

Electronic Supplementary Information (ESI) for “Chemical Equilibria in the Binary and Ternary Uranyl(VI) – Hydroxide – Peroxide Systems”.

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Preliminary experiments

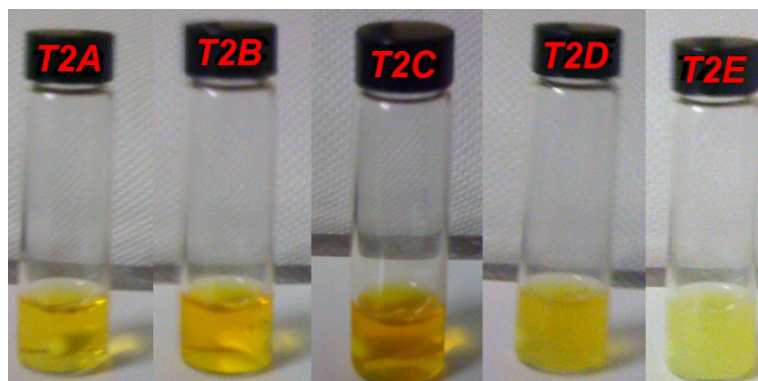


Figure S1. Color changes in the ternary U(VI) – hydroxide – peroxide system where the composition of the various test solutions are given in the following table (Table S1).

Table S1. Test solutions used for the preliminary titrations in the binary U(VI) – hydroxide system. C_U , C_{OH} and $C_{H_2O_2}$ are the total concentrations of UO_2^{2+} , OH^- , and H_2O_2 in these solutions.

Photo	$C_{H_2O_2}$ mM	C_{OH} mM	C_U mM	$R = C_{H_2O_2}/C_M$	Comments
A	97.6	95.1	4.88	20.00	
B	95.2	90.5	9.52	10.00	
C	93.0	86.1	13.95	6.67	
D	90.9	81.8	18.18	5.00	Opalescence, ppt -
E	88.9	77.8	22.22	4.00	ppt ++

Potentiometric Data

Table S2. Test solutions used to study formation of uranyl(VI) hydroxide complexes in the acid $p[H^+]$ region of the binary U(VI) – hydroxide system; V^0 is the initial volume of the solutions titrated; C_U^0 and C_H^0 are the total concentrations of UO_2^{2+} and H^+ in these solutions; $C_{OH,tit}$ is the total concentration of tetra-ethyl ammonium hydroxide in the titrant.

	V^0 (mL)	C_U^0 (mM)	C_H^0 (mM)	$C_{OH,tit}$ (mM)
1	21.80	1.099	9.75	100.4
2	32.55	0.555	7.13	100.4
3	23.71	2.188	9.83	100.4
4	25.20	4.782	10.64	100.4
5	38.36	0.309	5.96	100.4

