

## Electronic Supplementary Information (ESI) for " Chemical equilibria in the $\text{UO}_2^{2+}$ - $\text{H}_2\text{O}_2$ - $\text{F}^-$ / $\text{OH}^-$ systems and possible solution precursors for the formation of $[\text{Na}_6(\text{OH}_2)_{24}]@[(\text{UO}_2)(\text{O}_2)\text{F}]_{24}^{18-}$ and $[\text{Na}_6(\text{OH}_2)_{24}]@[(\text{UO}_2)(\text{O}_2)\text{OH}]_{24}^{18-}$ clusters.

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### Strategy for the analysis of the potentiometric data.

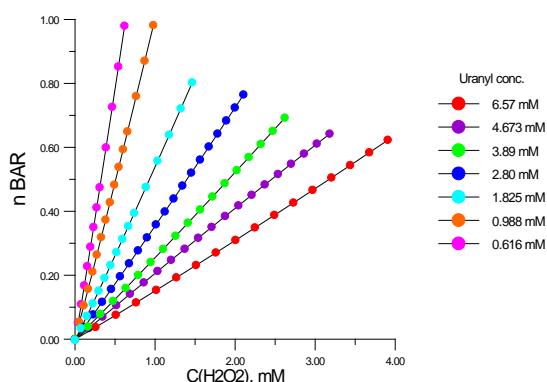
The analysis of the experimental data begins by determination of the average number,  $\bar{n}$

of coordinated peroxide and fluoride per uranyl unit as this provides insight into the stoichiometry of the complexes formed. Figure S1 shows the average number of coordinated peroxides as a function of the *total* concentration of hydrogen peroxide.

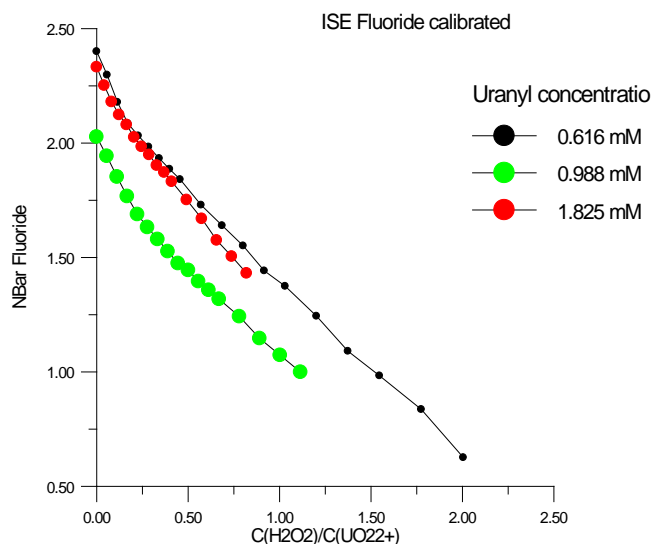
$$\bar{n}_{\text{H}_2\text{O}_2} = \frac{C_{\text{OH}} - C_{\text{H}}}{2C_{\text{U}}}$$

$C_{\text{OH}}$  is the total concentrations of hydroxide after addition of a volume  $v$  from the titrant to the titration vessel.  $C_{\text{H}}$  and  $C_{\text{U}}$  are the total concentrations of strong acid and uranyl(VI) in the titration vessel after adding the titrant.

The linear curves demonstrate that the amount of free hydrogen peroxide in the test solutions is negligible in comparison with the concentration of the different complexes, as expected from the very high stability of uranyl peroxide complexes<sup>1</sup>. The average number of coordinated peroxides is less than one, suggesting that all complexes have a ratio peroxide / uranyl  $\leq 1$ . The  $\text{p}[\text{H}^+]$  data are not very sensitive to variations in the number of coordinated fluoride and this has instead to be determined from the measurements of the free fluoride concentration,  $[\text{F}^-]$  as shown in Figure S2.



