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Hydrolysis of Thorium(IV) at Variable Temperatures

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Electronic Supplementary Information.

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Figure S2. ESI mass spectrum of thorium hydroxide clusters, singly charged cluster anions favored.

Figure S3. ESI mass spectrum of thorium hydroxide clusters, doubly charged cluster anions favored.

Table S1. Experimental conditions of potentiometry. I = 0.100 mol dm^{-3} $(CH_3\ CH_2)_4NClO_4$.

t, °C	Cup Solution			Titrant, $(CH_3\ CH_2)_4NOH$
	V^0, cm^3	C_{Th}, mmol dm^{-3}	C_H, mmol dm^{-3}	C_{OH}, mmol dm^{-3}
10	30.0	4.96	41.57	102.2
	29.7	3.40	30.60	102.2
	30.7	2.41	25.16	102.2
	82.6	0.487	8.48	102.2
25	20.0	6.41	32.5	101.8
	40.0	3.21	16.2	101.8
	70.3	1.83	9.24	101.8
	135.0	0.95	4.74	101.8
40	45.0	2.85	14.5	101.8
	85.0	1.51	7.70	101.8
	120.3	1.07	5.55	101.8
	135.0	0.64	3.45	101.8
55	45.0	2.85	14.4	101.8
	85.0	1.51	7.65	101.8
	120.0	1.07	5.42	101.8
	120.0	1.07	5.42	101.8
	125.1	0.64	3.27	101.8
70	45.0	2.85	14.45	101.8
	85.0	1.51	7.65	101.8
	85.0	1.51	7.65	101.8
	120.0	1.07	5.42	101.8
	125.1	0.644	3.27	101.8
85	45.0	2.85	14.45	101.8
	85.0	1.51	7.65	101.8
	64.0	2.01	10.20	101.8

Table S2. Experimental conditions of calorimetry. $I = 0.100$ mol dm^{-3} $(CH_3\ CH_2)_4NClO_4$.

	t, °C	Cup Solution			Titrant, $(CH_3\ CH_2)_4NOH$
		V^0, cm^3	C_{Th}, mmol dm^{-3}	C_H, mmol dm^{-3}	C_{OH}, mmol dm^{-3}
1	10	2.63	4.66	4.10	102.2
2		2.50	2.40	12.04	102.2
3		2.48	1.28	12.01	102.2
4		2.52	0.60	5.29	44.0
5		2.53	0.29	5.56	44.0
6		2.50	5.02	25.22	102.2
1	25	2.64	3.70	1.275	102.2
2		2.57	1.91	0.421	102.2
3		2.53	0.97	0.553	102.2
4		2.48	7.44	10.23	101.0
5		2.52	7.44	10.23	101.0
6		2.48	3.74	5.145	101.0
7		2.49	3.72	5.113	101.0
8		2.49	1.18	1.616	57.2
9		2.42	0.60	0.828	57.2
10		2.45	0.59	0.808	57.2
1	40	2.53	0.958	0.839	102.2
2		2.54	1.94	2.12	102.2
3		2.56	2.90	3.15	102.2
4		2.61	3.78	3.58	102.2
5		2.52	4.38	-9.03	-100.3
6		2.49	2.23	-4.59	-100.3
1	55	0.900	2.30	5.98	55.0
2		0.900	3.06	7.98	100.0
3		0.908	4.55	10.98	100.0
1	70	0.903	4.58	11.60	100.0
2		0.908	1.14	2.48	55.0
3		0.902	2.29	5.85	55.0
4		0.902	3.06	7.74	100.0
5		0.904	1.14	2.74	55.0
1	85	0.900	1.15	2.99	55.0
2		0.900	2.30	5.98	55.0
3		0.900	2.30	5.98	55.0
4		0.900	3.06	7.98	100.0
5		0.900	4.59	11.97	100.0
6		0.900	2.30	5.98	55.0

