Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Modelling the Metal Atom Positions of the Photosystem II Water Oxidising Complex: A Density Functional Theory Appraisal of the 1.9 Å Resolution Crystal Structure

Supplementary material

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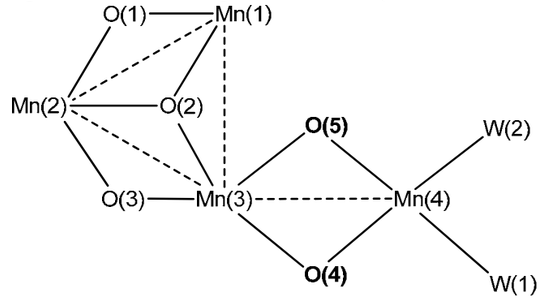
Table S1. Optimized metal-metal bond distances and deviation from the 1.9 Å XRD parameters for simplified models (in the 'low oxidation state' paradigm) of the form



						r(Mn—Mn) / Å [f]					*r*(Ca—Mn) / Å				RMSD		
***S* state**[a]	***q***[b]	**O(4)**[c]	**O(5)**[c]	**Coupling**[d]	**OSP**[e]	**Mn(12)**	**Mn(23)**	**Mn(13)**	**Mn(34)**	**Mn(14)**	**Mn(1)**	**Mn(2)**	**Mn(3)**	**Mn(4)**	**(short)**[g]	**(long + Ca)**[h]	**(all)**[i]
Shen 1.9 Å [j]						**2.80**	**2.90**	**3.30**	**2.94**	**4.98**	**3.49**	**3.33**	**3.43**	**3.80**			
S_0	-2	OH	O	F	3332	2.976	2.953	3.173	2.964	4.913	3.303	3.120	3.190	3.724	0.112	0.171	0.148
				AF		2.991	2.909	3.150	2.937	4.883	3.317	3.111	3.171	3.718	0.122	0.180	0.156
S_0	-2	O	OH	F	3332	2.887	2.942	3.406	3.020	5.101	3.665	3.166	3.522	3.885	0.082	0.133	0.113
				AF		2.848	2.925	3.427	2.925	4.964	3.664	3.164	3.538	3.794	0.069	0.118	0.099
S_0	-1	OH	OH	F	3332	2.922	2.977	3.387	3.164	5.382	3.558	3.237	3.587	3.809	0.140	0.200	0.176
				AF		2.895	2.965	3.403	3.074	5.323	3.565	3.232	3.615	3.748	0.102	0.184	0.153
S_1	-2	O	O	F	3333	2.943	2.935	3.241	2.755	4.749	3.362	3.114	3.295	3.840	0.122	0.165	0.147
				AF		2.903	2.856	3.263	2.721	4.677	3.408	3.139	3.238	3.944	0.124	0.196	0.168
S_1	-1	OH	O	F	3342	2.764	2.920	3.292	2.914	5.056	3.426	3.251	3.213	3.855	0.025	0.115	0.087
				AF		2.744	2.848	3.329	2.891	5.049	3.425	3.213	3.234	3.829	0.048	0.111	0.089
S_1	-1	OH	O	AF	4332	2.767	2.844	3.241	2.902	3.559	3.153	3.266	3.660	3.815	0.048	0.662	0.494
S_1	-1	OH	O	F	2442	2.879	2.771	3.402	2.920	4.941	3.499	3.118	3.288	3.735	0.092	0.119	0.108
				AF		2.819	2.745	3.296	2.894	4.752	3.439	3.125	3.286	3.703	0.081	0.159	0.131
S_1	-1	O	OH	F	3432	2.746	2.829	3.455	3.027	5.181	3.582	3.238	3.574	3.975	0.099	0.147	0.128
				AF		2.709	2.804	3.466	2.925	5.087	3.585	3.259	3.617	3.922	0.106	0.123	0.116
S_1	-1	O	OH	F	3342	2.734	2.952	3.475	2.933	5.422	3.516	3.233	3.346	4.376	0.097	0.330	0.254
				AF		2.713	2.873	3.511	2.894	5.463	3.510	3.203	3.360	4.340	0.117	0.331	0.258
S_1	-1	O	OH	F	2442	2.837	2.784	3.671	2.942	5.527	3.663	3.130	3.443	4.261	0.195	0.341	0.286
				AF		2.774	2.775	3.612	2.896	5.517	3.635	3.130	3.427	4.287	0.170	0.343	0.279
S_1	0	OH	OH	F	3342	2.752	2.938	3.404	3.078	5.346	3.509	3.268	3.388	4.132	0.092	0.224	0.178
				AF		2.759	2.830	3.409	3.035	5.351	3.509	3.242	3.429	4.018	0.083	0.197	0.157
S_1	0	OH	OH	AF	4332	2.759	2.813	3.214	3.270	5.392	3.430	3.226	3.699	4.674	0.177	0.452	0.357
S_1	0	OH	OH	F	3432	2.754	2.821	3.398	3.133	5.383	3.518	3.271	3.539	4.057	0.117	0.221	0.183
				AF		2.740	2.799	3.387	3.111	5.361	3.516	3.266	3.542	4.054	0.112	0.213	0.176
S_2	-1	O	O	F	2443	2.883	2.754	3.402	2.700	4.602	3.479	3.119	3.383	3.621	0.155	0.211	0.188
				AF		2.824	2.747	3.395	2.673	4.648	3.480	3.121	3.364	3.637	0.161	0.192	0.179
S_2	0	OH	O	F	3433	2.741	2.879	3.513	2.864	5.210	3.550	3.220	3.430	3.779	0.117	0.118	0.117
				AF		2.721	2.854	3.472	2.855	5.213	3.552	3.223	3.413	3.788	0.106	0.118	0.113
S_2	0	O	OH	F	3442	2.736	2.818	3.428	2.991	5.497	3.575	3.259	3.470	4.330	0.086	0.335	0.256
				AF		2.720	2.805	3.420	3.107	5.857	3.563	3.252	3.464	4.699	0.120	0.564	0.428
S_2	0	O	OH	AF	4342	2.712	2.788	3.065	3.188	5.330	3.507	3.274	3.666	5.066	0.185	0.597	0.462

