Supporting Information

On the Structure and Relative Stability of Uranyl(VI) Sulfate Complexes in Solution.

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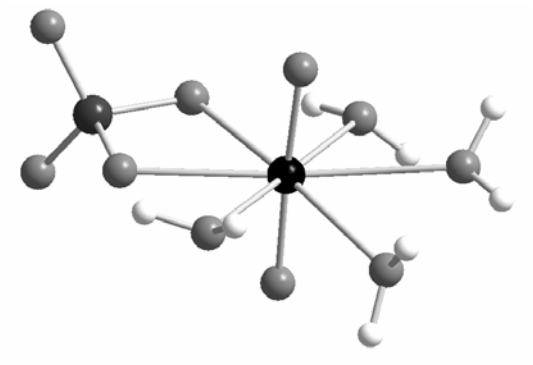

Figure S1. Structure of the six coordinated isomer $[UO_2(SO_{4\text{-chel}})(OH_2)_4]$. The average distance U – O_{eq} is 2.51 Å. There are only very weak hydrogen bond interactions within the first coordination sphere with H – O distances larger than 2.1 Å.

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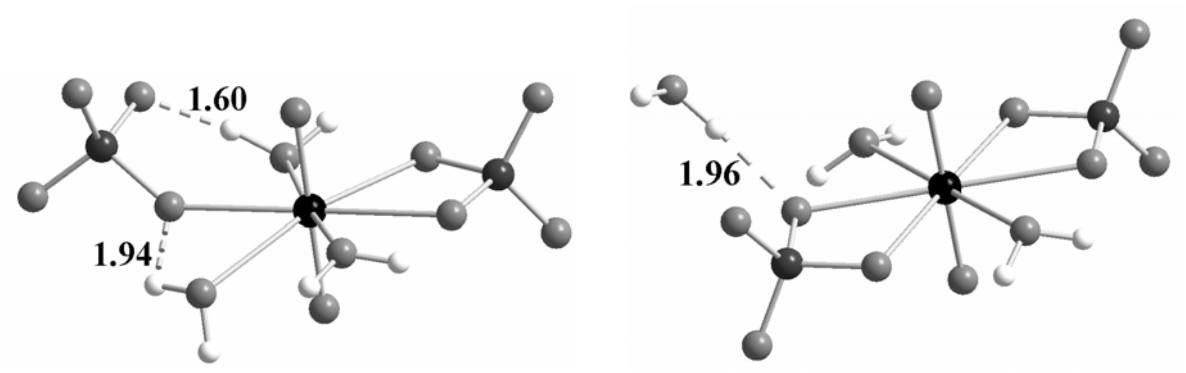

a. **b.**

Figure S2. Structure of the six coordinated bonding isomer of $UO_2(SO_4)_2^{2-}$: a. $[UO_2(SO_{4\text{-}chel})(SO_{4\text{-}mono})(OH_2)_3]^{2-}$ and b. $[UO_2(SO_{4\text{-}chel})_2(H_2O)_2]^{2-}$,$(OH_2)$. The dashed lines denote hydrogen bonds. In a. there is only one reasonably strong hydrogen bond at 1.60 Å; the hydrogen bond interactions of the other two water ligands are very weak. In b. the second sphere water is very weakly bonded to one sulfate group. There are no hydrogen-bond interactions involving the coordinated water.

Table S1. Total electronic energies in au for the various complexes computed at the DFT-B3PW91 and MP2 levels in the CPCM solvent model.

Complex	E(B3PW91)	G(B3PW91)	E(MP2)	G(MP2)
$UO_2(SO_4\text{-mono})(OH_2)_4$	-1632.62016456	-1632.552129	-1629.3577438738	-1629.289708
$[UO_2(SO_4\text{-mono})(OH_2)_4]$,Na	-1794.82900804	-1794.829008	-1791.1874599669	-1791.123513
$[UO_2(SO_4\text{-chel})(OH_2)_3]$,$(H_2O)$	-1632.62483164	-1632.557076	-1629.3639421147	-1629.296187
$[UO_2(SO_4\text{-chel})(OH_2)_3]$,$(H_2O)$,Na	-1794.82900804	-	-1791.1913741436	-
$[UO_2(SO_4\text{-mono})_2(OH_2)_3]^{2-}$	-2255.53025205	-2255.473006	-2251.3634496638	-2251.306204
$[UO_2(SO_4\text{-chel})(SO_4\text{-mono})(OH_2)_2]^{2-}$,$(H_2O)$	-2255.52910522	-	-2251.3631341250	-
$[UO_2(SO_4\text{-chel})(SO_4\text{-mono})(OH_2)_3]^{2-}$	-2255.52093766	-2255.461753	-2251.3592256576	-2251.300041
$[UO_2(SO_4\text{-chel})_2(OH_2)]^{2-}$,$(H_2O)_2$	-2255.52426795	-2255.475267	-2251.3601842663	-2251.311183
$[UO_2(SO_4\text{-chel})_2(H_2O)_2]^{2-}$,$(OH_2)$	-2255.52911480	-2255.471836	-2251.3702361557	-2251.312957

