingmar Grenthe



**Figure S1.** A comparison of the stepwise reaction heats (observed, cyan diamonds; calculated, red crosses) for titration T1 of the system  $\text{Li}^+ - \text{UO}_2^{++} - \text{H}_2\text{O}_2 - \text{OH}^-$ . The speciation curves were calculated using the selected best fit model of Table 1. —,  $[(\text{UO}_2)(\text{OH})_3]^-$ ; - - -,  $[(\text{UO}_2)(\text{OH})_4]^{2-}$ ; - - -,  $[(\text{UO}_2)(\text{O}_2)(\text{OH})]^-$ ; —,  $\text{Li}[(\text{UO}_2)(\text{O}_2)(\text{OH})_2]^-$ ; - - -,  $\text{Li}[(\text{UO}_2)(\text{O}_2)(\text{OH})_4]^{3-}$ .



**Figure S2.** A comparison of the stepwise reaction heats (observed, blue diamonds; calculated, red crosses) for titration T3 of the system  $\text{Na}^+ - \text{UO}_2^{++} - \text{H}_2\text{O}_2 - \text{OH}^-$ . The speciation curves were calculated using the selected best fit model of Table 1. —,  $[(\text{UO}_2)(\text{OH})_3]^-$ ; - - -,  $[(\text{UO}_2)(\text{OH})_4]^{2-}$ ; · · ·,  $[(\text{UO}_2)(\text{O}_2)(\text{OH})]^-$ ; —,  $\text{Na}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_2^-$ ; - - -,  $\text{Na}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_4^{3-}$ .



**Figure S3.** A comparison of the stepwise reaction heats (observed, black diamonds; calculated, red crosses) for titration T3 of the system  $\text{K}^+ - \text{UO}_2^{++} - \text{H}_2\text{O}_2 - \text{OH}^-$ . The speciation curves were calculated using the selected best fit model of Table 1. —,  $[(\text{UO}_2)(\text{OH})_3]^-$ ; - - -,  $[(\text{UO}_2)(\text{OH})_4]^{2-}$ ; · · ·,  $[(\text{UO}_2)(\text{O}_2)(\text{OH})]^-$ ; —,  $\text{K}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_2^-$ ; - - -,  $\text{K}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_4^{3-}$ .

## Tables S1 - S3

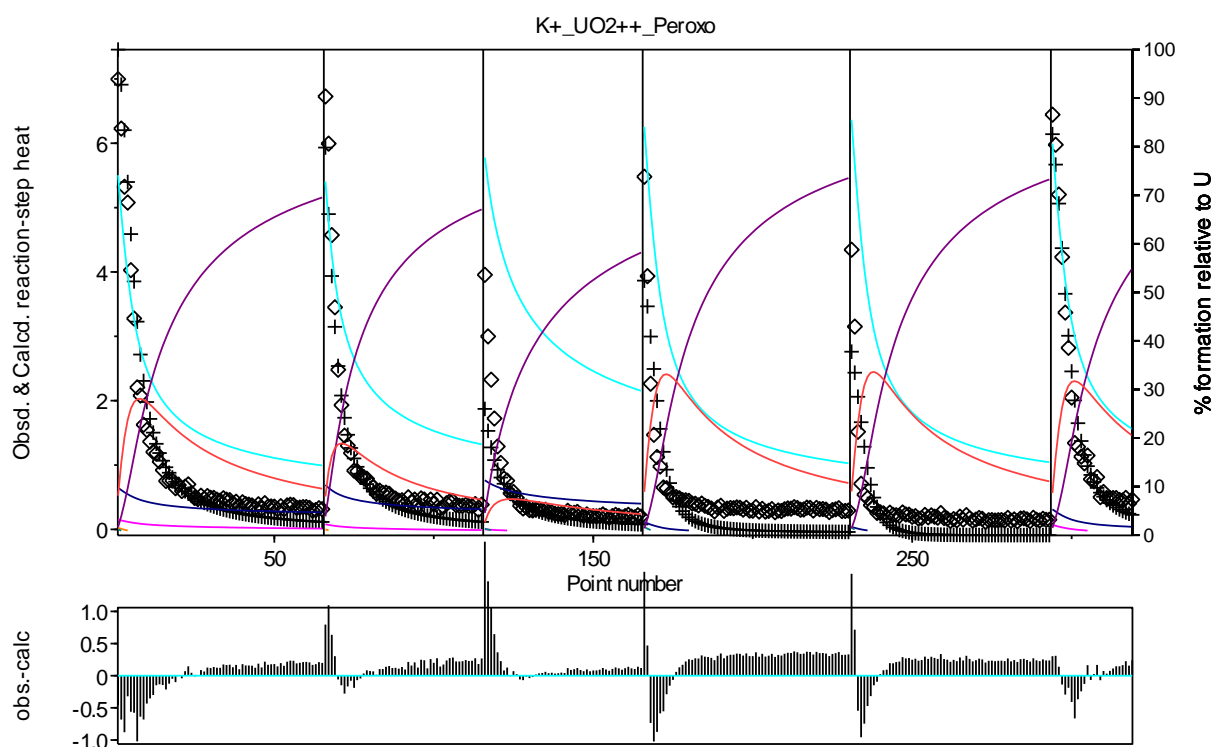
Composition of solutions used in the calorimetric titrations in the  $K^+$ ,  $Na^+$  and  $Li^+$  - uranyl(VI) - peroxide – hydroxide systems.