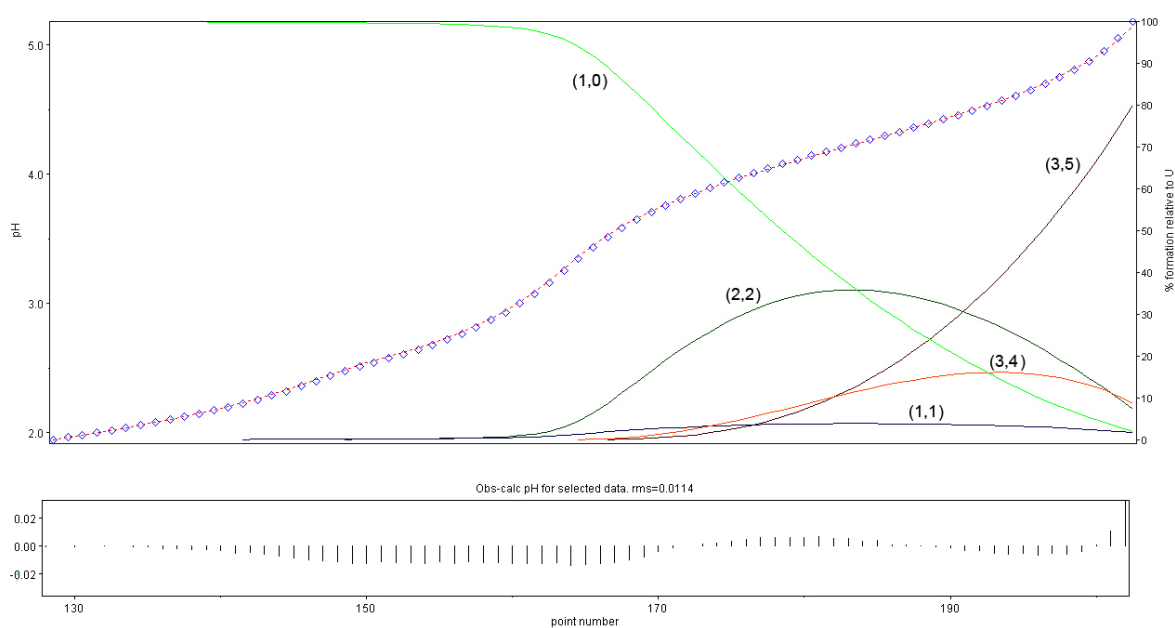


Figure S2. Typical agreement between experimental and calculated titration curves in the acid $p[H^+]$ region. The figure refers to titration 4 in Table S2 and includes the percentages of the various complexes. The strip below the figure shows the difference between measured and calculated $p[H^+]$.

Table S3. Test solutions used to study formation of uranyl(VI) hydroxide complexes in the neutral and alkaline $p[H^+]$ region of the binary U(VI) – hydroxide system. V^0 is the initial volume of the solutions titrated; C^0_U and C^0_{OH} are the total concentrations of UO_2^{2+} and OH^- in these solutions; $C_{H,tit}$ is the total concentration of nitric acid in the titrant.

	V_0	C^0_U (mM)	C^0_{OH} (mM)	$C_{H,tit}$ (mM)
1	29.67	0.668	16.71	100.3
2	32.99	2.027	14.35	100.3
3	35.02	1.151	13.86	100.3

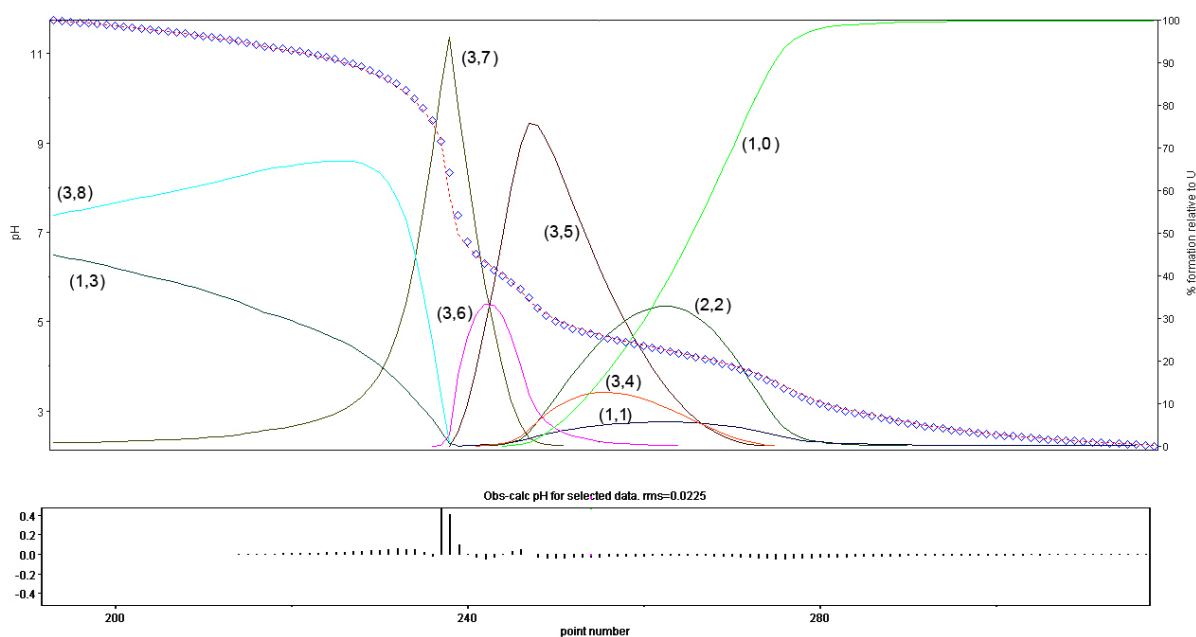


Figure S3. Typical agreement between experimental and calculated titration curves for the alkaline region. The figure refers to tit. 2 in Table S3 and includes the percentages of the various complexes. The equilibrium constants used to calculate the percentages of the species formed in the acid range are those in Table 1. The strip below the figure shows the difference between measured and calculated $p[H^+]$.