S_2	+1	OH	OH	F	3442	2.762	2.801	3.425	3.114	5.512	3.582	3.274	3.487	4.068	0.120	0.272	0.218
				AF		2.746	2.788	3.411	3.077	5.504	3.580	3.265	3.481	4.091	0.108	0.274	0.216
S_3	0	O	O	F	3443	2.767	2.785	3.193	2.693	4.463	3.438	3.223	3.412	3.613	0.147	0.252	0.212
				AF		2.738	2.782	3.271	2.669	4.645	3.478	3.215	3.403	3.666	0.152	0.170	0.162
S_3	+1	OH	O	F	3443	2.782	2.790	3.313	2.872	4.815	3.513	3.256	3.505	3.862	0.066	0.092	0.082
				AF		2.774	2.773	3.322	2.832	4.865	3.543	3.251	3.503	3.827	0.085	0.075	0.080
S_3	+1	O	OH	F	3443	2.757	2.798	3.390	2.911	5.446	3.551	3.292	3.535	4.193	0.073	0.278	0.213
				AF		2.743	2.787	3.383	2.932	5.475	3.556	3.281	3.523	4.198	0.076	0.289	0.222
S_3	+1	O	OH	AF	4433	2.732	2.800	3.205	3.243	5.536	3.342	3.310	3.578	4.724	0.170	0.491	0.383
S_3	+2	OH	OH	F	3443	2.753	2.771	3.407	3.053	5.612	3.632	3.307	3.549	4.295	0.104	0.369	0.283
				AF		2.782	2.758	3.403	3.027	5.572	3.657	3.311	3.546	4.244	0.098	0.343	0.264
S_3	+2	OH	OH	AF	4433	2.719	2.871	3.526	3.042	5.768	3.674	3.333	3.571	4.260	0.131	0.421	0.326

Notes:

a According to the 'low oxidation state' paradigm, in which S_0 implies a $Mn^{II}(Mn^{III})_3$ oxidation state distribution.

b Overall charge state of the indicated model structure

c Identity of the indicated Mn(3) / Mn(4) bridging species as either μ-O or μ-OH.

d Magnetic coupling (F = fully ferromagnetic coupling; AF = antiferromagnetic coupling. For antiferromagnetic coupling, the reported results are averaged from the 'AABB', 'ABAB', and 'ABBA' coupling patterns, where, for example, 'ABAB' denotes a complex in which Mn(1) is α-spin-dominant, Mn(2) β-spin-dominant, Mn(3) α-spin-dominant, and Mn(4) β-spin dominant.)

e Oxidation state pattern found for the indicated structure. For example, '3332' denotes a complex in which Mn(1), Mn(2) and Mn(3) are all Mn^{III}, Mn(4) is Mn^{II}.

f Mn—Mn distance between the indicated pair of Mn atoms.