### Potassium Complexes

Table S1 - Titrations with  $KNO_3$

	Cell contents				Titrant
	$V^\circ$ mL	$C^\circ_U$ mM	$C^\circ_{H_2O_2}$ mM	$C^\circ_{OH}$ mM	$C_{K,T}$ mM
T1	2.277	3.613	1.068	26.537	49.79
T2	2.255	2.413	2.441	16.986	49.79
T3	2.275	3.622	3.612	25.480	49.79
T4	2.249	1.207	1.281	8.443	49.79
T5	2.255	3.619	5.466	25.439	49.79
T6	2.262	3.621	7.130	28.885	49.95
T7	2.267	3.620	4.545	29.139	49.95
T8	2.262	0.000	0.000	0.000	49.79

The titrations T2 – T7 in the Table S1 were used to calculate the thermodynamic parameters. Titration T1, with a large concentration of hydroxide complexes, was discarded because of the possible presence of systematic errors (see Text). Titration T8 was carried out to measure the dilution heat.







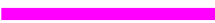
The observed ( $\diamond$ ) and calculated ( $+$ ) stepwise reaction heats for the six titrations carried out to measure the stability constants and the enthalpies of the reactions shown below. The full lines in the plots represent the species distribution during the titrations according to the given color code.

Reaction	$\log K \pm \sigma$	$\Delta H \pm \sigma$
$2\text{UO}_2^{2+} + 2\text{HO}_2^- + 2\text{H}_2\text{O} + \text{K}^+ \rightleftharpoons \text{K}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_2^- + 4\text{H}^+$	$0.9 \pm 0.2$	$-85.0 \pm 1.0$
$4\text{UO}_2^{2+} + 4\text{HO}_2^- + 4\text{H}_2\text{O} + \text{K}^+ \rightleftharpoons \text{K}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_4^{3-} + 8\text{H}^+$	$1.3 \pm 0.2$	$-174 \pm 8$

$$\sigma = 0.3525 \text{ mJ}$$

$Q_{\text{obs}}$  ( $\diamond$ );  $Q_{\text{calc}}$  ( $+$ )

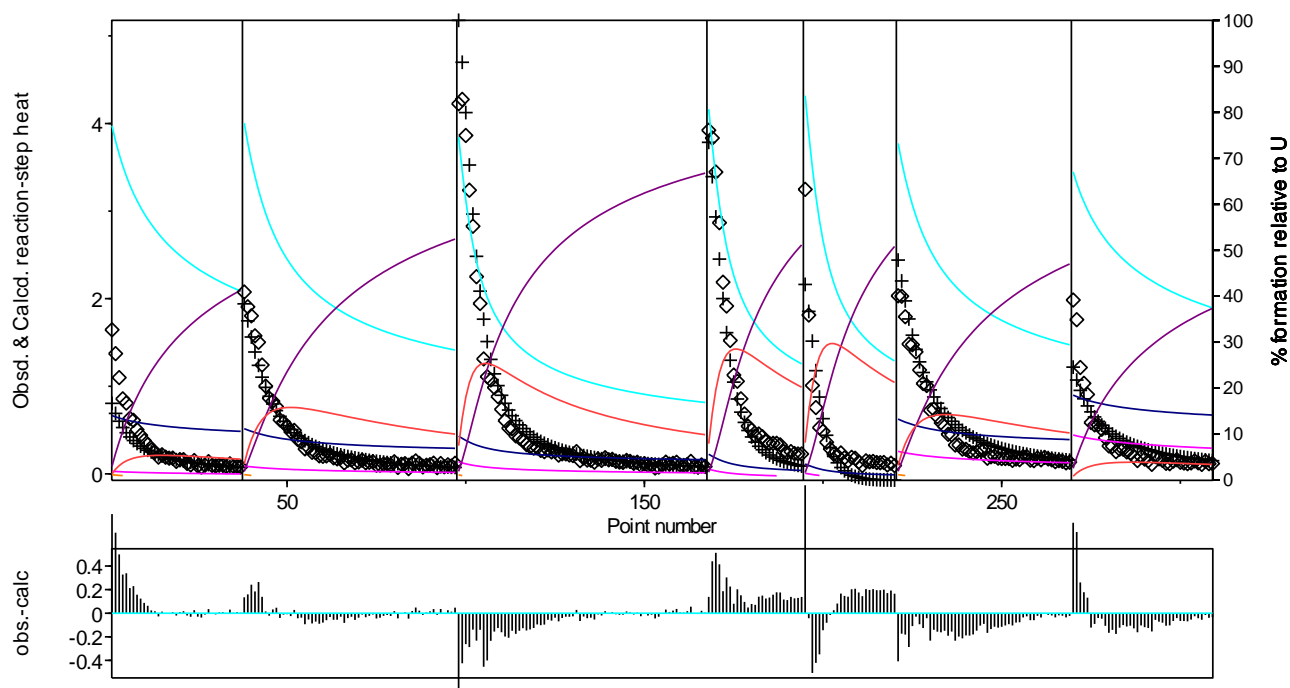
Color code for the speciations:

$[(\text{UO}_2)(\text{O}_2)(\text{OH})]^-$	
$\text{K}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_4^{3-}$	
$\text{K}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_2^-$	
$[(\text{UO}_2)(\text{OH})_3]^-$	
$[(\text{UO}_2)(\text{OH})_4]^{2-}$	

## Sodium Complexes

	Cell contents				Titrant
	V° mL	C° <sub>U</sub> mM	C° <sub>H2O2</sub> mM	C° <sub>OH</sub> mM	C <sub>Na,T</sub> mM
<b>T1</b>	2.247	1.211	1.216	9.762	24.895
<b>T2</b>	2.247	2.414	2.454	19.425	24.895
<b>T3</b>	2.247	3.625	3.721	29.166	49.98
<b>T4</b>	2.251	3.624	2.49	27.75	49.98
<b>T5</b>	2.251	2.428	2.422	28.112	24.895
<b>T6</b>	2.265	1.215	1.223	26.815	24.895
<b>T7</b>	2.263	3.627	4.512	30.066	49.98
<b>T8</b>	2.262	3.63	5.426	30.977	49.98
<b>T9</b>	2.249	3.627	1.192	26.726	49.98
<b>T10</b>	2.246	0.000	0.000	0.000	24.895

The titrations T1 – T7 in the Table S2 were used to calculate the thermodynamic parameters. Titrations T8 and T9, with a large concentration of hydroxide complexes, were discarded because of the possible presence of systematic errors (see Text). Titration T10 was carried out to measure the dilution heat.








