Supporting Information

EXAFS investigation of U(VI), U(IV) and Th(IV) sulfato complexes in aqueous solution

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Figure F1: UV-vis spectra of U(VI) and U(IV) aquo sulfato species. The spectra were obtained from the starting solution (solid line, sample **D**) and after reduction (dotted line, sample **O**).

Figure F2: Origin of the splitting in the O_{eq} shell. The figure shows the fit result as sum of the O_{ax} and O_{eq} contribution, each represented only by a single shell. The peak at $R+\Delta = 1.7 \text{ \AA}$ originates from a superposition of the O_{eq} shell with a side lobe of the O_{ax} shell. The asymmetry of the O_{eq} shell may originate from a nonlinearity of the k -dependent scattering phase function [B.K. Teo, EXAFS Basic principles and data analysis (1986)] or a mixture of $UO_2(H_2O)_5^{2+}$ and $UO_2(H_2O)_4^{2+}$ [Neuefeind et al. J. Phys. Chem. A 108 (2004) 2733].

U L_3 -edge k^3 weighted EXAFS data (left), and the corresponding Fourier transforms (right) of U(VI) hydrate (sample **A**).

Table S1: List of U(VI) sulfato samples at pH 2

ID	Chemical composition	Speciation	pH	$[\text{SO}_4^{2-}]_{\text{total}}$
Q	0.05 M UO_2SO_4 0.03 M H_2SO_4 0.32 M $(\text{NH}_4)_2\text{SO}_4$	5.6 % UO_2^{2+} 18.2 % $\text{UO}_2\text{SO}_4(\text{aq})$ 69.1 % $\text{UO}_2(\text{SO}_4)_2^{2-}$ 6.9 % $\text{UO}_2(\text{SO}_4)_3^{4-}$	1.91	0.4
R	0.05 M UO_2SO_4 0.04 M H_2SO_4 1.21 M $(\text{NH}_4)_2\text{SO}_4$	1.3 % UO_2^{2+} 13.8 % $\text{UO}_2\text{SO}_4(\text{aq})$ 81.7 % $\text{UO}_2(\text{SO}_4)_2^{2-}$ 3.1 % $\text{UO}_2(\text{SO}_4)_3^{4-}$	2.02	1.3
S	0.05 M UO_2SO_4 0.05 M H_2SO_4 1.90 M $(\text{NH}_4)_2\text{SO}_4$	16.6 % UO_2^{2+} 81.6 % $\text{UO}_2(\text{SO}_4)_2^{2-}$	2.04	2

Electrolytically prepared U(IV) samples and their starting U(VI) solutions contain 0.1 M NaCl in order to enforce the anode reaction.

Figure F3: U L_3 -edge k^3 weighted EXAFS data (left), and the corresponding Fourier transforms (right) of U(VI) sulfato species at pH 2.

Table S2: EXAFS fit parameters of U(VI) sulfato complexes at pH 2, k range 3.2-16.7 Å⁻¹.

Sample	Scattering path	R [Å]	N	σ^2 [Å ²]	ΔE	F
Q	U–O _{ax}	1.77	2.0	0.0015	4.1	0.13
	U–O _{eq1}	2.35	2.7	0.0055 [*]		
	U–O _{eq2}	2.48	1.9	0.0055 [*]		
	U–S _{bid}	3.11	1.1	0.0060 [*]		
R	U–O _{ax}	1.77	2.0	0.0017	4.3	0.13
	U–O _{eq1}	2.35	2.3	0.0055 [*]		
	U–O _{eq2}	2.48	2.3	0.0055 [*]		
	U–S _{bid}	3.12	1.9	0.0060 [*]		
S	U–O _{ax}	1.77	2.0	0.0016	4.2	0.12
	U–O _{eq1}	2.35	2.3	0.0055 [*]		
	U–O _{eq2}	2.49	2.4	0.0055 [*]		
	U–S _{bid}	3.12	2.0	0.0060 [*]		

^{*}Value fixed during the fit procedure.