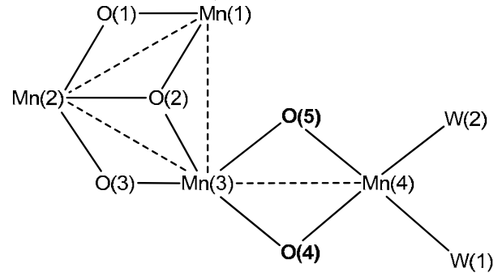
g Root-mean-square deviation from the corresponding 1.9 Å resolution XRD values for the directly-bridged Mn-Mn distances (viz., Mn(1)—Mn(2), Mn(2)—Mn(3), Mn(1)—Mn(3) and Mn(3)—Mn(4)) against the corresponding averaged Shen XRD values.

h Root-mean-square deviation from the corresponding 1.9 Å resolution XRD values for the Mn(1)—Mn(4) and Ca—Mn(*n*) distances.

i Root-mean-square deviation from the corresponding 1.9 Å resolution XRD values for both 'short' and 'long' metal—metal distances.

j Distances obtained from the 1.9 Å resolution XRD of Umena et al.[7] Results shown are the average of monomer A and monomer B values.

Table S2. Metal-metal bond distances and Mn atom spin densities for hydroxide-ligated S_1 state models (in the 'low oxidation state' paradigm) of the form[a]

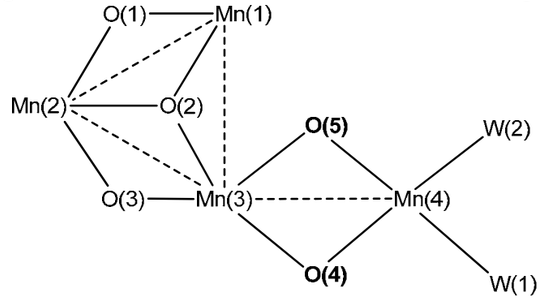


						r(Mn—Mn) / Å					*r*(Ca—Mn) / Å				RMSD		
q	**O(4)**	**O(5)**	**W(OH)?**	**Coupling**	**OSP**	**Mn(12)**	**Mn(23)**	**Mn(13)**	**Mn(34)**	**Mn(14)**	**Mn(1)**	**Mn(2)**	**Mn(3)**	**Mn(4)**	**(short)**	**(long + Ca)**	**(all)**
Shen 1.9 Å						**2.80**	**2.90**	**3.30**	**2.94**	**4.98**	**3.49**	**3.33**	**3.43**	**3.80**			
-2	OH	O	(1)	F	3333	3.005	3.136	3.245	2.886	5.401	3.384	3.223	3.143	3.731	0.161	0.240	0.208
				AF		2.993	3.133	3.262	2.855	5.425	3.391	3.206	3.115	3.711	0.158	0.257	0.219
				F	2433	2.877	2.804	3.624	2.955	5.523	3.504	3.120	3.272	3.742	0.173	0.271	0.233
				AF		2.827	2.793	3.589	2.906	5.490	3.481	3.095	3.234	3.749	0.156	0.267	0.224
-2	O	OH	(1)	F	3333	2.896	2.947	3.307	2.963	5.138	3.478	3.193	3.397	3.764	0.055	0.096	0.080
				AF		2.870	2.928	3.319	2.986	5.108	3.470	3.195	3.402	3.764	0.045	0.086	0.071
				F	2433	2.840	2.801	3.700	3.166	5.852	3.686	3.168	3.682	3.609	0.236	0.430	0.357
				AF		2.754	2.799	3.649	3.210	5.849	3.690	3.176	3.691	3.574	0.227	0.433	0.357
-1	OH	OH	(1)	F	3333	2.931	3.002	3.355	3.072	5.476	3.658	3.178	3.445	3.758	0.110	0.245	0.196
				AF		2.901	2.998	3.360	3.062	5.529	3.663	3.170	3.430	3.756	0.098	0.268	0.210
				F	3342	2.751	2.937	3.326	3.305	5.914	3.396	3.249	3.209	4.691	0.186	0.588	0.456
				AF		2.721	2.889	3.434	3.284	6.127	3.391	3.194	3.210	4.907	0.189	0.724	0.554
				F	2433	2.870	2.802	3.605	3.169	5.598	3.574	3.105	3.492	4.037	0.200	0.316	0.271
				AF		2.845	2.773	3.567	3.163	5.608	3.570	3.113	3.462	4.029	0.187	0.317	0.267
-2	OH	O	(2)	F	3333	2.747	2.986	3.622	2.965	5.101	3.403	3.145	3.183	3.677	0.169	0.163	0.166
				AF		2.722	2.956	3.613	2.957	5.094	3.399	3.136	3.182	3.675	0.164	0.165	0.164
				F	3342	2.762	2.904	3.234	2.947	4.811	3.388	3.274	3.168	3.746	0.038	0.151	0.115
				AF		2.720	2.868	3.364	2.873	5.094	3.434	3.215	3.200	3.857	0.063	0.131	0.106
-2	O	OH	(2)	F	3333	2.890	2.943	3.305	2.966	5.076	3.474	3.201	3.421	3.759	0.052	0.075	0.065
				AF		2.861	2.920	3.324	3.013	5.033	3.531	3.183	3.442	3.783	0.050	0.073	0.064
				F	3342	2.729	2.968	3.554	2.989	5.634	3.495	3.208	3.316	4.238	0.138	0.360	0.284
				AF		2.708	2.888	3.559	2.963	5.633	3.504	3.185	3.322	4.238	0.138	0.361	0.284
-1	OH	OH	(2)	F	3333	2.916	2.966	3.327	3.166	5.250	3.556	3.230	3.559	3.952	0.132	0.159	0.148
				AF		2.790	2.894	3.378	3.164	5.294	3.553	3.246	3.508	3.961	0.119	0.168	0.148
				F	3432	2.783	2.811	3.150	3.276	5.255	3.251	3.264	3.415	4.380	0.189	0.308	0.262
				AF		2.798	2.752	3.202	3.245	5.123	3.249	3.227	3.466	4.374	0.176	0.290	0.246
				F	3342	2.770	2.920	3.204	3.353	5.627	3.354	3.297	3.236	4.653	0.213	0.491	0.392
				AF		2.766	2.831	3.219	3.319	5.651	3.343	3.252	3.280	4.561	0.198	0.465	0.371