The observed ( $\diamond$ ) and calculated ( $\+$ ) stepwise reaction heats for the seven titrations carried out to measure the stability constants and the enthalpies of the reactions shown below. The full lines in the plots represent the species distribution during the titrations according to the given color code.

Reaction	$\log\beta\pm\sigma$	$\Delta H\pm\sigma$
$2\text{UO}_2^{++}+2\text{HO}_2^-+2\text{H}_2\text{O}+\text{Na}^+ \rightleftharpoons \text{Na}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_2^- + 4\text{H}^+$	$0.7\pm 0.1$	$-77.8 \pm 0.2$
$4\text{UO}_2^{++}+4\text{HO}_2^-+4\text{H}_2\text{O}+\text{Na}^+ \rightleftharpoons \text{Na}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_4^{3-} + 8\text{H}^+$	$1.0\pm 0.1$	$-164 \pm 3$

$$\sigma = 0.1826 \text{ mJ}$$

$Q_{\text{obs}}$  ( $\diamond$ );  $Q_{\text{calc}}$  ( $\+$ )

Color code for the speciations:

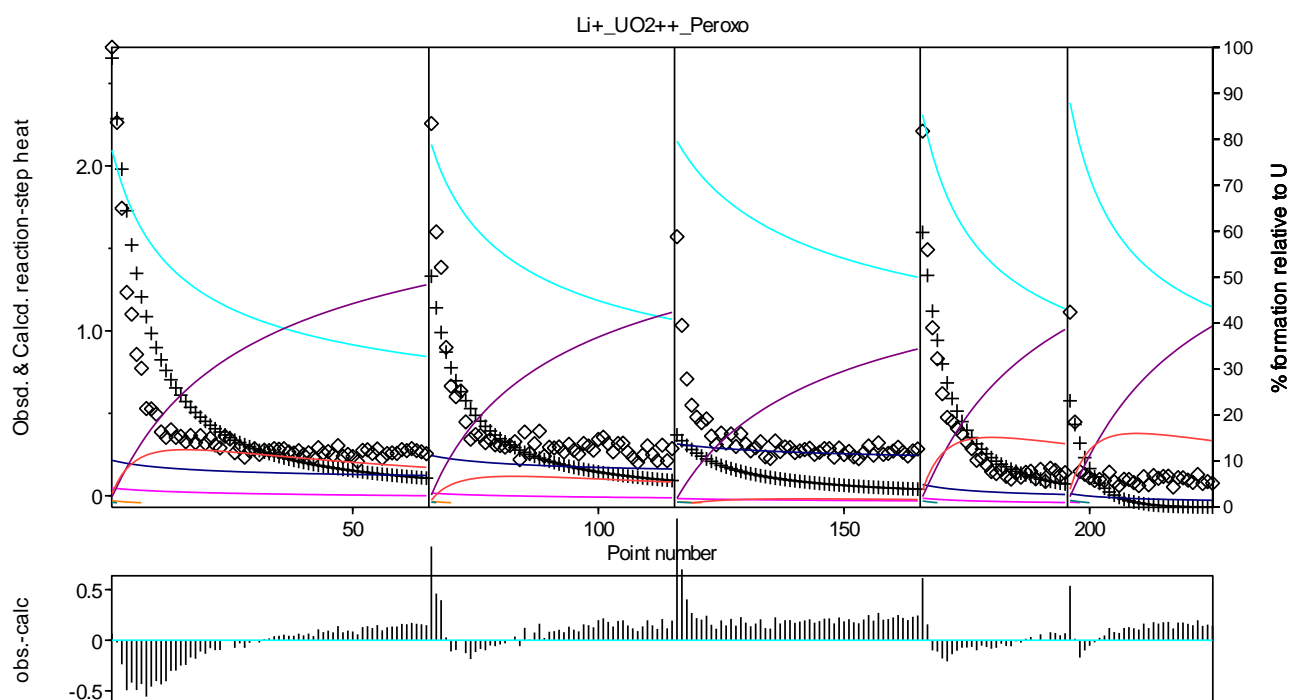
$[(\text{UO}_2)(\text{O}_2)(\text{OH})]^-$	
$\text{Na}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_4^{3-}$	
$\text{Na}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_2^-$	
$[(\text{UO}_2)(\text{OH})_3]^-$	
$[(\text{UO}_2)(\text{OH})_4]^{2-}$	

## Lithium Complexes

Table S3 - Titrations with LiNO<sub>3</sub>

	Cell contents			Titrant	
	V° mL	C <sup>o</sup> <sub>U</sub> mM	C <sup>o</sup> <sub>H<sub>2</sub>O<sub>2</sub></sub> mM	C <sup>o</sup> <sub>OH</sub> mM	C <sub>Li,T</sub> mM
T1	2.274	3.623	3.664	29.033	49.72
T2	2.258	2.405	2.449	19.321	49.72
T3	2.247	1.210	1.230	9.701	49.72
T4	2.262	3.620	4.725	29.080	49.72
T5	2.256	3.638	5.782	29.238	49.82
T6	2.263	0.000	0.000	0.000	49.72

The titrations T1 – T5 in the Table were used to calculate the thermodynamic parameters. Titration T5 was carried out to measure the dilution heat.



The observed ( $\diamond$ ) and calculated ( $+$ ) stepwise reaction heats for the five titrations carried out to measure the stability constants and the enthalpies of the reactions shown below. The full lines in the plots represent the species distribution during the titrations according to the given color code.