Table S4. Constitution and equilibrium constants for different chemical models deduced from titrations in the binary U(VI) – hydroxide system. The dissociation constant of water was determined in separate titrations and used as a constant value, $\log K_w = -13.81 \pm 0.03$, in the least-squares refinements.

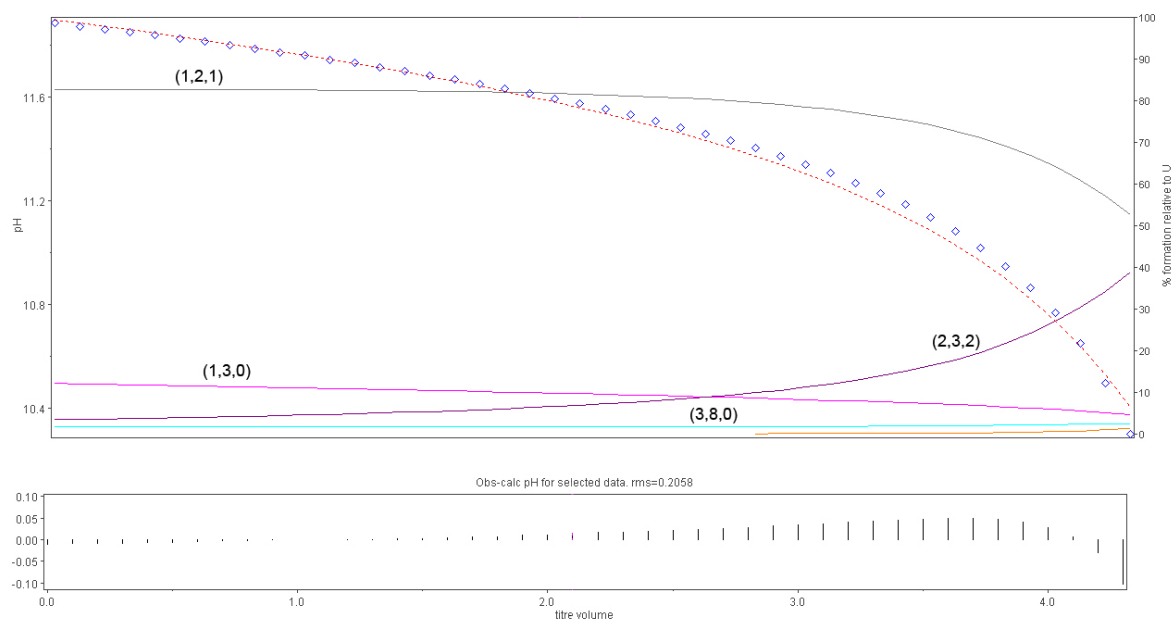
Chemical model	$\log \beta_{p,q} \pm 3\sigma$	Goodness of fit
Titrations in acid solutions		
(1, 1)	-5.20 ± 0.10	0.524
(2, 2)	-5.95 ± 0.03	
(3, 4)	-12.25 ± 0.08	
(3, 5)	-16.43 ± 0.02	
(1, 1)	-5.21 ± 0.18	0.745
(2, 2)	-5.84 ± 0.04	
(3, 5)	-16.38 ± 0.02	
(2, 2)	-12.28 ± 0.12	0.669
(3, 4)	-16.42 ± 0.02	
(3, 5)	-5.84 ± 0.03	
Titrations in neutral / alkaline solution		
(1, 2);	-10.03 ± 0.15	1.93
(1, 3);	-18.65 ± 0.10	
(2, 5);	-23.97 ± 0.33	
(3, 7);	-28.98 ± 0.07	
(3, 8);	-39.06 ± 0.30	
(1, 2)	-10.15 ± 0.16	1.95
(1, 3)	-18.73 ± 0.10	
(3, 7)	-28.94 ± 0.07	
(3, 8)	-38.85 ± 0.17	
(1, 3)	-18.76 ± 0.10	1.87
(3, 6);	-22.77 ± 0.14	
(3, 7)	-28.98 ± 0.07	
(3, 8)	-38.92 ± 0.17	

Table S5. Compositions of test solutions used to study the ternary U(VI) – OH⁻ - hydrogen peroxide system. V^0 is the initial volume of the solutions titrated.