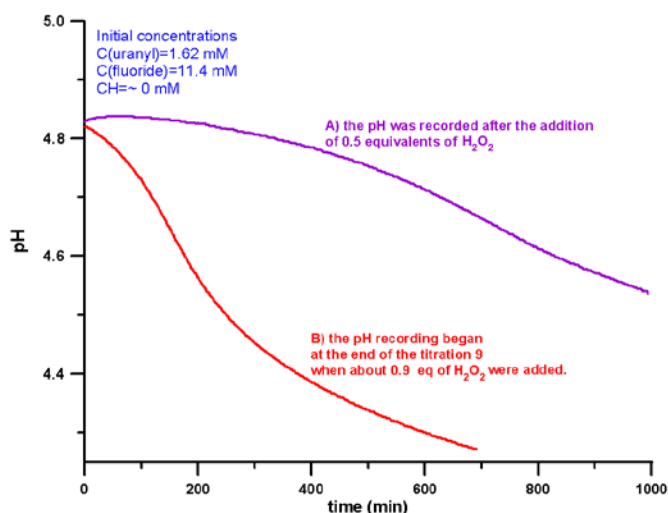
**Figure S1.** Average number of coordinated peroxides per uranyl unit as a function of the total concentration of hydrogen peroxide,  $C(\text{H}_2\text{O}_2)$ .



**Figure S2.** The average number of coordinated fluorides as a function of the ratio  $C_{(\text{H}_2\text{O}_2)} / C_{(\text{UO}_2^{2+})}$ .

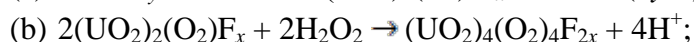
The data in Figure S2 demonstrate that the average number of coordinated fluorides decreases with increasing ratio  $C_{(\text{H}_2\text{O}_2)} / C_{(\text{UO}_2^{2+})}$ . The detailed analysis of the potentiometric data is based on titrations where there was no evidence for the formation of a solid phase, titrations that represent “quasi-equilibrium”, that is equilibrium between the species in solution, but not between these and the solid phase. There was no problem to separate the different reactions, as those in solution were much faster than the ones involving the solid phase.

Both in the present and previous studies<sup>1</sup> we observed slow chemical reactions, both decomposition of  $\text{H}_2\text{O}_2$  in the alkaline  $\text{p}[\text{H}^+]$  range and formation of precipitates. In the present study we did not observe formation of gas bubbles indicating decomposition of  $\text{H}_2\text{O}_2$ . Stable  $\text{p}[\text{H}^+]$  readings were obtained within a few minutes but we also observed a slow decrease in the readings after a longer time that was related to the slow precipitation of a solid, see Figure S3. This shows the time dependence of  $\text{p}[\text{H}^+]$  as a function of time in a test solution with the ratio  $C(\text{H}_2\text{O}_2) / C(\text{UO}_2^{2+}) = 0.5$ , demonstrating a near constancy of the  $\text{p}[\text{H}^+]$  over a period of 5 hours. After a longer time we observed a significant decrease of  $\text{p}[\text{H}^+]$  followed by the appearance of small amounts of precipitate. When the ratio  $C(\text{H}_2\text{O}_2) / C(\text{UO}_2^{2+})$  was close to, or larger than one the change in  $\text{p}[\text{H}^+]$  is larger with the formation of significant amounts of precipitate.

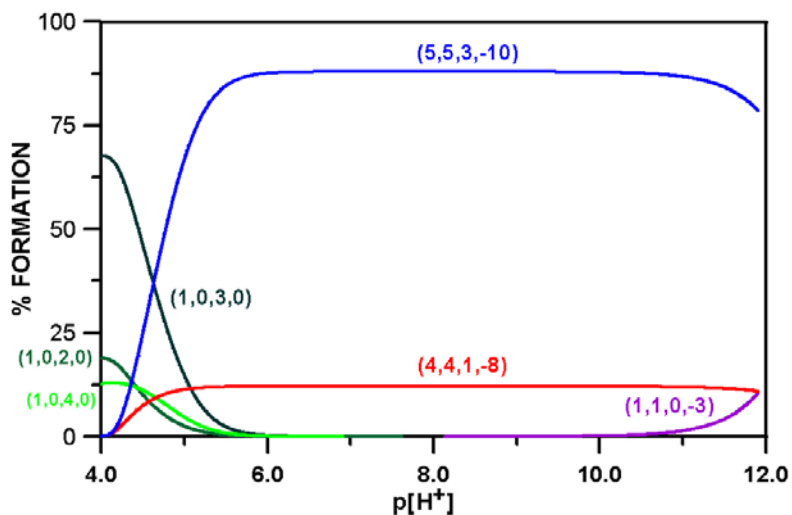


**Figure S3.** Time dependence of the experimental value of  $p[H^+]$  for two different values of the ratio  $C_{(H_2O_2)} / C_{(UO_{22+})}$ , 0.5 and approximately 1.