Table S3. Potentiometry Models tested

Model	T (K)	Reaction	log β*	sigma	Chi
A	283	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $6\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{9+} + 15\,H^+$	-5.26 0.09 -20.59 0.09 -39.95 0.08	1.497	26.2
	298	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $6\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{9+} + 15\,H^+$	-4.49 0.024 -18.09 0.026 -35.38 0.027	0.722	61.7
	313	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $6\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{9+} + 15\,H^+$	-4.01 0.04 -16.08 0.023 -32.25 0.04	0.707	30.3
	328	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $6\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{9+} + 15\,H^+$	-3.27 0.023 -14.48 0.023 -29.28 0.04	0.667	141.4
	343	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $6\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{9+} + 15\,H^+$	-3.14 0.05 -13.09 0.03 -26.72 0.08	0.911	103.4
	358	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $6\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{9+} + 15\,H^+$	-2.55 0.024 -11.90 0.024 -24.06 0.03	0.491	19.5
B	283	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $6\,Th^{4+} + 16\,H_2O = [Th_6(OH)_{16}]^{8+} + 16\,H^+$	-5.30 0.09 -20.52 0.06 -43.75 0.07	1.43	34.3
	298	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $6\,Th^{4+} + 16\,H_2O = [Th_6(OH)_{16}]^{8+} + 16\,H^+$	-4.51 0.023 -18.02 0.020 -38.78 0.027	0.67	108.2
	313	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $6\,Th^{4+} + 16\,H_2O = [Th_6(OH)_{16}]^{8+} + 16\,H^+$	-4.05 0.04 -16.04 0.020 -35.62 0.03	0.777	36.7
	328	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $6\,Th^{4+} + 16\,H_2O = [Th_6(OH)_{16}]^{8+} + 16\,H^+$	-3.28 0.024 -14.43 0.019 -32.44 0.029	0.725	161.4
	343	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $6\,Th^{4+} + 16\,H_2O = [Th_6(OH)_{16}]^{8+} + 16\,H^+$	-3.17 0.06 -13.06 0.029 29.677 0.05	0.988	108.0
	358	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $6\,Th^{4+} + 16\,H_2O = [Th_6(OH)_{16}]^{8+} + 16\,H^+$	-2.60 0.023 -11.80 0.016 -26.96 0.028	0.444	9.2
C	283	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$ $4\,Th^{4+} + 12\,H_2O = [Th_4(OH)_{12}]^{4+} + 12\,H^+$ $6\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{9+} + 15\,H^+$	-5.28 0.08 -20.59 0.07 -35.90 0.09 -40.18 0.11	1.374	29.9
	298	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$ $4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-4.39 0.022 -18.24 0.03	0.426	106.4