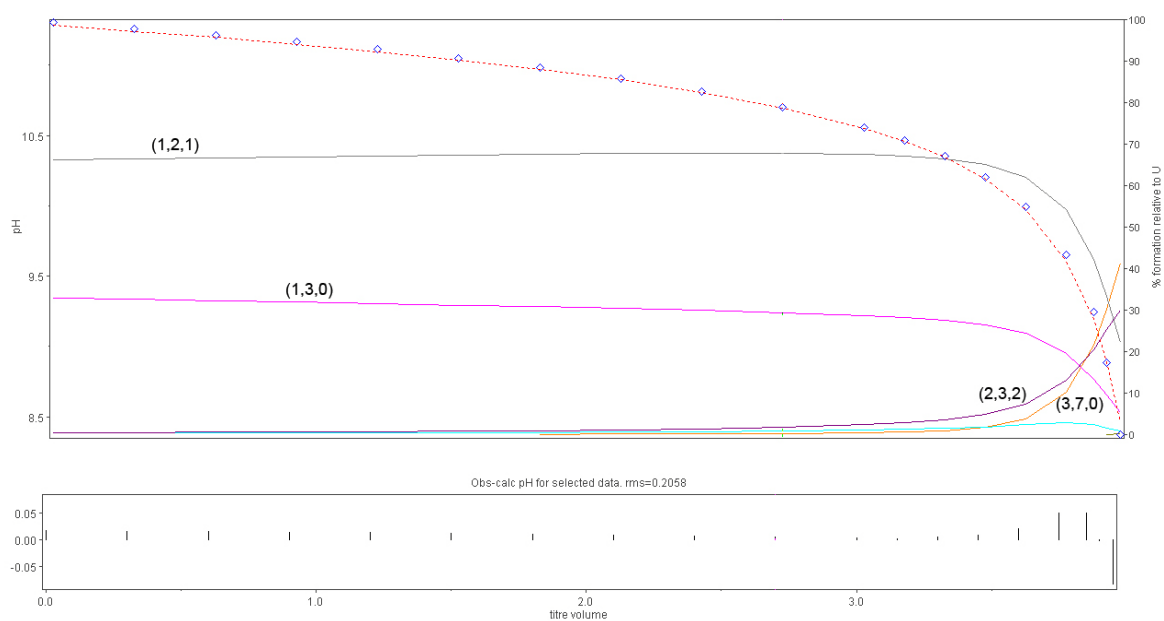
N	V_0 (mL)	Cup (mM)			Titrant (mM)		
		UO ₂ ²⁺	H ₂ O ₂	OH ⁻	UO ₂ ²⁺	H ₂ O ₂	H ⁺
1	32.00	2.488	0.000	18.06	0.000	20.4	0.0
2	31.72	2.488	0.000	18.10	0.000	20.4	0.0
3	31.12	2.497	0.000	17.64	0.000	50.3	-101.2
4	30.66	5.300	5.098	26.84	0.000	60.3	-30.03
5	32.19	6.198	6.110	31.21	0.000	0.000	100.7
6	29.65	3.094	3.146	28.92	0.000	0.000	100.7
7	32.30	1.575	1.586	30.87	0.000	0.000	100.7
8	32.50	1.522	2.168	30.16	0.000	0.000	100.7
9	21.41	0.201	0.205	16.37	0.000	0.000	19.61
10	23.00	0.215	0.210	8.72	0.000	0.000	19.61
11	23.00	0.211	0.211	8.65	0.000	0.000	19.61
12	24.60	0.319	0.318	4.01	0.000	0.000	19.61
13	24.74	0.317	0.315	3.959	0.000	0.000	19.61
14	26.41	0.615	0.615	3.57	0.000	0.000	19.61

Table S6. Least-squares refinement of experimental titration data from the ternary U(VI) – OH⁻ - peroxide system using two different sets of data. The p*K* value for the first dissociation constant for hydrogen peroxide was 11.49 ± 0.02 and the equilibrium constants for the binary complexes are kept constants at the values given in Table 1.

	$\log \beta_{1,2,1} \pm 3\sigma$	$\log \beta_{2,3,2} \pm 3\sigma$	Goodness of fit
All titrations	-2.67 ± 0.07	7.16 ± 0.16	1.27
Titrations 9 - 14	-2.52 ± 0.26	≈ 7.6	2.24



a.



b.

Figure S4. Typical agreement between experimental and calculated titration curves. Figure a. refers to titration 5 in Table S5 and Figure b. to titration 13. The equilibrium constants used to calculate the percentages of the solution species are those in Table 1 of the manuscript. The strip below the figure shows the difference between measured and calculated $p[H^+]$.