Table S2. Cartesian coordinates in Å of the various isomers of $[UO_2(H_2O)_5]^{2+}$,(H_2O), $UO_2(SO_4)$, and $UO_2(SO_4)_2^{2-}$ complexes. Geometries were optimized with DFT-B3PW91 in the CPCM solvent model.

Complex	Figure	Coordinates			
$[UO_2(OH_2)_5]^{2+}$,(H_2O)	-	U	-0.224313	0.022279	0.095159
		O	-0.508930	-0.044188	-1.626245
		O	1.791862	1.386900	-0.155043
		O	-0.879253	-2.307357	0.200912
		O	-0.042168	0.086177	1.830502
		O	1.752680	-1.415259	-0.051269
		O	-2.615897	0.090107	0.408957
		O	-0.794390	2.378962	0.002215
		H	-1.393355	-2.771969	-0.486926
		H	-0.939482	-2.840595	1.016720
		H	1.743944	-2.278346	-0.501510
		H	2.685593	-1.097982	-0.008505
		H	-3.293145	0.035617	-0.291821
		H	-3.082683	0.146232	1.264218
		H	1.811160	2.191705	-0.702690
		H	2.713861	1.041554	-0.082407
		H	-1.366302	2.777540	-0.681423
		H	-0.777104	2.995943	0.758789
		O	4.043229	-0.035257	0.080922
		H	4.683129	-0.069142	-0.653497
		H	4.571185	-0.006650	0.899652
$UO_2(SO_4$-mono$)(OH_2)_4$	Fig. 1a	U	-0.614795	-0.071315	-0.117260
		O	-0.516294	0.017170	1.636413
		O	-0.835550	-0.176963	-1.860933
		O	-0.519688	2.419061	-0.267682
		O	-2.903836	0.812099	-0.001099
		O	-2.200276	-2.004901	0.131325
		O	0.555968	-2.200887	-0.046763
		O	1.537511	0.435197	-0.313979
		S	2.959346	0.096948	0.315456
		O	3.967510	0.392471	-0.734301
		O	2.886972	-1.388905	0.627215

		O	3.117718	0.910983	1.546997
		H	0.330708	2.839732	-0.487034
		H	-1.216816	2.970768	-0.664053
		H	-3.367587	1.109615	0.803602
		H	-3.504066	0.967136	-0.754169
		H	-3.155077	-1.901347	0.288243
		H	-1.923186	-2.795369	0.627890
		H	1.518323	-2.012917	0.217822
		H	0.576194	-2.773395	-0.833452
$[UO_2(SO_4\text{-mono})(OH_2)_4]$,Na	-	O	-0.205041	0.008773	-1.605295
		U	-0.614944	-0.086998	0.099812
		O	-2.196447	-1.877227	-0.488917
		O	-0.476423	2.381800	0.345837
		O	1.485180	0.409345	0.743812
		S	2.998545	0.081550	0.488696
		O	3.497578	0.950919	-0.621264
		O	-1.157312	-0.233236	1.765150
		O	0.582933	-2.208070	0.201666
		O	-2.753437	1.021299	-0.410723
		O	3.040699	-1.384879	0.138035
		O	3.744005	0.392839	1.747734
		H	1.574026	-2.045073	0.186221
		H	0.396227	-2.839803	0.917879
		H	-3.192847	0.992266	-1.280328
		H	-3.445265	1.204283	0.251278
		H	-1.014046	3.011611	-0.164252
		H	0.340561	2.838949	0.609449
		H	-2.795872	-2.316940	0.141443
		H	-2.035194	-2.507082	-1.214809
		Na	5.158316	2.113734	0.758463
$[UO_2(SO_4\text{-chel})(OH_2)_3]$,$(H_2O)$	Fig 1b	U	0.541201	0.091317	-0.038117
		O	0.530672	-0.337283	-1.744650
		O	-1.384467	1.443566	-0.242006
		O	-3.269880	0.745323	1.243235
		O	0.705659	0.477282	1.670809
		O	0.913559	-2.241724	0.489187