The slow decrease in  $p[H^+]$  depends on the main reaction(s) taking place in solution as shown below where some charges have been omitted for clarity (the stoichiometry of the complexes in the test solutions are discussed in detail in the main text).

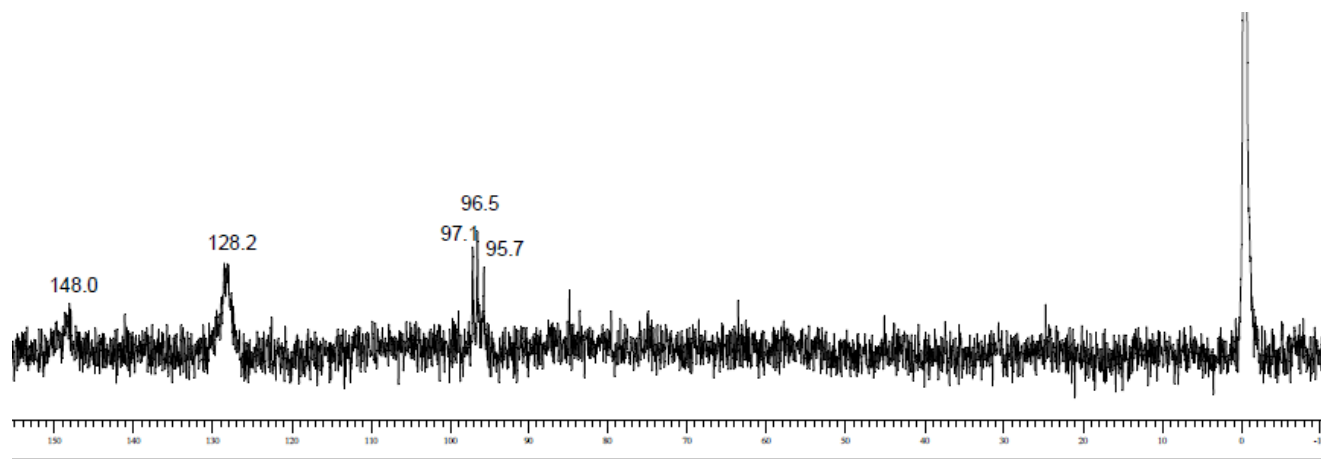


In both reactions (a) and (b) the removal of  $(UO_2)_4(O_2)_4F_x$  through precipitation will result in a decrease in  $p[H^+]$  and this information can be used to support the detailed analysis of the titration data as shown in the main text.