		$4\,Th^{4+} + 12\,H_2O = [Th_4(OH)_{12}]^{4+} + 12\,H^+$	-32.18	0.018		
		$6\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{9+} + 15\,H^+$	-35.44	0.028		
	313	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$	-3.95	0.04	0.790	46.0
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-16.16	0.029		
		$4\,Th^{4+} + 12\,H_2O = [Th_4(OH)_{12}]^{4+} + 12\,H^+$	-30.34	0.13		
		$6\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{9+} + 15\,H^+$	-32.16	0.05		
	328	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$	-3.29	0.035	1.046	167.8
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-14.40	0.026		
		$4\,Th^{4+} + 12\,H_2O = [Th_4(OH)_{12}]^{4+} + 12\,H^+$	-27.46	0.024		
		$6\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{9+} + 15\,H^+$	-29.67	0.06		
	343	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$	-3.15	0.07	1.157	133.7
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-13.10	0.03		
		$4\,Th^{4+} + 12\,H_2O = [Th_4(OH)_{12}]^{4+} + 12\,H^+$	-25.30	0.03		
		$6\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{9+} + 15\,H^+$	-27.00	0.08		
	358	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$	-2.59	0.026	0.466	24.8
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-11.84	0.023		
		$4\,Th^{4+} + 12\,H_2O = [Th_4(OH)_{12}]^{4+} + 12\,H^+$	-23.30	0.10		
		$6\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{9+} + 15\,H^+$	-24.38	0.11		
D	283	$Th^{4+} + H_2O = [Th(OH)]^{5+} + H^+$	-4.60	0.10	1.393	23.26
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-20.45	0.04		
		$5\,Th^{4+} + 15\,H_2O = [Th_6(OH)_{15}]^{5+} + 15\,H^+$	-43.47	0.06		
	298	$Th^{4+} + H_2O = [Th(OH)]^{5+} + H^+$	-3.99	0.04	0.718	112.3
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-17.93	0.026		
		$5\,Th^{4+} + 15\,H_2O = [Th_5(OH)_{15}]^{5+} + 15\,H^+$	-38.98	0.03		
	313	$Th^{4+} + H_2O = [Th(OH)]^{5+} + H^+$	-3.92	0.05	0.962	50.6
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-15.97	0.021		
		$5\,Th^{4+} + 15\,H_2O = [Th_5(OH)_{15}]^{5+} + 15\,H^+$	-36.10	0.03		
	328	$Th^{4+} + H_2O = [Th(OH)]^{5+} + H^+$	-3.42	0.04	1.168	73.7
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-14.28	0.025		
		$5\,Th^{4+} + 15\,H_2O = [Th_5(OH)_{15}]^{5+} + 15\,H^+$	-33.30	0.04		
	343	$Th^{4+} + H_2O = [Th(OH)]^{5+} + H^+$	-3.37	0.08	1.226	115.5
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-12.96	0.03		
		$5\,Th^{4+} + 15\,H_2O = [Th_5(OH)_{15}]^{5+} + 15\,H^+$	-30.59	0.05		
	358	$Th^{4+} + H_2O = [Th(OH)]^{5+} + H^+$	-2.89	0.021	0.436	36.2
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-11.77	0.015		
		$5\,Th^{4+} + 15\,H_2O = [Th_5(OH)_{15}]^{5+} + 15\,H^+$	-27.71	0.027		
E	283	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$	-5.38	0.10	1.381	29.6
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-20.45	0.04		
		$5\,Th^{4+} + 15\,H_2O = [Th_5(OH)_{15}]^{5+} + 15\,H^+$	-43.47	0.06		
	298	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$	-4.58	0.05	0.729	111.1
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-17.90	0.025		
		$5\,Th^{4+} + 15\,H_2O = [Th_5(OH)_{15}]^{5+} + 15\,H^+$	-39.03	0.03		
	313	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$	-4.20	0.08	1.014	22.7
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-15.96	0.021		
		$5\,Th^{4+} + 15\,H_2O = [Th_5(OH)_{15}]^{5+} + 15\,H^+$	-36.16	0.03		
	328	$2\,Th^{4+} + 2\,H_2O = [Th_2(OH)_2]^{6+} + 2\,H^+$	-3.46	0.05	1.234	97.9
		$4\,Th^{4+} + 8\,H_2O = [Th_4(OH)_8]^{8+} + 8\,H^+$	-14.27	0.026		
		$5\,Th^{4+} + 15\,H_2O = [Th_5(OH)_{15}]^{5+} + 15\,H^+$	-33.46	0.03		

	343	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-3.34 0.06	0.788	43.3
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-13.06 0.019		
		$5\ Th^{4+} + 15\ H_2O = [Th_5(OH)_{15}]^{5+} + 15\ H^+$	-31.03 0.028		
	358	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-2.66 0.026	0.472	33.7
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-11.75 0.015		
		$5\ Th^{4+} + 15\ H_2O = [Th_5(OH)_{15}]^{5+} + 15\ H^+$	-27.84 0.027		
F	283	$2\ Th^{4+} + 3\ H_2O = [Th_2(OH)_3]^{5+} + 3\ H^+$	-8.68 0.08	1.337	15.3
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-20.58 0.06		
		$5Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	-47.28 0.06		
	298	$2\ Th^{4+} + 3\ H_2O = [Th_2(OH)_3]^{5+} + 3\ H^+$	-7.72 0.08	0.957	137.0
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-17.97 0.04		
		$5Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	-42.68 0.04		
	313	$2\ Th^{4+} + 3\ H_2O = [Th_2(OH)_3]^{5+} + 3\ H^+$	-7.29 0.11	1.132	38.07
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-16.00 0.025		
		$5Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	-39.67 0.04		
	328	$2\ Th^{4+} + 3\ H_2O = [Th_2(OH)_3]^{5+} + 3\ H^+$	-6.62 0.3	1.872	56.9
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-14.29 0.08		
		$5Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	-37.15 0.05		
	343	$2\ Th^{4+} + 3\ H_2O = [Th_2(OH)_3]^{5+} + 3\ H^+$	-5.92 0.08	1.11	72.1
		$4\ Th^{4+} + 8\ H_2O = [Th_5(OH)_8]^{8+} + 8\ H^+$	-13.12 0.03		
		$5Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	-33.51 0.05		
	358	$2\ Th^{4+} + 3\ H_2O = [Th_2(OH)_3]^{5+} + 3\ H^+$	-5.15 0.026	0.510	45.8
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-11.98 0.021		
		$5Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	-30.76 0.025		
G	283	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-5.42 0.11	1.437	15.0
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-20.42 0.04		
		$5Th^{4+} + 17\ H_2O = [Th_5(OH)_{17}]^{3+} + 17\ H^+$	-50.99 0.08		
	298	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-4.59 0.03	0.812	143.6
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-17.91 0.017		
		$5Th^{4+} + 17\ H_2O = [Th_5(OH)_{17}]^{3+} + 17\ H^+$	-45.55 0.04		
	313	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-4.21 0.08	1.038	28.9
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-15.95 0.022		
		$5Th^{4+} + 17\ H_2O = [Th_5(OH)_{17}]^{3+} + 17\ H^+$	-42.86 0.05		
	328	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-3.37 0.03	0.894	103.6
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-14.33 0.019		
		$5Th^{4+} + 17\ H_2O = [Th_5(OH)_{17}]^{3+} + 17\ H^+$	-39.58 0.04		
	343	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-3.68 0.11	0.795	30.6
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-13.14 0.019		
		$5Th^{4+} + 17\ H_2O = [Th_5(OH)_{17}]^{3+} + 17\ H^+$	-36.79 0.04		
	358	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-2.72 0.03	0.549	43.5
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-11.71 0.017		
		$5Th^{4+} + 17\ H_2O = [Th_5(OH)_{17}]^{3+} + 17\ H^+$	-33.52 0.03		
H	283	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-5.27 0.08	1.406	27.64
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-20.60 0.08		
		$5\ Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	-48.05 0.12		
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	-40.01 0.08		