Reaction	$\log\beta\pm\sigma$	$\Delta H\pm\sigma$
$2\text{UO}_2^{++}+2\text{HO}_2^-+2\text{H}_2\text{O}+\text{Li}^+ \rightleftharpoons \text{Li}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_2^- + 4\text{H}^+$	$0.0\pm 0.2$	$-78.0 \pm 0.5$
$4\text{UO}_2^{++}+4\text{HO}_2^-+4\text{H}_2\text{O}+\text{Li}^+ \rightleftharpoons \text{Li}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_4^{3-} + 8\text{H}^+$	$-0.2\pm 0.3$	$-162 \pm 2$

$$\sigma = 0.2133 \text{ mJ}$$

$Q_{\text{obs}}$  ( $\diamond$ );  $Q_{\text{calc}}$  ( $+$ )

Color code for the speciations:

$[(\text{UO}_2)(\text{O}_2)(\text{OH})]^-$	<span style="display: inline-block; width: 20px; height: 10px; background-color: cyan; border: 1px solid black;"></span>
$\text{Li}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_4^{3-}$	<span style="display: inline-block; width: 20px; height: 10px; background-color: red; border: 1px solid black;"></span>
$\text{Li}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_2^-$	<span style="display: inline-block; width: 20px; height: 10px; background-color: purple; border: 1px solid black;"></span>
$[(\text{UO}_2)(\text{OH})_3]^-$	<span style="display: inline-block; width: 20px; height: 10px; background-color: blue; border: 1px solid black;"></span>
$[(\text{UO}_2)(\text{OH})_4]^{2-}$	<span style="display: inline-block; width: 20px; height: 10px; background-color: magenta; border: 1px solid black;"></span>



## Table S4

Test solutions with 10 mM uranyl, 70 mM TMAOH and 70 mM peroxide and varying concentration of  $\text{Na}^+$  used in the  $^{17}\text{O}$  NMR experiments. The ratio between the peak integrals at 1174 ppm assigned to  $\text{Na}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_4^{3-}$  and 1088 ppm assigned to  $\text{Na}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_2^-$  were used to calculate the equilibrium constant for reaction (6):  $2\text{Na}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_2^- \rightarrow \text{Na}[(\text{UO}_2)(\text{O}_2)(\text{OH})]_4^{3-} + \text{Na}^+$ ;

Test solution	$[\text{Na}^+]$ M	Ratio between 1074 and 1088 ppm peaks	$\log K(6)$
(b)	0.07	74/21	0.10
(c)	0.13	69/27	0.09

## Table S5

Electronic reaction in kJ/mol for different  $\text{Na}[(\text{UO}_2)(\text{O}_2)(\text{OH})_2]^-$  isomers computed at the M06L, M06, M06-2X and the MP2 level calculated in gas-phase. The coordinated water has not been included in the formulae for simplicity.

Isomer	Figure 4	MP2	M06L	M06	M06-2X
$\text{Na}_{\text{yl}}[(\text{O}_2)(\text{UO}_2)(\mu\text{-}\eta^2(\text{O}_2))(\text{UO}_2)(\text{OH})_2]^-$	a	0.0	0.0	0.0	0.0
$\text{Na}_{\text{yl}}[(\text{OH})(\text{O}_2)(\text{UO}_2)(\mu\text{-}\eta^2(\text{O}_2))(\text{UO}_2)(\text{OH})]^-$	b	139.1	103.7	126.2	137.7
$\text{Na}_{\text{term}}[(\text{O}_2)(\text{UO}_2)(\mu\text{-}\eta^2(\text{O}_2))(\text{UO}_2)(\text{OH})_2]^-$	c	11.7	16.8	14.9	10.2
$\text{Na}_{\text{term}}[(\text{O}_2)(\text{UO}_2)(\mu\text{-}(\text{OH})_2)(\text{UO}_2)(\text{OH})_2]^-$	d	70.9	52.1	64.5	76.3

## Table S6

The stability constants and reaction enthalpies of all the complexes involved into the solution equilibria and not containing the alkali ions, T 25 °C ,  $\mu = 0.100$  M TMANO<sub>3</sub>. Values taken from Ref. 1a

Reaction	$\log \beta$	$\Delta H^\circ \pm 3\sigma$ kJ/mol
$\text{UO}_2^{2+} + \text{H}_2\text{O} = [(\text{UO}_2)(\text{OH})]^+ + \text{H}^+$	$-5.20 \pm 0.10$	46.5 <sup>a</sup>
$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} = [(\text{UO}_2)_2(\text{OH})_2]^{2+} + 2\text{H}^+$	$-5.94 \pm 0.03$	$49.1 \pm 0.9$
$3\text{UO}_2^{2+} + 4\text{H}_2\text{O} = [(\text{UO}_2)_3(\text{OH})_4]^{2+} + 4\text{H}^+$	$-12.25 \pm 0.08$	$94.2 \pm 3.0$
$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} = [(\text{UO}_2)_3(\text{OH})_5]^+ + 5\text{H}^+$	$-16.43 \pm 0.02$	$123.5 \pm 1.0$
$3\text{UO}_2^{2+} + 6\text{H}_2\text{O} = [\text{M}_3(\text{OH})_6]_{(\text{aq})} + 6\text{H}^+$	$-22.69 \pm 0.12$	$132.2 \pm 4.0$
$3\text{UO}_2^{2+} + 7\text{H}_2\text{O} = [(\text{UO}_2)_3(\text{OH})_7]^- + 7\text{H}^+$	$-28.97 \pm 0.07$	$198.2 \pm 2.1$
$3\text{UO}_2^{2+} + 8\text{H}_2\text{O} = [(\text{UO}_2)_3(\text{OH})_8]^{2-} + 8\text{H}^+$	$-38.84 \pm 0.14$	$230.2 \pm 2.7$
$\text{UO}_2^{2+} + 3\text{H}_2\text{O} = [(\text{UO}_2)(\text{OH})_3]^- + 3\text{H}^+$	$-18.81 \pm 0.17$	$93.7 \pm 1.8$
$\text{UO}_2^{2+} + 4\text{H}_2\text{O} = [(\text{UO}_2)(\text{OH})_4]^{2-} + 4\text{H}^+$	$-31.25 \pm 0.5$	$167.6 \pm 1.7$
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	$-13.81 \pm 0.03$	$57.4 \pm 0.3$
$\text{H}^+ + \text{HO}_2^- = \text{H}_2\text{O}_2$	$11.49 \pm 0.02$	$-26.2 \pm 0.6$
$\text{UO}_2^{2+} + \text{HO}_2^- + \text{H}_2\text{O} = [(\text{UO}_2)(\text{O}_2)(\text{OH})]^- + 2\text{H}^+$	$-2.56 \pm 0.07$	$-43.4 \pm 1.5$
$2\text{UO}_2^{2+} + 2\text{HO}_2^- + \text{H}_2\text{O} = [(\text{UO}_2)_2(\text{O}_2)_2(\text{OH})]^- + 3\text{H}^+$	$7.34 \pm 0.16$	$-91 \pm 9$