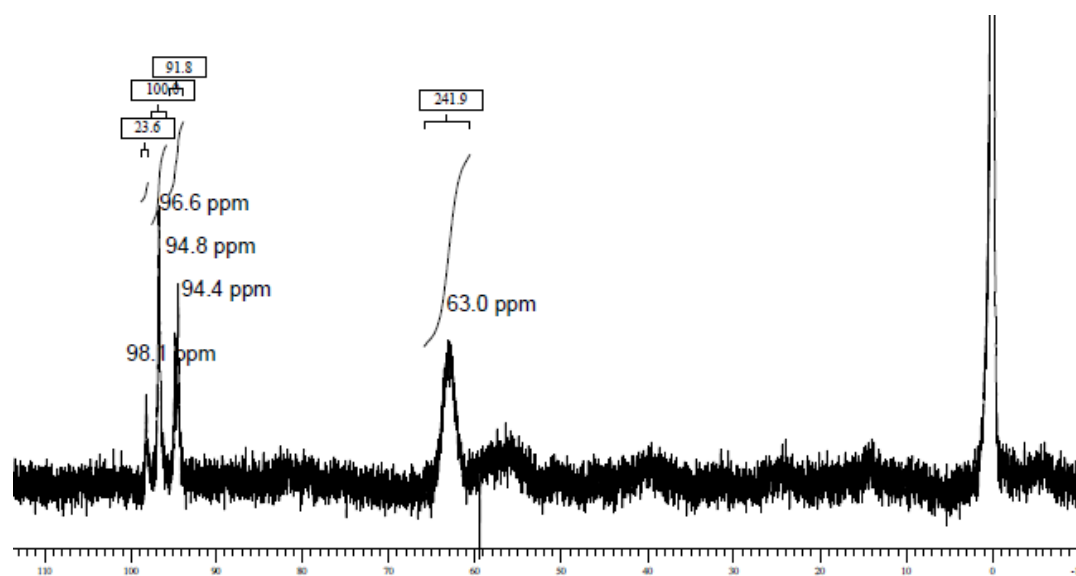


**Figure S4.** Speciation in test solutions used to prepare the solid phases. Note that there is no significant concentration of ternary uranyl(VI) – peroxide – hydroxide complexes present.

All slow reactions might not be detected from the potentiometric data and we therefore used  $^{19}\text{F}$ -NMR to obtain additional information on this issue. However, the measurements were complicated because of the low total concentrations that were necessary to avoid precipitation; even so there were always precipitates in the NMR tubes after the experiment. The data collection required up to twenty hours and even so the signal to noise ratio in the spectra was poor, cf. Fig. S5. Because of these difficulties we did not continue the NMR studies.

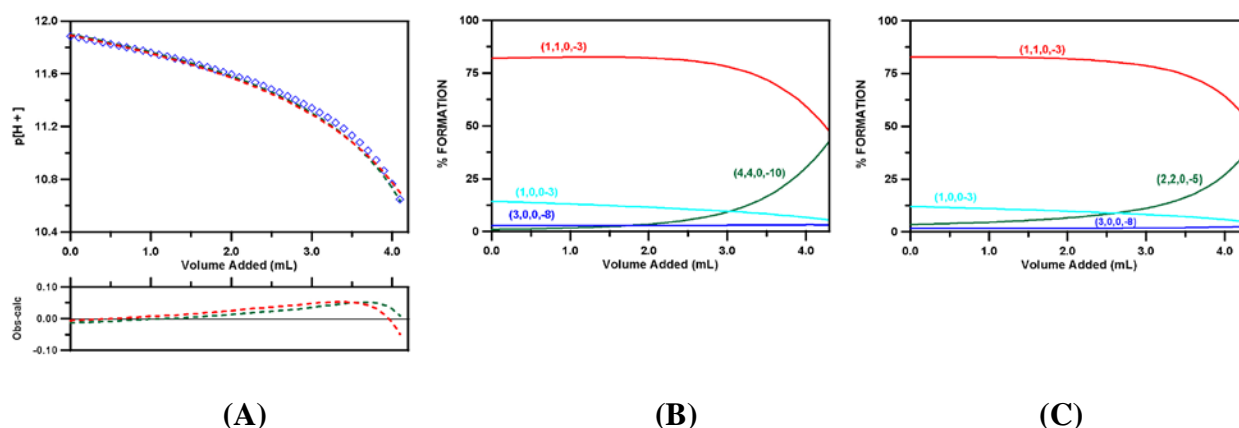


(a)