		O	2.968155	0.053731	-0.152325
		O	1.207785	2.424657	-0.613072
		O	-1.633964	-0.860782	0.245773
		O	-3.361480	0.244149	-1.191201
		O	-1.198760	-3.582396	-0.173405
		S	-2.522634	0.407473	0.014109
		H	0.183066	-2.875366	0.206538
		H	1.202099	-2.507277	1.379882
		H	3.505843	-0.221585	-0.917988
		H	3.583059	0.257741	0.576629
		H	0.520898	3.109651	-0.700937
		H	1.895638	2.635317	-1.269615
		H	-1.760999	-2.787870	-0.182529
		H	-1.288335	-3.990727	-1.049866
$[UO_2(SO_4\text{-chel})(OH_2)_3],(H_2O),Na$	-	U	0.225281	0.152580	-0.011316
		O	0.174333	-0.450695	-1.663826
		O	-1.482125	1.778116	-0.423026
		O	-3.397903	1.566264	1.156588
		O	0.429154	0.713055	1.644394
		O	0.278882	-2.101212	0.767040
		O	2.621991	-0.309694	-0.065921
		O	1.282307	2.243002	-0.805611
		O	-2.066033	-0.382102	0.359460
		O	-3.650069	0.787318	-1.186238
		O	0.051120	-4.286531	-0.610150
		S	-2.741342	0.959116	-0.034551
		H	0.187945	-2.940635	0.220381
		H	0.278150	-2.348739	1.707578
		H	3.115320	-0.733245	-0.791281
		H	3.265272	-0.080216	0.628721
		H	0.964400	3.111546	-0.499680
		H	1.558876	2.360922	-1.732418
		H	-0.725176	-4.355551	-1.190680
		H	0.812714	-4.528736	-1.163103
		Na	-5.368287	2.372707	1.925872
$[UO_2(SO_4\text{-chel})(OH_2)_4]$	Fig. S1	U	0.485642	0.129034	-0.050409

		O	0.465777	-0.255139	-1.766385
		O	-1.481919	1.523299	-0.172658
		O	-3.386480	0.740154	1.245341
		O	0.605643	0.483175	1.668078
		O	0.186343	-2.309758	0.631986
		O	2.802678	1.240416	-0.136768
		O	0.717810	2.558595	-0.764035
		O	-1.738420	-0.789680	0.153740
		O	-3.458609	0.402151	-1.213615
		O	2.568580	-1.364129	-0.155128
		S	-2.620353	0.480573	0.004848
		H	-0.725793	-2.486402	0.916185
		H	0.771049	-2.768874	1.258011
		H	3.597569	0.684435	-0.116405
		H	2.989480	2.022814	0.410672
		H	-0.137793	2.944059	-1.016977
		H	1.357365	2.796776	-1.456020
		H	2.575063	-2.081627	-0.813572
		H	3.023536	-1.716710	0.631988
$[UO_2(SO_4\text{-mono})_2(OH_2)_3]^{2-}$	Fig. 2a	U	-0.013626	0.413752	-0.154064
		O	0.020730	0.942428	-1.844445
		O	-0.087572	-0.045992	1.550642
		O	-2.004498	-0.655723	-0.517516
		O	-4.374563	-1.208532	-0.901249
		O	-3.740174	0.474902	0.814857
		O	-3.267443	-1.934724	1.202577
		O	0.559172	-1.888520	-0.810957
		O	-1.784903	2.073855	0.318923
		O	0.995603	2.633607	0.517311
		O	2.262825	0.214166	-0.146903
		O	3.803106	-0.541884	1.651378
		O	3.039493	-2.119417	-0.113288
		O	4.615895	-0.282928	-0.683245
		S	-3.399534	-0.864439	0.173769
		S	3.491102	-0.701468	0.202332
		H	-0.017953	-2.620660	-0.535888