Spectrophotometric data.

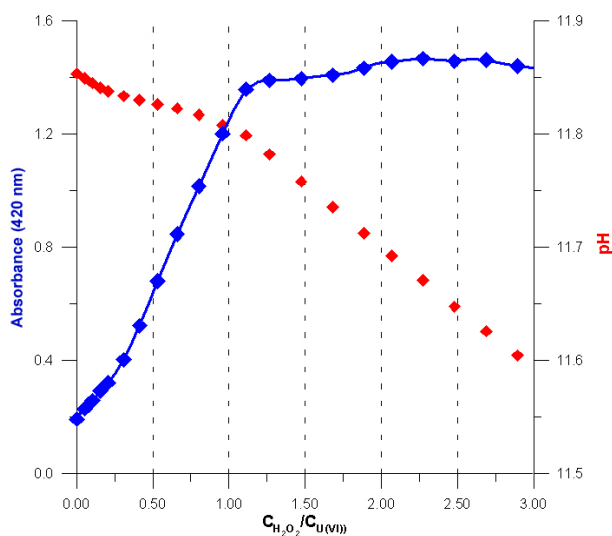


Figure S5. Spectrophotometric titration with measured absorbance as a function of the ratio $R = C_{H_2O_2} / C_{U(VI)}$. At $R \geq 1$, the absorbance is very near constant, indicating that only one peroxide per uranium is coordinated. The red curve shows the change in $p[H^+]$ during the titration. The data in the figure refer to tit. 2 in Table S5.

Table S7. Titrations used to determine the absorption spectra of $[UO_2(OH)(O_2)]^-$ and $[(UO_2)_2(OH)(O_2)_2]^-$.

	Cup (mM)			Titrant (mM)		
	UO_2^{2+}	H_2O_2	OH^-	UO_2^{2+}	H_2O_2	H^+
A	2.00	0.000	100	0.0	201	0.0
B	0.50	0.000	100	0.0	201	0.0
C	2.00	9.94??	100	0.0	0.0	100.0