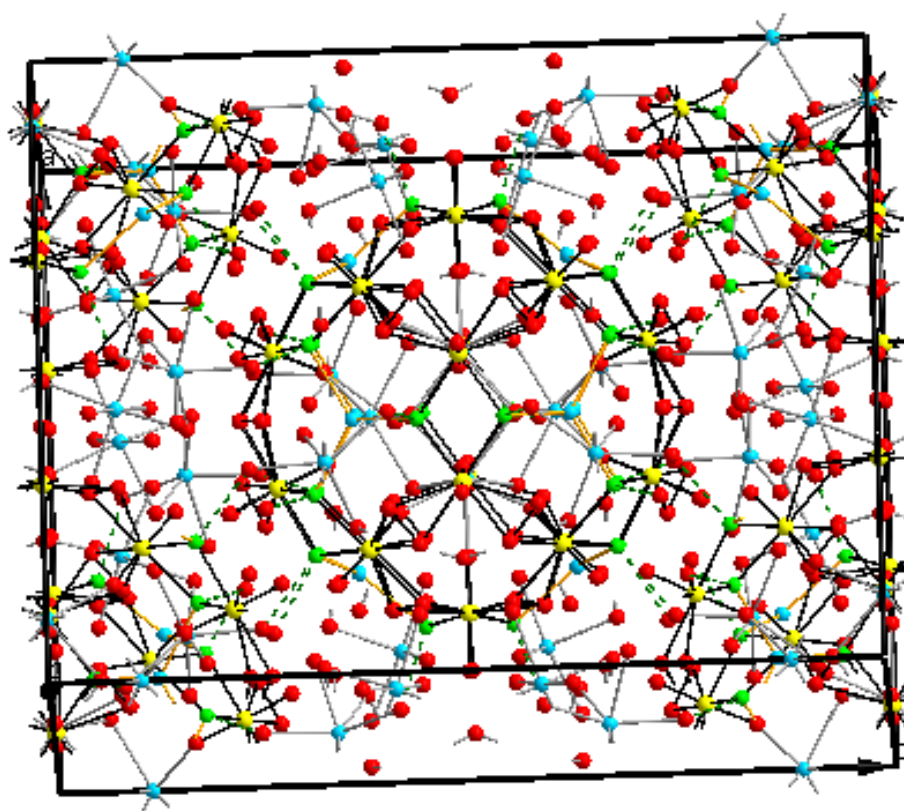


(b)

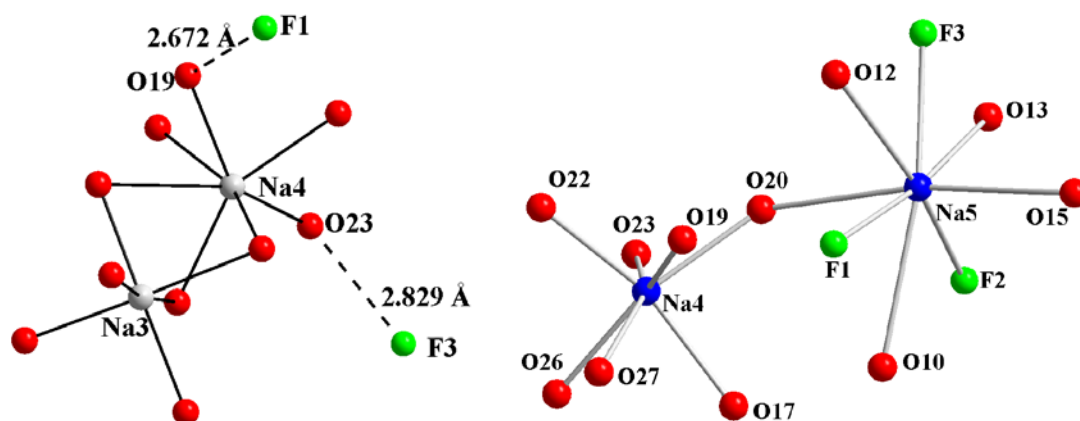
**Figure S5.**  $^{19}\text{F}$ -NMR spectra of test solutions where the ratio  $\text{H}_2\text{O}_2/\text{U} \approx 2$ .