298					
	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-4.39	0.023		
	$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-18.22	0.04	0.426	108.5
	$5\ Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	-42.98	0.05		
	$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	-35.38	0.03		
313					
	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-3.96	0.04		
	$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-16.14	0.026	0.760	39.3
	$5\ Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	-40.32	0.09		
	$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	-32.17	0.04		
328					
	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-3.29	0.03		
	$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-14.67	0.04	1.091	136.1
	$5\ Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	-37.42	0.06		
	$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	-29.30	0.04		
343					
	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-3.42	0.07		
	$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-13.24	0.025	0.717	17.49
	$5\ Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	-34.30	0.19		
	$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	-27.08	0.085		
358					
	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-2.60	0.026		
	$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-11.82	0.022	0.452	7.61
	$5\ Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	-31.03	0.08		
	$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	-24.33	0.07		

Table S4. Calorimetric data.

Model	T (K)	Reaction	ΔH*	sigma
A	283	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	119 (4)	1.03
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	243 (4)	
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	559 (4)	
	298	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	118 (3)	1.51
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	236 (7)	
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	554 (4)	
	313	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	134 (3)	0.640
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	273 (2)	
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	552 (2)	
	328	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	137 (2)	0.832
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	270 (5)	
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	582 (3)	
	343	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	155 (3)	0.442
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	270 (4)	
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	597 (4)	
	358	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	126 (3)	0.358
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	275 (3)	
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	537 (4)	
H	283	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	118 (5)	1.02
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	276 (3)	
		$5\ Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	649 (6)	
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	546 (7)	
	298	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	109 (2)	0.774
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	274 (4)	
		$5\ Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	619 (4)	
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	551 (3)	
	313	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	119 (3)	0.586
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	267 (2)	
		$5\ Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	555 (2)	
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	519 (2)	
	328	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	170 (2)	0.255
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	324 (3)	
		$5\ Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	653 (2)	
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	638 (2)	
	343	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	163(3)	0.280
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	258(3)	
		$5\ Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	617(3)	
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	585(2)	
	358	$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	115(4)	0.353
		$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	263(3)	
		$5\ Th^{4+} + 16\ H_2O = [Th_5(OH)_{16}]^{4+} + 16\ H^+$	451(4)	
		$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	572(6)	

Table S5. The values of stability constants selected by NEA for the hydrolysis of thorium(IV) have been used, together with SIT, to calculate the corresponding values in 0.1 m $TEAClO_4$ medium.