Table S3: Coordination numbers and interatomic distances in selected crystal structures of U(VI) sulfates.

Compound	N_{total}	N_O	$[\text{SO}_4]^{2-}_{\text{mon}}$		$[\text{SO}_4]^{2-}_{\text{bid}}$			H_2O		Ref.
			$R_{\text{U-O}}$	$R_{\text{U-S}}$	N_O	$R_{\text{U-O}}$	$R_{\text{U-S}}$	N_O	$R_{\text{U-O}}$	
$\text{Mn}_2\text{UO}_2(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$	5	4	2.347	3.612	-	-	-	1	2.461	[1]
$\text{MgUO}_2(\text{SO}_4)_2 \cdot 11\text{H}_2\text{O}$	5	4	2.350	3.627	-	-	-	1	2.425	[2]
$\text{UO}_2(\text{SO}_4)(\text{H}_2\text{SO}_4) \cdot 5\text{H}_2\text{O}$	5	4	2.359	3.647	-	-	-	1	2.459	[3]
$(\text{C}_3\text{H}_{12}\text{N}_2)_2[\text{UO}_2(\text{H}_2\text{O})_2(\text{SO}_4)_2]_2 \cdot 2\text{H}_2\text{O}$	5	3	2.366	3.629	-	-	-	2	2.428	[4]
$[\text{UO}_2\text{SO}_4]_2 \cdot 7\text{H}_2\text{O}$	5	3	2.364	3.678	-	-	-	2	2.429	[5]
$\text{Na}_{10}[(\text{UO}_2)(\text{SO}_4)_4](\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$	5	3	2.304	3.629	2	2.452	3.091	-	-	[6]
$\text{KNa}_5[(\text{UO}_2)(\text{SO}_4)_4] \cdot \text{H}_2\text{O}$	5	3	2.345	3.600	2	2.474	3.091	-	-	[7]
$\text{Na}_6[(\text{UO}_2)(\text{SO}_4)_4] \cdot 2\text{H}_2\text{O}$	5	3	2.320	3.596	2	2.481	3.102	-	-	[8]

N_{total} – total coordination number for O_{eq} ; the coordination number of the axial oxygen atoms O_{ax} is always 2 and not considered in the table. N_O refers to the partial coordination number of oxygen atoms related to the given bonding mode, R – distance in Å, O – oxygen, S – sulfur, U – uranium. All distances are given as average values.

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[4] Doran, M. B.; Norquist, A. J.; O'Hare, D. *Acta Cryst. E* **2005**, 61, m881-m884.

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Table S4: Coordination numbers and interatomic distances in selected crystal structures of Th(IV) and U(IV) sulfates.

Compound	N_{total}	$[\text{SO}_4]^{2-}_{\text{mon}}$			$[\text{SO}_4]^{2-}_{\text{bid}}$			O/OH/H ₂ O		Ref.
		N_O	$R_{\text{M-O}}$	$R_{\text{M-S}}$	N_O	$R_{\text{M-O}}$	$R_{\text{M-S}}$	N_O	$R_{\text{M-O}}$	
$\text{K}_4\text{Th}(\text{SO}_4)_4(\text{H}_2\text{O})_2$	9	5	2.329	3.715	2	2.502	3.119	2	2.565 ^a	[1]
$\text{Th}(\text{SO}_4)_2(\text{H}_2\text{O})_8$	10	-	-	-	4	2.558	3.193	6	2.488 ^a	[2]
$\text{Na}_2\text{Th}(\text{SO}_4)_3(\text{H}_2\text{O})_3$	9	6	2.384	3.785	-	-	-	3	2.591 ^a	[3]
$\text{Cs}_2\text{Th}(\text{SO}_4)_3(\text{H}_2\text{O})_2$	10	2	2.401	3.741	6	2.538	3.173	2	2.547 ^a	[4]
$\text{ThSO}_4(\text{OH})_2$	8	4	2.414	3.766	-	-	-	4	2.432 ^c	[5]
$\text{U}(\text{SO}_4)_2(\text{H}_2\text{O})_4$	8	4	2.412	3.690	-	-	-	4	2.386 ^a	[6]
$\text{U}_6\text{O}_4(\text{SO}_4)_6(\text{OH})_4$	8	4	2.367	3.706	-	-	-	4	2.369 ^b	[7]
$\text{U}(\text{SO}_4)(\text{OH})_2$	8	4	2.394	3.709	-	-	-	4	2.341 ^c	[8]