## Table S7

Distortion energies in kJ/mol computed at the MP2 level in gas-phase of the four-membered rings  $[(\text{UO}_2)(\text{O}_2)(\text{OH}_2)_2]_4$  with geometries corresponding to those obtained with a coordinated  $\text{M}^+$ -cation.

Geometry	$\Delta E$ [kJ/mol]
$[\text{UO}_2(\text{O}_2)(\text{OH}_2)_2]_4$	0.0
$\text{Li}[\text{UO}_2(\text{O}_2)(\text{OH}_2)_2]_4^+$	10.2
$\text{Na}[\text{UO}_2(\text{O}_2)(\text{OH}_2)_2]_4^+$	13.2
$\text{K}[\text{UO}_2(\text{O}_2)(\text{OH}_2)_2]_4^+$	12.7
$\text{Rb}[\text{UO}_2(\text{O}_2)(\text{OH}_2)_2]_4^+$	12.1
$\text{Cs}[\text{UO}_2(\text{O}_2)(\text{OH}_2)_2]_4^+$	10.4

## Table S8

Cartesian coordinates in Å of the four-membered rings without and with cations (TPSSH gas-phase geometries)

### [UO<sub>2</sub>(O<sub>2</sub>)(OH<sub>2</sub>)<sub>2</sub>]<sub>4</sub>

U	-2.1152133	-1.9922471	0.5257544
O	-1.9523047	0.0581017	1.5316624
O	-2.9107135	-2.7459649	1.9441268
O	-1.5514052	-1.4980376	-1.0939239
O	-3.2233898	0.0941849	0.8206087
U	-1.9922471	2.1152133	0.5257544
O	-2.7459649	2.9107135	1.9441268
O	-1.4980376	1.5514052	-1.0939239
O	0.0581017	1.9523047	1.5316624
O	0.0941849	3.2233898	0.8206087
U	2.1152133	1.9922471	0.5257544
O	2.9107135	2.7459649	1.9441268
O	1.5514052	1.4980376	-1.0939239
O	1.9523047	-0.0581017	1.5316624
O	3.2233898	-0.0941849	0.8206087
U	1.9922471	-2.1152133	0.5257544
O	2.7459649	-2.9107135	1.9441268
O	1.4980376	-1.5514052	-1.0939239
O	-0.0581017	-1.9523047	1.5316624
O	-0.0941849	-3.2233898	0.8206087
O	-2.4212556	-4.5427507	-0.1718177
H	-2.5818096	-4.8076317	0.7509345
H	-1.5104421	-4.8302310	-0.3473347
O	-4.2334489	-2.3248115	-1.0102488
H	-3.7896755	-2.0587639	-1.8330822
H	-4.4177895	-3.2712116	-1.1166795
O	-4.5427507	2.4212556	-0.1718177
H	-4.8076317	2.5818096	0.7509345
H	-4.8302310	1.5104421	-0.3473347
O	-2.3248115	4.2334489	-1.0102488
H	-2.0587639	3.7896755	-1.8330822
H	-3.2712116	4.4177895	-1.1166795
O	2.4212556	4.5427507	-0.1718177
H	2.5818096	4.8076317	0.7509345
H	1.5104421	4.8302310	-0.3473347
O	4.2334489	2.3248115	-1.0102488
H	3.7896755	2.0587639	-1.8330822
H	4.4177895	3.2712116	-1.1166795
O	4.5427507	-2.4212556	-0.1718177
H	4.8076317	-2.5818096	0.7509345
H	4.8302310	-1.5104421	-0.3473347
O	2.3248115	-4.2334489	-1.0102488
H	2.0587639	-3.7896755	-1.8330822
H	3.2712116	-4.4177895	-1.1166795