Reaction	$I_m = 0$	$I_m = 0.1m$ ($TEAClO_4$)
$Th^{4+} + H_2O = [Th(OH)]^{3+} + H^+$	-2.50	-3.15
$Th^{4+} + 2\ H_2O = [Th\ (OH)_2]^{2+} + 2\ H^+$	-6.20	-7.28
$Th^{4+} + 4\ H_2O = [Th\ (OH)_4](aq) + 4\ H^+$	-17.4	-18.70
$2\ Th^{4+} + 2\ H_2O = [Th_2(OH)_2]^{6+} + 2\ H^+$	-5.90	-5.25
$2\ Th^{4+} + 3\ H_2O = [Th_2(OH)_3]^{5+} + 3\ H^+$	-6.80	-7.22
$4\ Th^{4+} + 8\ H_2O = [Th_4(OH)_8]^{8+} + 8\ H^+$	-20.40	-19.53
$4\ Th^{4+} + 12\ H_2O = [Th_4(OH)_{12}]^{4+} + 12\ H^+$	-26.60	-30.47
$6\ Th^{4+} + 14\ H_2O = [Th_6(OH)_{14}]^{10+} + 14\ H^+$	-36.8	-34.83
$6\ Th^{4+} + 15\ H_2O = [Th_6(OH)_{15}]^{9+} + 15\ H^+$	-36.8	-36.78

Table S6. $\Delta H_{nm,exp}$ vs. $\Delta H_{nm,fit}$ (kJ mol^{-1})

Species	experimental	van't Hoff fit
(2,2)	118 ± 4	59 ± 3
(8,4)	236 ± 7	212 ± 3
(15,6)	554 ± 4	405 ± 7

ESI-MS.

A preliminary ESI-MS study was performed to evaluate the influence of solution pH on the formation of thorium hydroxide clusters, two methanol solutions (360 μmol dm^{-3} $Th(ClO_4)_4$) were prepared by dilution of stock solutions with higher pH (2.9 and 3.7) and studied by ESI-MS. For the stock solution with pH 2.9, the intensities of thorium hydroxide clusters decreased dramatically such that no peaks were evident above *m/z* 1000. The $Th(ClO_4)_5^-$ peak was still present in the spectrum, but its intensity was reduced by about 90%. For the solution with pH 3.7, no thorium-containing species appeared, with sodium perchlorate clusters as the only species observed in the ESI mass spectrum. Fig. S2 shows the ESI-MS data for a solution of 360 μmol dm^{-3} $Th(ClO_4)_4$ in methanol (nominally 0.1% water) that was diluted from the stock solution at pH 2.5.

Table S7. Stoichiometry of the Th(IV) species observed by ESI-MS.

$[Th_x(OH)_y(ClO_4)_z\text{-}aH_2O]^-$					$[Th_x(OH)_y(ClO_4)_z\text{-}aH_2O]^{2-}$				
x	y	z	a	m/z	x	Y	z	a	m/z
2	4	5	0	1029	3	6	8	1	787.7
2	3	6	0	1111	3	5	9	2	819.6
2	3	6	1	1093	4	8	10	2	1010.6
2	2	7	0	1195	4	8	10	4	992.8
2	2	7	1	1177	5	12	10	4	1142.6
3	6	7	1	1477	5	11	11	4	1183.5
3	5	8	1	1559	5	10	12	4	1225.4
3	4	9	1	1641	5	9	13	4	1266.4
3	3	10	1	1723	6	14	12	6	1357.4
4	8	9	1	1941	6	13	13	5	1407.3
4	7	10	2	2005					
4	6	11	1	2107					
4	6	11	2	2089					