N_{total} – total coordination number, N_O refers to the partial coordination number of oxygen atoms, R – distance in Å, O – oxygen, S – sulfur, M – metal (Th or U). All distances are given as average values. Coordinated O from H₂O (a), coordinated O (b) or OH (c) from a M–O–M bridge.

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[8] Lundgren, G. *Arkiv foer Kemi* **1952**, 4, 421-428.

Figure F4: The structures of a $\text{UO}_2(\text{SO}_4)_2(\text{H}_2\text{O})_2^{2-}$ complex with $N_{\text{Oeq}} = 6$, and $\text{UO}_2(\text{SO}_4)_3^{4-}$, optimized at the DFT level in solvent.

Fig. F4a

U	-0.00027	0.00613	-0.00372
O	-0.00203	0.01567	-1.78185
O	0.00214	0.00188	1.77488
O	2.20975	1.18946	-0.07677
O	2.14931	-1.15641	0.01281
O	-2.15549	-1.16543	-0.00189
H	-0.81326	3.03273	-0.05987
O	-0.00615	2.51935	0.12229
H	0.76083	3.03045	-0.19033
O	-2.19289	1.17698	-0.05469
S	-3.15541	-0.00795	-0.00769
O	-3.99477	-0.05122	-1.2128
O	-3.94558	0.00573	1.23113
S	3.15587	-0.0049	-0.00753
O	4.00003	-0.07539	-1.20835
O	3.94199	0.01697	1.23415
H	-0.79105	-3.0128	0.2811
O	0.00276	-2.52832	-0.00928
H	0.78844	-3.00269	0.31746

Fig. F4b

U	-0.0079	-0.00708	0.00514
O	-0.00644	-0.00754	1.79286
O	0.00061	-0.02306	-1.78164
O	1.91322	1.57681	0.02458
O	-0.25622	2.47042	-0.02247
O	-2.33878	0.86851	-0.01837
O	-2.01691	-1.45688	0.01488
S	-3.14064	-0.42717	-0.00472
O	-3.96376	-0.52597	1.21245
O	-3.95489	-0.55717	-1.22534
S	1.19918	2.92106	-0.00468
O	1.49418	3.70249	1.21099
O	1.53501	3.67084	-1.23023
O	2.2707	-0.98259	-0.01745
O	0.43558	-2.44494	-0.01691
S	1.95873	-2.47468	-0.00216
O	2.48349	-3.13755	-1.20951
O	2.46055	-3.11034	1.23019

Figure F5: The structures of $\text{UO}_2(\text{SO}_4)_2(\text{H}_2\text{O})_n^{2-}$ complexes with $N_{\text{Oeq}} = 5$ optimized at the DFT level in solvent. The Gibbs energy of one monodentate and one bidentate sulfate (Figure 3a) is 9.2 kJ/mol higher than bidentate sulfate (Figure F5b). The Gibbs energy of two monodentate (Figure 3a) is 16.6 kJ/mol higher than one monodentate and one bidentate sulfate (Figure 5a).