**Li[UO<sub>2</sub>(O<sub>2</sub>)(OH<sub>2</sub>)<sub>2</sub>]<sub>4</sub><sup>+</sup>**

O	-3.9578280	-0.6430688	1.8881172
U	-2.8533437	-0.4517539	0.5068279
O	-4.9283795	0.7266508	-0.5375620
O	-1.5749326	1.1418240	1.5362679
U	-0.4517539	2.8533437	0.5068279
O	0.7266508	4.9283795	-0.5375620
O	-1.9594157	-0.3307213	-1.0656407
O	-2.5917885	1.8789017	0.8055224
O	-1.1418240	-1.5749326	1.5362679
O	-1.8789017	-2.5917885	0.8055224
U	0.4517539	-2.8533437	0.5068279
O	-0.7266508	-4.9283795	-0.5375620
O	-0.6430688	3.9578280	1.8881172
O	-0.3307213	1.9594157	-1.0656407
O	1.1418240	1.5749326	1.5362679
U	2.8533437	0.4517539	0.5068279
O	4.9283795	-0.7266508	-0.5375620
O	1.8789017	2.5917885	0.8055224
O	3.9578280	0.6430688	1.8881172
O	1.9594157	0.3307213	-1.0656407
O	1.5749326	-1.1418240	1.5362679
O	2.5917885	-1.8789017	0.8055224
O	0.6430688	-3.9578280	1.8881172
O	0.3307213	-1.9594157	-1.0656407
O	-4.3913252	-2.1833839	-0.6567106
O	-2.1833839	4.3913252	-0.6567106
O	4.3913252	2.1833839	-0.6567106
O	2.1833839	-4.3913252	-0.6567106
H	-4.7695320	-2.7798069	0.0093040
H	-3.8992696	-2.7550285	-1.2669548
H	-5.4866384	0.1337391	-1.0650877
H	-5.4926805	1.0278415	0.1924513
H	-2.7798069	4.7695320	0.0093040
H	-2.7550285	3.8992696	-1.2669548
H	0.1337391	5.4866384	-1.0650877
H	1.0278415	5.4926805	0.1924513
H	4.7695320	2.7798069	0.0093040
H	3.8992696	2.7550285	-1.2669548
H	5.4866384	-0.1337391	-1.0650877
H	5.4926805	-1.0278415	0.1924513
H	2.7798069	-4.7695320	0.0093040
H	2.7550285	-3.8992696	-1.2669548
H	-0.1337391	-5.4866384	-1.0650877
H	-1.0278415	-5.4926805	0.1924513
Li	0.0000000	0.0000000	-1.3861391

**Na[UO<sub>2</sub>(O<sub>2</sub>)(OH<sub>2</sub>)<sub>2</sub>]<sub>4</sub><sup>+</sup>**

O	-3.9055021	-0.6353641	1.8673696
U	-2.8910956	-0.4622357	0.4145877
O	-5.0406318	0.7085694	-0.4787010
O	-1.5550740	1.1238201	1.3673693
U	-0.4622357	2.8910956	0.4145877
O	0.7085694	5.0406318	-0.4787010
O	-2.1371315	-0.3710201	-1.2286480
O	-2.5998370	1.8780298	0.6951281
O	-1.1238201	-1.5550740	1.3673693
O	-1.8780298	-2.5998370	0.6951281
U	0.4622357	-2.8910956	0.4145877
O	-0.7085694	-5.0406318	-0.4787010
O	-0.6353641	3.9055021	1.8673696
O	-0.3710201	2.1371315	-1.2286480
O	1.1238201	1.5550740	1.3673693
U	2.8910956	0.4622357	0.4145877
O	5.0406318	-0.7085694	-0.4787010
O	1.8780298	2.5998370	0.6951281
O	3.9055021	0.6353641	1.8673696
O	2.1371315	0.3710201	-1.2286480
O	1.5550740	-1.1238201	1.3673693
O	2.5998370	-1.8780298	0.6951281
O	0.6353641	-3.9055021	1.8673696
O	0.3710201	-2.1371315	-1.2286480
O	-4.5263735	-2.2308136	-0.5432530
O	-2.2308136	4.5263735	-0.5432530
O	4.5263735	2.2308136	-0.5432530
O	2.2308136	-4.5263735	-0.5432530
H	-4.8527268	-2.7627425	0.2005688
H	-4.0844567	-2.8590593	-1.1356421
H	-5.6423107	0.1189555	-0.9598012
H	-5.5401458	1.0047396	0.2990508
H	-2.7627425	4.8527268	0.2005688
H	-2.8590593	4.0844567	-1.1356421
H	0.1189555	5.6423107	-0.9598012
H	1.0047396	5.5401458	0.2990508
H	4.8527268	2.7627425	0.2005688
H	4.0844567	2.8590593	-1.1356421
H	5.6423107	-0.1189555	-0.9598012
H	5.5401458	-1.0047396	0.2990508
H	2.7627425	-4.8527268	0.2005688
H	2.8590593	-4.0844567	-1.1356421
H	-0.1189555	-5.6423107	-0.9598012
H	-1.0047396	-5.5401458	0.2990508
Na	0.0000000	0.0000000	-1.9921154

**K[UO<sub>2</sub>(O<sub>2</sub>)(OH<sub>2</sub>)<sub>2</sub>]<sub>4</sub><sup>+</sup>**

O	-3.8807028	-0.6244500	1.8567439
U	-2.9012171	-0.4610571	0.3765953
O	-5.0859132	0.6946288	-0.4628693
O	-1.5496829	1.1220871	1.3043585
U	-0.4610571	2.9012171	0.3765953
O	0.6946288	5.0859132	-0.4628693
O	-2.2115175	-0.3839236	-1.2920911
O	-2.6026070	1.8836029	0.6514165
O	-1.1220871	-1.5496829	1.3043585
O	-1.8836029	-2.6026070	0.6514165
U	0.4610571	-2.9012171	0.3765953
O	-0.6946288	-5.0859132	-0.4628693
O	-0.6244500	3.8807028	1.8567439
O	-0.3839236	2.2115175	-1.2920911
O	1.1220871	1.5496829	1.3043585
U	2.9012171	0.4610571	0.3765953
O	5.0859132	-0.6946288	-0.4628693
O	1.8836029	2.6026070	0.6514165
O	3.8807028	0.6244500	1.8567439
O	2.2115175	0.3839236	-1.2920911
O	1.5496829	-1.1220871	1.3043585
O	2.6026070	-1.8836029	0.6514165
O	0.6244500	-3.8807028	1.8567439
O	0.3839236	-2.2115175	-1.2920911
O	-4.5832985	-2.2487937	-0.4764856
O	-2.2487937	4.5832985	-0.4764856
O	4.5832985	2.2487937	-0.4764856
O	2.2487937	-4.5832985	-0.4764856
H	-4.8755429	-2.7310532	0.3142381
H	-4.1553604	-2.9134417	-1.0384956
H	-5.7021217	0.0822856	-0.8948102
H	-5.5480512	1.0005457	0.3340979
H	-2.7310532	4.8755429	0.3142381
H	-2.9134417	4.1553604	-1.0384956
H	0.0822856	5.7021217	-0.8948102
H	1.0005457	5.5480512	0.3340979
H	4.8755429	2.7310532	0.3142381
H	4.1553604	2.9134417	-1.0384956
H	5.7021217	-0.0822856	-0.8948102
H	5.5480512	-1.0005457	0.3340979
H	2.7310532	-4.8755429	0.3142381
H	2.9134417	-4.1553604	-1.0384956
H	-0.0822856	-5.7021217	-0.8948102
H	-1.0005457	-5.5480512	0.3340979
K	0.0000000	0.0000000	-2.6907939