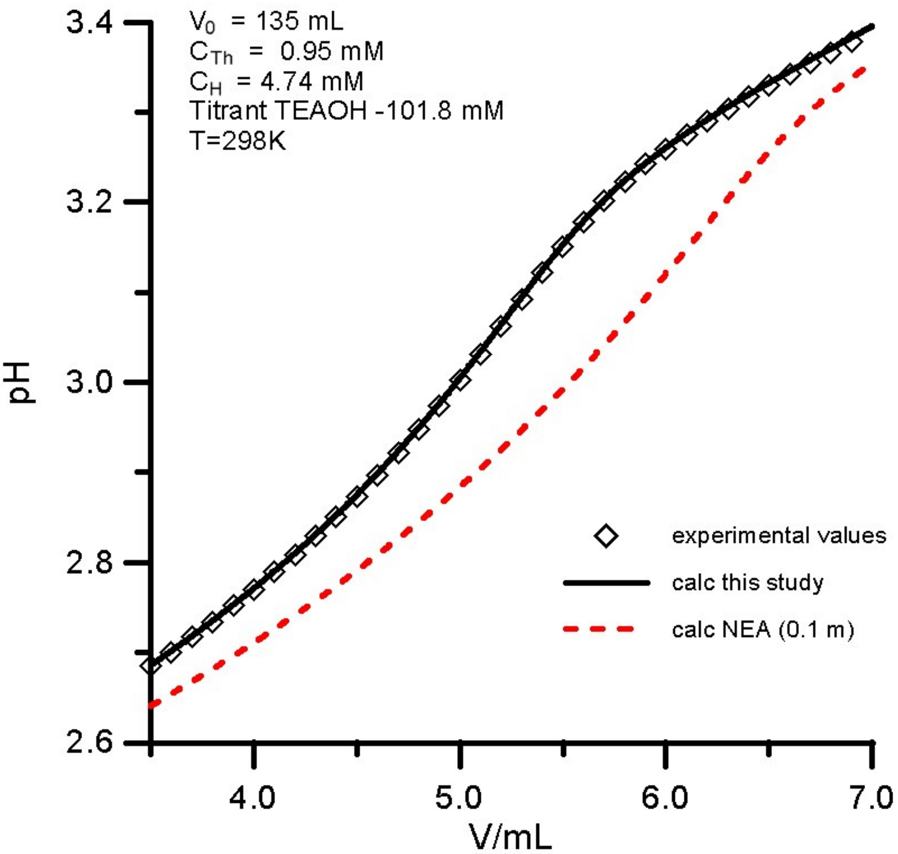

Fig. S1. The values reported in Table S5 for I_m =0.1 m $TEAClO_4$ have been used to calculate the pH (dashed red curve) in the case of the most diluted titration made at 298 K.

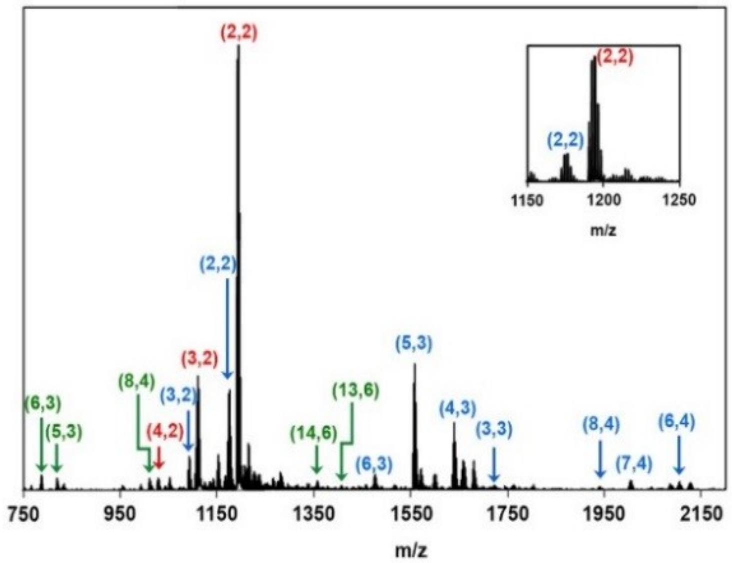

Fig. S2. ESI mass spectrum of thorium hydroxide clusters. Numbers in parenthesis denote the number of Th and OH in each cluster (red: non-dehydrated hydroxide clusters $[Th_x(OH)_y(ClO_4)_z]^-$; blue: dehydrated clusters $[Th_x(OH)_y(ClO_4)_z\text{-}aH_2O]^-$; green: doubly charged cluster anions $[Th_x(OH)_y(ClO_4)_z\text{-}aH_2O]^{2-}$). The inset shows the isotopic splitting of peaks around *m/z* 1200 due to chlorine isotopes, which is characteristic of all peaks in the spectrum and enables peak assignments.