Fig. F5a				Fig. F5b			
U	-0.00015	0.15823	-0.16181	U	0.18586	0.03724	0.06889
O	-0.00108	0.789	1.5021	O	0.27277	0.66901	-1.59327
O	0.00136	-0.36079	-1.86487	O	0.11292	-0.5173	1.75868
O	-2.40116	0.42901	-0.2574	O	2.52283	0.63629	0.38959
O	-1.49012	-1.62789	0.45505	O	1.99325	-1.51529	-0.41568
O	1.48722	-1.63148	0.44831	O	-0.67037	-2.14716	-0.69976
H	0.0228	2.70692	-1.87163	H	-0.27703	-2.67137	-1.42068
O	0.01063	2.44472	-0.93022	H	-1.65926	-2.22321	-0.72477
H	0.00511	3.27138	-0.3732	H	0.01172	2.51623	1.84562
O	2.40125	0.42761	-0.25153	O	0.06238	2.30828	0.89304
S	2.85207	-0.9615	0.22558	H	0.06555	3.16291	0.38474
O	3.58949	-0.86037	1.489	O	-2.0902	0.18425	0.00791
O	3.60197	-1.6527	-0.82732	S	-3.49648	-0.46672	-0.01899
S	-2.85427	-0.95863	0.22407	O	-3.28135	-1.87855	-0.47076
O	-3.5976	-0.85181	1.48297	O	-4.05136	-0.41769	1.34516
O	-3.59903	-1.65463	-0.82889	O	-4.31321	0.28785	-0.98633
H	-0.76406	4.72761	1.14987	S	3.21321	-0.65755	-0.05673
O	-0.004	4.63512	0.54498	O	4.04641	-0.41852	-1.24164
H	0.79415	4.7725	1.08946	O	3.96063	-1.25806	1.05481
				O	0.0748	4.59769	-0.44218
				H	0.8668	4.78886	-0.97856
				H	-0.69078	4.74299	-1.02905

Figure F6: The structures of $\text{UO}_2\text{SO}_4(\text{H}_2\text{O})_n(\text{aq})$ complexes optimized at the DFT level in solvent. The Gibbs energy of a 4-fold coordinated complex including one monodentate sulfate (Fig. F6b) is 30.4 kJ/mol higher than that of the bidentate complex in Figure 5b.

Fig. F6a				Fig. F6b			
U	0.32392	0.09336	-0.16208	U	0.7712	0.02006	-0.03937
O	0.69781	-0.10295	1.55812	O	1.18396	0.04681	-1.7608
O	0.09584	0.37681	-1.89574	O	0.53469	-0.00492	1.7126
O	2.68024	-0.10809	-0.588	O	3.15148	-0.15563	0.39833
O	0.8682	2.45715	0.07149	O	0.82545	-2.39571	-0.05036
O	-1.78795	1.09546	0.34347	H	3.85781	-0.236	-0.27693
H	3.08828	0.01434	-1.46864	H	3.57116	-0.24988	1.2797
H	3.409	-0.24149	0.08327	H	0.75952	-2.98036	0.73392
H	0.98316	2.92147	0.92622	H	0.99163	-2.96266	-0.83267
H	0.72104	3.1393	-0.61578	H	0.71348	2.99292	0.79156
H	0.11095	-3.03284	-0.41117	O	0.90532	2.42619	0.01416
O	0.76196	-2.32336	-0.57587	H	1.00673	3.01491	-0.76421
H	1.63586	-2.74021	-0.70738	O	-1.34715	0.07827	-0.44737
O	-1.65638	-1.22302	0.00451	S	-2.87191	-0.02062	0.02907
S	-2.70427	-0.14182	0.33627	O	-2.86384	-0.78798	1.2811
O	-3.27913	-0.37014	1.66091	O	-3.3157	1.37231	0.2005
O	-3.69905	-0.04499	-0.73082	O	-3.56176	-0.71609	-1.06996
O	4.59764	-0.4339	1.17765				
H	4.5788	-1.25766	1.70038				
H	4.70694	0.2937	1.81872				

Table S5

Coordinates of the complexes obtained by DFT calculations.