**Rb[UO<sub>2</sub>(O<sub>2</sub>)(OH<sub>2</sub>)<sub>2</sub>]<sub>4</sub><sup>+</sup>**

O	-3.8760395	-0.6143717	1.8577354
U	-2.9055413	-0.4538961	0.3705714
O	-5.1033799	0.6902254	-0.4558277
O	-1.5460830	1.1255116	1.2911895
U	-0.4538961	2.9055413	0.3705714
O	0.6902254	5.1033799	-0.4558277
O	-2.2341524	-0.3772829	-1.3040386
O	-2.5992972	1.8917351	0.6435083
O	-1.1255116	-1.5460830	1.2911895
O	-1.8917351	-2.5992972	0.6435083
U	0.4538961	-2.9055413	0.3705714
O	-0.6902254	-5.1033799	-0.4558277
O	-0.6143717	3.8760395	1.8577354
O	-0.3772829	2.2341524	-1.3040386
O	1.1255116	1.5460830	1.2911895
U	2.9055413	0.4538961	0.3705714
O	5.1033799	-0.6902254	-0.4558277
O	1.8917351	2.5992972	0.6435083
O	3.8760395	0.6143717	1.8577354
O	2.2341524	0.3772829	-1.3040386
O	1.5460830	-1.1255116	1.2911895
O	2.5992972	-1.8917351	0.6435083
O	0.6143717	-3.8760395	1.8577354
O	0.3772829	-2.2341524	-1.3040386
O	-4.5965418	-2.2498268	-0.4592522
O	-2.2498268	4.5965418	-0.4592522
O	4.5965418	2.2498268	-0.4592522
O	2.2498268	-4.5965418	-0.4592522
H	-4.8721070	-2.7238404	0.3424851
H	-4.1659351	-2.9178339	-1.0152247
H	-5.7163634	0.0653506	-0.8743610
H	-5.5587170	0.9934480	0.3461056
H	-2.7238404	4.8721070	0.3424851
H	-2.9178339	4.1659351	-1.0152247
H	0.0653506	5.7163634	-0.8743610
H	0.9934480	5.5587170	0.3461056
H	4.8721070	2.7238404	0.3424851
H	4.1659351	2.9178339	-1.0152247
H	5.7163634	-0.0653506	-0.8743610
H	5.5587170	-0.9934480	0.3461056
H	2.7238404	-4.8721070	0.3424851
H	2.9178339	-4.1659351	-1.0152247
H	-0.0653506	-5.7163634	-0.8743610
H	-0.9934480	-5.5587170	0.3461056
Rb	0.0000000	0.0000000	-2.9715644



Cs[ $\text{UO}_2(\text{O}_2)(\text{OH}_2)_2$ ] $^{4+}$

O	-3.8774327	-0.6133331	1.8562719
U	-2.9021783	-0.4519359	0.3717499
O	-5.1008323	0.6906781	-0.4587378
O	-1.5474461	1.1277077	1.2989976
U	-0.4519359	2.9021783	0.3717499
O	0.6906781	5.1008323	-0.4587378
O	-2.2287637	-0.3727083	-1.3013591
O	-2.5986363	1.8931369	0.6467432
O	-1.1277077	-1.5474461	1.2989976
O	-1.8931369	-2.5986363	0.6467432
U	0.4519359	-2.9021783	0.3717499
O	-0.6906781	-5.1008323	-0.4587378
O	-0.6133331	3.8774327	1.8562719
O	-0.3727083	2.2287637	-1.3013591
O	1.1277077	1.5474461	1.2989976
U	2.9021783	0.4519359	0.3717499
O	5.1008323	-0.6906781	-0.4587378
O	1.8931369	2.5986363	0.6467432
O	3.8774327	0.6133331	1.8562719
O	2.2287637	0.3727083	-1.3013591
O	1.5474461	-1.1277077	1.2989976
O	2.5986363	-1.8931369	0.6467432
O	0.6133331	-3.8774327	1.8562719
O	0.3727083	-2.2287637	-1.3013591
O	-4.5936740	-2.2514235	-0.4515823
O	-2.2514235	4.5936740	-0.4515823
O	4.5936740	2.2514235	-0.4515823
O	2.2514235	-4.5936740	-0.4515823
H	-4.8715387	-2.7090069	0.3589729
H	-4.1563134	-2.9298138	-0.9894549
H	-5.7136258	0.0637771	-0.8745255
H	-5.5542336	0.9930446	0.3446690
H	-2.7090069	4.8715387	0.3589729
H	-2.9298138	4.1563134	-0.9894549
H	0.0637771	5.7136258	-0.8745255
H	0.9930446	5.5542336	0.3446690
H	4.8715387	2.7090069	0.3589729
H	4.1563134	2.9298138	-0.9894549
H	5.7136258	-0.0637771	-0.8745255
H	5.5542336	-0.9930446	0.3446690
H	2.7090069	-4.8715387	0.3589729
H	2.9298138	-4.1563134	-0.9894549
H	-0.0637771	-5.7136258	-0.8745255
H	-0.9930446	-5.5542336	0.3446690
Cs	0.0000000	0.0000000	-3.2069796