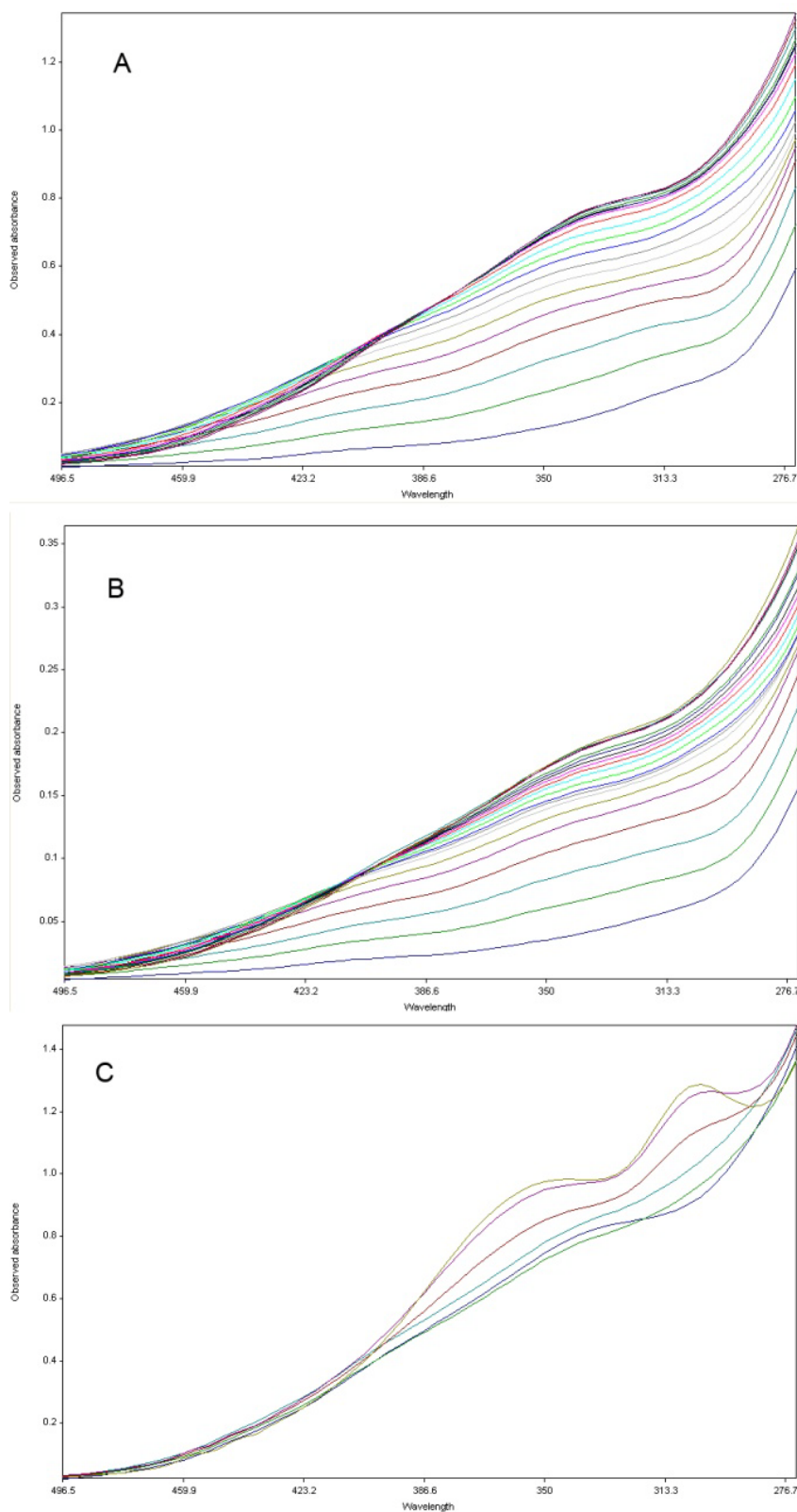


Figure S6. Absorption spectra in titrations A, B and C. The measured absorbances at selected wave lengths were extracted from the experimental spectra in order to calculate the molar absorptivity of the solution species. In Figure 1 of the main text the difference between the experimental and calculated absorbance at 386.6 nm are plotted. The speciation at three different positions in the three titrations 1, 2 and 3 in Figure 1, are shown in Table S9.

Table S8. The relative amounts of the complexes $[\text{UO}_2(\text{OH})_3]^-$ (1, 3), $[\text{UO}_2(\text{OH})(\text{O}_2)]^-$ (1, 2, 1), $[(\text{UO}_2)_2(\text{OH})_2(\text{O}_2)_2]^-$ (2, 3, 2) and $[(\text{UO}_2)_3(\text{OH})_8]^{2-}$ (3, 8) at positions 1, 2, 3 in Figure 1 of the main text.

Titration	% (1,-3,0)	% (1,-2,1)	% (2,-3,2)	% (3,-8,0)
A				
A1	18.3	67.5	0	14.2
A2	13.0	86.7	0.2	0.1
A3	4.8	95.0	0.2	0
B				
B1	21.0	77.7	<0.1	1.3
B2	18.2	81.8	<0.1	0
B3	8.5	91.5	<0.1	0
C				
C1	5.2	94.6	0.2	0
C2	1.3	97.5	1.2	0
C3	0.3	86.2	13.5	0

Table S9. Comparison between the stability constants for the binary U(VI) – hydroxide complexes in 0.100 M TMANO₃ obtained with the present work (P.W.) and the equilibrium constants in 0.100 M tetramethylammonium trifluoromethanesulfonate reported by Palmer and Nguyen-Trung⁶ and re-evaluated by Guillaumont et al.^{7 b}. In this Table only the stability constants for complexes which form at $\text{p}[\text{H}^+] < 7.2$ are reported in column 4.

Complex Notation	Palmer and Nguyen-Trung	Guillaumont et al, $\text{p}[\text{H}^+] < 7.2$	P.W. $\text{p}[\text{H}^+] < 7.2$
(1, 1)	-5.50 (fixed)	-5.50 (fixed)	-5.20 ± 0.10
(2, 2)	-5.77 ± 0.01	-5.79 ± 0.10	-5.95 ± 0.03
(3, 4)	-	-	-12.25 ± 0.08
(3, 5)	-16.10 ± 0.01	-16.38 ± 0.15	-16.43 ± 0.02
(3, 6)	-	-	-22.68 ± 0.23
(3, 7)	-28.25 ± 0.04	-28.68 ± 0.23	-28.95 ± 0.12
(3, 8)	-37.62 ± 0.07	-	-
(3, 10)	-60.53 ± 0.08	-	-
(4, 7)	-22.67 (fixed)	-22.67 (fixed)	-