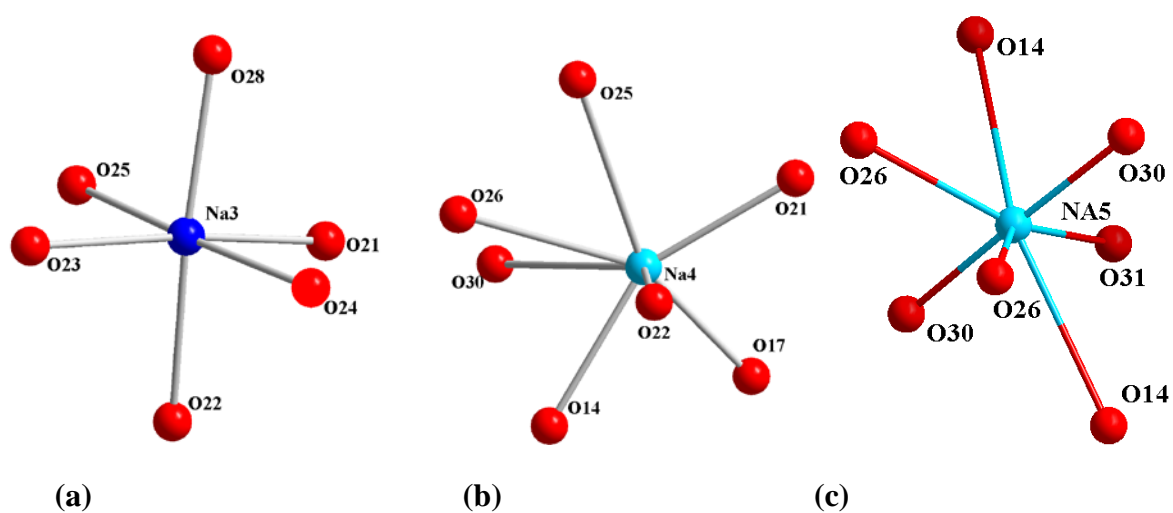
**Figure S6.** Test of the experimental data from the ternary uranyl(VI) – peroxide – hydroxide system using a chemical model comprised of  $\text{UO}_2(\text{O}_2)(\text{OH})^-$  and  $(\text{UO}_2)_4(\text{O}_2)_4(\text{OH})_2^{2-}$  (red and green curves in Figure S6(B), respectively), the latter replacing  $(\text{UO}_2)_2(\text{O}_2)_2(\text{OH})^-$  in the original model (see red and green curves in Figure S6(C), respectively). The original model is slightly better ( $\sigma = 1.27$  as compared to  $\sigma = 1.42$ ) as judged by the overall fit (Figure S6(A)), but the second model can not be excluded. The plot in Figure S6(B) was calculated with the equilibrium constants  $\log\beta = -14.16$  for (1, 1, 0, -3) and ,  $\log\beta = -29.27$  for (4, 4, 0, -10).



**Figure S7.** The unit cell in the uranyl- peroxide – fluoride structure. Color code: U (yellow); O (red); F (green) and Na (blue). The suggested hydrogen bonds between the oxygen donor and the fluoride acceptor are dashed.



**Figure S8.** The water coordination around the external  $\text{Na}^+$  in the ternary uranyl(VI) – peroxide- fluoride structure. (a) The coordination around Na3 and Na4 where the water molecules O19 and O23 are hydrogen bonded to the bridging fluorides F1 and F3. (b) The coordination around Na4 and Na5 in the same compound.



**Figure S9.** The water coordination around the external  $\text{Na}^+$  in the ternary uranyl(VI) – peroxide - hydroxide structure. (a) The Na3 coordination (b) The Na4 coordination in the same compound (c) The Na5 coordination.

**Table S1.** Composition of solutions used to prepare the solid phases used in the X-ray experiment. All concentrations are given in mM/L.

Label	V <sub>tot</sub> (mL)	C(U)	C(H <sub>2</sub> O <sub>2</sub> )	C(F)	C(OH)	Note
A	5.66	4.59	8.81	44.66	12.4	
B	5.47	9.49	9.39	26.88	53.7	
C	8.66	6.02	11.67	24.93	16.3	Faint ppt mother liquor
D	8.77	5.95	5.97	24.28	38.8	Ppt in mother liquor
E	4.92	5.27	8.07	16.30	33.0	
F	6.79	3.79	4.39	7.84	29.3	

**Table S2.** Composition of test solutions used in the potentiometric measurements. V<sub>o</sub> is the initial volume in the titration vessel. The black entries refer to titrations with p[H<sup>+</sup>] data alone, the blue entries refer to titrations with both with p[H<sup>+</sup>] and p[F<sup>-</sup>] data.