**Table S9**

Cartesian coordinates in Å of Na[(UO<sub>2</sub>)(O<sub>2</sub>)(OH)<sub>2</sub>]<sup>-</sup> isomers (TPSSH-PCM geometries)

Na<sub>yl</sub>[(O<sub>2</sub>)(UO<sub>2</sub>)(μ-η<sup>2</sup>(O<sub>2</sub>))(UO<sub>2</sub>)(OH)<sub>2</sub>]<sup>-</sup>

O	2.074188	0.340426	-1.840008
U	2.266522	0.089276	-0.058689
O	0.085387	-0.754506	0.223594
U	-2.172403	-0.003329	-0.101023
O	-2.303076	-0.258535	1.716640
O	0.059575	0.708828	0.447675
O	2.494267	-0.179121	1.729645
O	2.827398	2.208355	0.188389
O	4.815157	-0.440486	-0.528030
O	2.809718	-2.097525	-0.446482
O	-4.251957	0.712739	-0.260992
O	-4.227217	-0.717829	-0.460754
O	-1.842363	0.240612	-1.877250
O	-2.235044	2.553810	0.222102
O	-2.156642	-2.558712	-0.431717
H	2.824374	2.787203	-0.587933
H	4.388827	-1.333808	-0.651285
H	5.132845	-0.169167	-1.402446
H	2.852869	-2.687429	0.320333
H	-3.048055	2.896140	-0.181933
H	-1.513565	3.052927	-0.190959
H	-1.600156	-3.066601	0.178544
H	-3.058226	-2.889543	-0.292811
Na	0.005593	-0.391786	2.619726

**Na<sub>4</sub>[(OH)(O<sub>2</sub>)(UO<sub>2</sub>)(μ-η<sup>2</sup>(O<sub>2</sub>))(UO<sub>2</sub>)(OH)]<sup>-</sup>**

O	-1.676877	-0.370761	1.563184
U	0.093107	-0.048274	1.533924
O	-0.284239	1.617190	0.058522
O	0.673693	-2.188646	0.974060
O	0.649251	-2.083395	2.434732
U	0.044591	-4.484173	1.869384
O	0.239219	-4.317150	-0.819178
O	1.831714	0.424709	1.569151
O	0.092128	0.054920	4.083710
O	-0.548106	2.302548	2.562000
O	1.890386	-4.684004	1.878926
O	-0.301584	-6.656835	2.116096
O	-0.276460	-6.360717	0.700506
O	-1.740982	-4.069760	1.840084
O	0.034490	-4.537119	4.111687
Na	2.967402	-2.582812	1.807525
H	0.654477	-0.614688	4.503097
H	-0.618962	2.493937	1.589385
H	-1.453574	2.352089	2.905390
H	0.506695	2.038715	-0.310428
H	-0.827578	-4.438803	4.540088
H	1.063390	-3.869430	-1.063252
H	0.434858	-5.269439	-0.878316
H	0.378389	0.907574	4.447031

**Na<sup>term</sup>[(O<sub>2</sub>)(UO<sub>2</sub>)(μ-η<sup>2</sup>(O<sub>2</sub>))(UO<sub>2</sub>)(OH)<sub>2</sub>]<sup>-</sup>**

O	-1.561330	0.602177	2.982015
U	0.032837	0.533833	2.123390
O	0.368117	2.663734	2.623387
O	-0.879999	1.356321	0.060304
O	-1.088423	-0.072568	0.243671
U	-0.324635	0.047926	-1.955361
O	0.106626	-2.244703	-0.821847
O	1.693846	0.413850	1.438926
O	-0.061299	-1.914783	1.833775
O	1.447891	0.313471	-1.592594
O	0.297559	-1.207509	-3.690980
O	0.219837	0.187600	-4.121842
O	-2.088039	-0.159366	-2.359012
Na	2.502641	-0.329840	-3.684617
O	0.966660	-1.065888	3.993606
O	-0.517290	2.507898	-2.697996
H	-0.959915	-2.236481	2.004790
H	0.390114	-1.172196	4.765217
H	0.621687	-1.716231	3.296178
H	1.194452	3.067634	2.320256
H	-0.461413	-2.994395	-1.049585
H	0.043365	-2.146309	0.187483
H	-0.721121	2.561145	-3.644898
H	-1.222167	3.004678	-2.254265

**Na<sup>term</sup>[(O<sub>2</sub>)(UO<sub>2</sub>)(μ-(OH)<sub>2</sub>)(UO<sub>2</sub>)(OH)<sub>2</sub>]<sup>-</sup>**

O	-1.698149	-0.547191	1.826840
U	0.117451	-0.477590	1.775860
O	1.944946	-0.485221	1.633747
O	0.138911	-2.394001	3.582518
O	0.247085	1.383101	2.975559
O	0.334327	0.250076	3.883294
O	-0.075224	1.179857	0.103234
U	-0.220198	0.126430	-2.186907
O	-0.905904	-2.391831	-2.549413
O	0.099901	-1.629653	-0.303348
O	0.414614	2.677507	-1.931705
O	-1.997231	0.400771	-1.886787
O	1.581137	-0.161094	-2.250463
O	-0.485638	-0.285401	-4.327129
O	-0.247410	1.123032	-4.140900
Na	2.554844	1.076070	3.485840
H	-0.514816	-3.105158	3.496598
H	-0.120543	-1.903247	4.379490
H	-0.570368	-2.515925	-1.621811
H	-0.294454	-2.872844	-3.126779
H	0.518984	2.466396	-0.970637
H	1.303190	2.849715	-2.276283
H	1.040587	-1.803106	-0.473509
H	-0.976910	1.522724	0.212692