Notes:

a Column headings used are as defined in Table 3.

Table S3. Metal-metal bond distances and Mn atom spin densities for hydroxide-ligated S_3 state models (in the 'low oxidation state' paradigm) of the form[a]



						r(Mn—Mn) / Å					*r*(Ca—Mn) / Å				RMSD		
q	**O(4)**	**O(5)**	**W(OH)?**	**Coupling**	**OSP**	**Mn(12)**	**Mn(23)**	**Mn(13)**	**Mn(34)**	**Mn(14)**	**Mn(1)**	**Mn(2)**	**Mn(3)**	**Mn(4)**	**(short)**	**(long + Ca)**	**(all)**
Shen 1.9 Å						**2.80**	**2.90**	**3.30**	**2.94**	**4.98**	**3.49**	**3.33**	**3.43**	**3.80**			
0	OH	O	(1)	F	3443	2.768	2.793	3.327	2.834	5.109	3.482	3.284	3.393	3.712	0.078	0.075	0.076
				AF		2.758	2.781	3.340	2.817	5.130	3.500	3.286	3.384	3.725	0.090	0.080	0.085
0	O	OH	(1)	F	3443	2.747	2.812	3.397	2.905	5.460	3.551	3.239	3.404	4.089	0.073	0.256	0.197
				AF		2.729	2.801	3.413	2.907	5.449	3.557	3.239	3.397	4.052	0.085	0.244	0.190
1	OH	OH	(1)	F	3443	2.769	2.787	3.376	2.930	5.286	3.588	3.320	3.587	3.808	0.070	0.160	0.128
				AF		2.753	2.777	3.381	2.922	5.231	3.606	3.316	3.576	3.809	0.078	0.140	0.117
0	OH	O	(2)	F	3443	2.770	2.794	3.265	2.846	4.805	3.489	3.265	3.433	3.695	0.074	0.096	0.087
				AF		2.758	2.787	3.309	2.831	4.940	3.516	3.262	3.432	3.755	0.081	0.042	0.063
				F	4343	2.788	2.900	2.822	3.234	4.835	3.256	3.352	3.336	4.414	0.281	0.304	0.294
				AF		2.754	2.778	2.827	3.294	5.018	3.236	3.276	3.336	4.415	0.303	0.302	0.302
0	O	OH	(2)	F	3443	2.740	2.803	3.415	2.911	5.346	3.580	3.288	3.477	4.082	0.082	0.212	0.168
				AF		2.723	2.790	3.411	2.905	5.356	3.577	3.275	3.455	4.057	0.089	0.209	0.167
1	OH	OH	(2)	F	3443	2.784	2.770	3.155	3.382	5.756	3.451	3.308	3.410	4.731	0.242	0.542	0.435
				AF		2.774	2.759	3.198	3.361	5.767	3.464	3.301	3.398	4.703	0.228	0.536	0.428
				F	3434	2.781	2.786	3.392	3.200	5.344	3.632	3.261	3.621	4.049	0.150	0.226	0.196
				AF		2.763	2.764	3.356	3.195	5.355	3.639	3.266	3.608	4.042	0.148	0.227	0.196
				F	4433	2.758	2.804	3.189	3.339	5.480	3.333	3.338	3.679	4.599	0.214	0.442	0.359
				AF		2.747	2.787	3.209	3.347	5.505	3.325	3.346	3.705	4.630	0.218	0.462	0.374

Notes:

a Column headings used are as defined in Table 3.