		H	1.505511	-2.115950	-0.556545
		H	-2.031680	2.697607	-0.386858
		H	-2.617857	1.546069	0.542545
		H	0.681870	3.513938	0.244339
		H	1.967298	2.678476	0.543980
$[UO_2(SO_4\text{-chel})(SO_4\text{-mono})(OH_2)_2]^{2-}$,(H_2O)	Fig. 2b	U	0.039985	-0.378812	-0.098205
		O	-0.148675	-0.532458	1.653189
		O	0.222336	-0.291631	-1.856758
		O	-2.206160	-0.252470	-0.364231
		S	-3.529833	0.441650	0.128143
		O	-3.160074	1.905712	0.309189
		O	-4.543736	0.267608	-0.950188
		O	-3.939518	-0.181541	1.418250
		O	-0.579231	2.001442	0.060257
		H	-0.171861	2.537802	0.761022
		H	-1.577574	2.083634	0.166092
		O	-0.394007	-2.784710	-0.318918
		H	-0.853019	-3.342495	0.336195
		H	-0.347628	-3.294408	-1.148910
		O	2.042370	0.968172	0.196826
		S	3.126389	-0.154472	0.237743
		O	3.802450	-0.172506	1.558324
		O	2.221383	-1.401463	0.063411
		O	4.060934	-0.017371	-0.905854
		H	2.503041	2.760212	-0.156040
		O	2.710391	3.699647	-0.305345
		H	2.515862	3.843643	-1.242840
$[UO_2(SO_4\text{-chel})(SO_4\text{-mono})(OH_2)_3]^{2-}$	Fig. S2a	U	0.110179	-0.262988	-0.080712
		O	0.354733	-0.237565	-1.830474
		O	-0.129219	-0.293526	1.666318
		O	-2.261148	-0.267958	-0.284553
		S	-3.552530	0.283117	0.413138
		O	-3.277677	1.752018	0.696922
		O	-4.674675	0.126443	-0.561246
		O	-3.782562	-0.476275	1.677380
		O	2.558249	-0.455714	0.202560

		S	2.972528	1.028778	0.324521
		O	1.581119	1.691951	0.194441
		O	3.569298	1.303561	1.658623
		O	3.858396	1.429660	-0.800400
		O	-1.160599	-2.513470	-0.729515
		H	-0.922003	-2.915512	-1.584158
		H	-2.036723	-2.109558	-0.852372
		O	1.225121	-2.554407	0.288549
		H	0.898181	-3.429464	0.026225
		H	2.193959	-2.562848	0.236404
		O	-0.881863	2.010241	-0.246257
		H	-0.343526	2.709955	0.155383
		H	-1.807268	2.052511	0.135792
$[UO_2(SO_4\text{-chel})_2(H_2O)]^{2-}$,$(OH_2)_2$	Fig. 2c	U	-0.003093	-0.001188	0.276154
		O	-1.731691	0.354795	0.381089
		O	-0.339800	-1.532170	-1.547164
		S	-0.620213	-2.849920	-0.752809
		O	-2.000228	-3.323215	-1.014512
		O	0.067077	-0.001306	2.711813
		O	1.728652	-0.357507	0.289355
		O	0.502515	2.312335	0.676994
		S	0.563516	2.848498	-0.778983
		O	-0.493234	3.860955	-1.011260
		O	-0.486051	-2.315655	0.698984
		O	0.239756	1.532410	-1.559863
		O	1.929375	3.318982	-1.110474
		O	0.425603	-3.859518	-1.040788
		H	-0.682666	0.168988	3.312991
		H	0.858433	-0.138971	3.266144
		H	0.718541	-1.693629	-3.133834
		O	1.266291	-1.818497	-3.927727
		H	1.834672	-2.570871	-3.708148
		H	-0.910031	1.702751	-3.082493
		O	-1.498186	1.832926	-3.845958
		H	-2.086454	2.551760	-3.573020
$[UO_2(SO_4\text{-chel})_2(H_2O)_2]^{2-}$,$(OH_2)$	Fig.	U	-0.071119	0.054091	0.136465

	S2b	O	1.654400	0.276557	-0.180555
		O	-1.797784	-0.167634	0.449941
		O	-0.046862	-1.938912	-1.296029
		S	0.217492	-3.056327	-0.257531
		O	0.315137	-2.201854	1.028958
		O	1.507527	-3.741517	-0.535501
		O	-0.934126	-3.994012	-0.185568
		O	-0.448307	2.342992	-0.744661
		S	-0.425227	3.168620	0.572230
		O	-0.168410	2.032537	1.587915
		O	0.701402	4.137025	0.560924
		O	-1.744419	3.808576	0.813180
		O	0.545762	-0.197407	2.583805
		H	0.227724	0.485001	3.198251
		H	0.390853	-1.064872	2.993965
		O	-0.653268	0.315968	-2.318735
		H	-0.992538	-0.491802	-2.741098
		H	-1.258722	1.041125	-2.549316
		H	0.541756	3.141032	-2.176228
		O	1.001349	3.599478	-2.901426
		H	1.373931	4.389345	-2.484028