Besides the mononuclear species such as $Th(ClO_4)_5^-$, $Th(CH_3O)(ClO_4)_4^-$, and $Th(OH)(ClO_4)_4^-$, a series of polynuclear thorium hydroxide clusters were observed above *m/z* 750. The overall intensities of these clusters in the mass spectrum are higher than those of the mononuclear species; the abundances of clusters decrease drastically as the number of thorium atoms increases. For dinuclear thorium hydroxide clusters, the *m/z* 1195 peak corresponding to $Th_2(OH)_2(ClO_4)_7^-$ is the most intense, followed by $Th_2(OH)_3(ClO_4)_6^-$ and $Th_2O(ClO_4)_7^-$, the latter of which can be considered as dehydrated $Th_2(OH)_2(ClO_4)_7^-$. Several trinuclear clusters appear between *m/z* 1400 and 1800 with $Th_3O(OH)_3(ClO_4)_8^-$ and $Th_3O(OH)_2(ClO_4)_9^-$ being the most abundant. Peaks around *m/z* 2000 arising from tetranuclear thorium hydroxide clusters have much lower intensities. It should be noted that non-dehydrated hydroxide clusters in the form of $Th_x(OH)_y(ClO_4)_z^-$ were observed only for dinuclear clusters, while trinuclear and tetranuclear clusters always appear as dehydration products of hydroxide clusters. Although the spectrum is dominated by singly charged anions, dehydrated doubly charged $Th_x(OH)_y(ClO_4)_z^{2-}$ anions were observed as well. The presence of these clusters is manifested as several low-intensity peaks ranging from *m/z* 780 to 1400 (Fig. S2). By varying the instrumental parameters, the intensities of singly charged anions could be greatly diminished relative to those of doubly charged anions such that the latter species dominate the spectrum (Fig. S3). Under these experimental conditions, peaks corresponding to tetra- and pentanuclear clusters are most intense followed by those for hexa- and trinuclear clusters. All the observed thorium hydroxide clusters are listed in Table S7. Evidently, a much larger number of thorium hydroxide clusters were observed in the ESI-MS experiments than that of thorium hydrolyzed species invoked to describe the hydrolysis of thorium in acidic aqueous solutions by this study. The observation of the dimers, tetramers, and hexamers, by ESI-MS is in accord with the selected model by this study ((2,2), (8,4), and (15,6)). The other clusters observed by ESI-MS in this work, such as the trimers and pentamers, were either mentioned in previous database[*] or identified as thorium hydroxide cluster cations embedded in small water droplets with a nano ESI time-of-flight mass spectrometer.[†]

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[*] Thorium in The Chemistry of the Actinide Elements, 3rd ed. (Eds. Morss, L. R.; Edelstein, N. M. and Fuger, J.), Springer, Dordrecht, 2006, Chapter 3, 52-161.

[†] C. Walther, J. Rothe, B. Schimmelpfennig and M. Fuss, Dalton Trans., 2012, 41, 10941-10947.

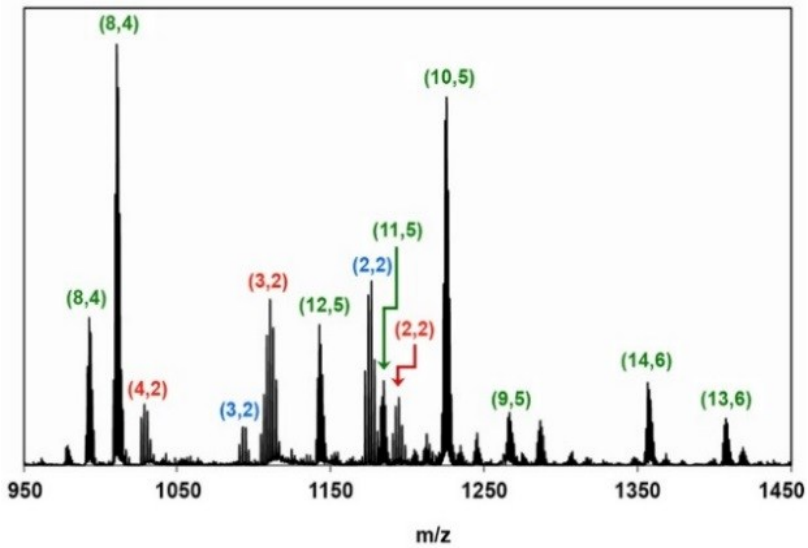

Fig. S3. ESI mass spectrum of thorium hydroxide clusters under instrumental conditions which comparatively favor doubly over singly charged cluster anions. Numbers in parenthesis denote the number of Th and OH in each cluster (red: non-dehydrated hydroxide clusters $[Th_x(OH)_y(ClO_4)_z]^-$; blue: dehydrated clusters $[Th_x(OH)_y(ClO_4)_z\text{-}aH_2O]^-$; green: doubly charged cluster anions $[Th_x(OH)_y(ClO_4)_z\text{-}aH_2O]^{2-}$).