approx.			Cup (mM)					Titrant (mM)				
	pH <sub>in</sub>	pH <sub>fin</sub>	V <sub>o</sub>	C <sub>UO<sub>2</sub></sub>	C <sub>F</sub>	C <sub>H</sub>	C <sub>H<sub>2</sub>O<sub>2</sub></sub>	C <sub>U</sub>	C <sub>F</sub>	C <sub>OH</sub>	C <sub>H<sub>2</sub>O<sub>2</sub></sub>	R <sub>max</sub> (H <sub>2</sub> O <sub>2</sub> /U)
1	5.5	4.55	51.7	6.57	29.7	0.021	0	0	0	62.2	75.2	0.63
2	5.6	4.6	83.5	3.89	18.62	0.013	0	0	0	64.2	71.6	0.70
3	5.5	4.65	116.6	2.80	14.165	0.012	0	0	0	62.3	75.4	0.77
4	5.3	4.5	123.9	1.82	8.34	0.018	0	0	0	64.7	70.6	0.90
5	5.7	4.7	130.3	0.998	6.42	-0.08	0	0	0	58.2	83.6	1.23
6	5.2	5.0	131.2	0.616	3.93	-0.00	0	0	0	60.9	78.2	2.22
7	5.8	5.0	74.2	5.65	44.29	0.025	0	0	0	54.64	80.70	0.87
8	5.8	4.8	73.1	3.06	19.86	-	0	0	0	59.34	81.30	1.01
9	5.65	4.8	108.9	1.617	11.37	0.011	0	0	0	57.50	85.01	0.94
10	5.5	5.0	127.0	0.766	6.14	0.012	0	0	0	59.34	81.30	2.08

**Table S3.** Equilibrium constants for the binary and ternary U(VI) complexes that do not contain peroxide. Only the equilibrium constants denoted with a star are required in the modeling of the uranyl(VI) – peroxide – fluoride system.

Complex	Notation	$\log \beta$	References
0, 0, 0,-1	$pK_W$	-14.67	1b
0, 1, 0, -1	$\text{HO}_2^-$	-11.83	1b
2, 0, 0, -2	$(\text{UO}_2)_2(\text{OH})_2^{2+}$	-6.73	1b
3, 0, 0, -5	$(\text{UO}_2)_3(\text{OH})_5^+$	-18.56	1b
0, 0, 1, 1*	HF	2.73	2 and van' t Hoff
1, 0, 1, 0	$\text{UO}_2\text{F}^+$	4.73 (5.12)*	2
1, 0, 2, 0	$\text{UO}_2\text{F}_2$	8.11 (8.77)*	2
1, 0, 3, 0	$\text{UO}_2\text{F}_3^-$	10.50 (10.97)*	2
1, 0, 4, 0	$\text{UO}_2\text{F}_4^{2-}$	11.61 (11.11)*	2
1, 1, 0, -3*	$\text{UO}_2(\text{O}_2)(\text{OH})^-$	-14.16	1a
2, 2, 0,-5*	$(\text{UO}_2)_2(\text{O}_2)_2(\text{OH})^-$	-15.83	1a

\* The equilibrium constants have been based on data obtained in separate titrations at 0 °C in 0.5 M  $\text{NaClO}_4$  and then recalculated to 0.100 M  $\text{NaClO}_4$  using the specific ion-interaction model (SIT) as described in Ref. 2, Appendix B. We tested the consistency of the values in Table S3 with the data selected in Ref. 2 by recalculating them to 25 °C and zero ionic strength (values are given within parenthesis), the values agreed within the estimated uncertainty range.

## References.

1. (a) P. L. Zanonato, P. Di Bernardo and I. Grenthe, *Dalton. Trans.* 2012, **41**, 3380 – 3386. (b) . P. L.Zanonato, P. Di Bernardo, Z. Szabó and I. Grenthe, *Dalton. Trans.* 2012, **41**, 11635 - 11641.
2. I. Grenthe, J. Fuger, R. Konings, R. J. M. Lemire, A. B. Mueller, C. Nguyen-Trung and H. Wanner, *Chemical Thermodynamics of Uranium*, (ed. H. Wanner and I. Fourest), North Holland, Elsevier, 1992.