Fig. 3a

U	0.18849	0.22788	-0.04618
O	0.28976	0.32621	-1.82019
O	0.09161	0.21029	1.72982
O	2.50492	0.94337	0.09032
O	2.01659	-1.35971	-0.01193
O	-0.65554	-2.08464	-0.12394
H	-0.30121	-2.7757	-0.71327
H	-1.64344	-2.16183	-0.07172
H	-0.23424	3.19711	0.82152
O	0.03139	2.68343	0.0326
H	-0.08573	3.26339	-0.74629
O	-2.07983	0.36162	-0.17584
S	-3.48096	-0.26143	0.06296
O	-3.25421	-1.73902	0.153
O	-4.01462	0.28006	1.32465
O	-4.31898	0.08395	-1.09902
S	3.22119	-0.41331	0.08122
O	4.0746	-0.54233	-1.10508
O	3.94934	-0.62475	1.33703

Fig. 3b

U	-0.0183	0.41886	-0.03541
O	-0.14576	0.42472	1.73892
O	0.10063	0.5451	-1.80657
O	1.94715	-0.74621	0.03322
O	4.01708	0.51652	-0.05695
O	-0.87295	2.75745	-0.04086
H	-0.98405	3.3204	0.75006
H	-0.77229	3.3547	-0.80791
H	0.05835	-2.68697	-0.48543
O	-0.52299	-2.00531	-0.10402
H	-1.46963	-2.27774	-0.19084
O	-2.2703	0.10349	-0.23586
S	-3.55877	-0.70521	0.05486
O	-3.16605	-2.1444	-0.07571
O	-4.01325	-0.39235	1.42199
O	-4.55145	-0.32589	-0.96753
S	3.48746	-0.8823	0.04041
O	3.87804	-1.51914	1.31197
O	3.88156	-1.68202	-1.1331
H	1.91941	2.75611	0.80086
O	1.88148	2.0655	0.11381
H	2.76739	1.61939	0.07263

Fig. 3c

U	-0.00028	0.3963	0.00038
O	-0.00015	0.45755	1.77843
O	-0.00008	0.4721	-1.77724
O	-2.39603	0.68214	0.00069
O	-1.47922	-1.49104	-0.00285
O	1.47724	-1.4917	-0.00883
H	0.018	3.42078	-0.78609
O	0.00773	2.84378	0.00463
H	0.00574	3.42414	0.7934
O	2.39643	0.68038	0.00467
S	2.84591	-0.7897	-0.00079
O	3.5826	-1.11077	1.22447
O	3.59154	-1.09818	-1.22376
S	-2.84715	-0.78762	-0.00092
O	-3.58834	-1.10252	1.2231
O	-3.589	-1.10017	-1.22518

Fig 5a

U	-0.76159	-0.00001	-0.01035
O	-0.97946	0.04064	-1.76788
O	-0.72929	0.00571	1.76048
O	-0.46243	-2.48061	-0.05696
O	-2.40454	1.82581	0.08192
O	0.43886	2.15463	-0.01794
H	-1.15888	-3.14867	-0.20323
H	0.40006	-2.89216	-0.25681
H	-2.84536	2.24519	-0.6846
H	-2.61486	2.36264	0.8727
H	0.17886	2.9263	-0.55602
H	1.42817	2.06637	-0.03431
H	-3.41689	-1.37167	0.94966
O	-2.92633	-1.17251	0.12643
H	-3.53626	-1.3276	-0.62327
O	1.41688	-0.4359	-0.16461
S	2.93196	-0.08227	0.01801
O	2.97098	1.41161	0.02853
O	3.37042	-0.65213	1.29894
O	3.64495	-0.64015	-1.13887

Fig. 5b

U	-0.57603	-0.03331	-0.00102
O	-0.65249	-0.05766	1.76726
O	-0.66634	-0.08612	-1.76777
O	-2.98889	0.32902	-0.0012
O	-1.24372	-2.37399	0.01776
O	1.51064	-1.17888	0.00515
H	-3.56842	0.35754	-0.79081
H	-3.56454	0.39423	0.78983
H	-1.26118	-2.94521	0.81364
H	-1.26862	-2.96254	-0.76516
H	-0.21023	3.0756	0.11052
O	-0.9302	2.42862	-0.02243
H	-1.77864	2.90995	0.04227
O	1.47761	1.16625	-0.01293
S	2.49591	0.00664	-0.00087
O	3.28772	0.02844	1.22665
O	3.29467	0.01035	-1.22403