Spectroscopic and Computational Investigation of Second-Sphere Contributions to Redox Tuning in *Eschericia coli* Iron Superoxide Dismutase

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Table S1. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Fe^{3+}SOD (starting coordinates based on PDB file 1ISA).[1]

Atom	x	y	z
C	-1.968597	-0.456619	-5.893906
C	-0.434052	-0.331833	-5.839310
C	0.073029	-0.201645	-4.444107
N	1.414871	-0.312622	-4.107727
C	1.542755	-0.177109	-2.763229
N	0.352158	0.008377	-2.210205
C	-0.564423	0.007126	-3.243607
H	-2.314743	-0.979446	-4.994080
H	-2.299759	-1.080933	-6.749741
H	-2.446884	0.545868	-5.888855
H	0.045212	-1.229431	-6.255859
H	-0.085388	0.510208	-6.455994
H	2.218536	-0.527237	-4.715576
H	2.482437	-0.210602	-2.228134
H	-1.612732	0.201080	-3.058609
C	-9.049591	4.085724	0.871033
C	-7.550095	4.171616	1.188934
C	-6.875168	2.823883	1.361450
C	-7.460892	1.774292	2.088531
C	-6.768250	0.587524	2.336487
C	-5.477905	0.419403	1.824722
O	-4.708557	-0.716415	2.063600
C	-4.912308	1.407974	1.021484
C	-5.605728	2.599945	0.816986
H	-9.594696	3.642136	1.717743
H	-9.223541	3.414169	-0.002731
H	-9.489578	5.094696	0.744843
H	-7.016357	4.723923	0.400574
H	-7.403366	4.762131	2.110809
H	-8.474716	1.872757	2.477859
H	-7.222916	-0.196335	2.947906
H	-5.084366	-1.185242	2.854630
H	-3.916611	1.261246	0.607162
H	-5.116882	3.407288	0.268127
C	-3.714249	4.955048	4.015640
C	-4.569885	3.690872	4.204483
C	-3.965317	2.670090	5.201019
C	-2.617400	2.097778	4.770996
O	-1.560196	2.481186	5.301376
N	-2.623657	1.162170	3.783844
H	-2.654100	4.652328	3.942505
H	-3.741028	5.643478	4.898224
H	-3.966217	5.460144	3.035736
H	-5.579285	3.957870	4.547775
H	-4.721848	3.174561	3.245514
H	-3.785034	3.137527	6.175690
H	-4.676453	1.840103	5.341248
H	-1.753159	0.746063	3.428711
H	-3.492889	0.825424	3.380554
C	0.262772	6.143784	-0.882065
C	-0.994980	5.453308	-1.455429
C	-1.146942	4.054962	-0.950729
N	-1.775070	3.777557	0.250046
C	-1.601669	2.479355	0.563248
N	-0.893524	1.876648	-0.389175
C	-0.603622	2.851105	-1.338257
H	1.107208	5.446121	-0.976257
H	0.214523	6.445328	0.204086
H	0.500427	6.991974	-1.534424
H	-1.896530	6.029495	-1.210632
H	-0.936569	5.417023	
H	-2.347977	4.433121	-2.550446
H	-1.954208	2.023300	0.789261
H	0.003662	2.641571	1.478592
C	5.486649	1.471573	-2.210892
C	4.801361	2.844086	6.376343
C	3.429016	2.808319	6.163834
C	2.227432	2.513336	5.562836
N	1.191971	2.535141	6.210678
C	1.682373	2.863449	5.318375
C	1.008102	3.039276	4.067917
C	1.762878	3.448242	2.862808
C	3.147476	3.672531	1.759842
C	3.822525	3.477875	1.868637
C	3.086823	3.059097	3.072189
H	5.670441	0.967133	4.194900
H	4.840714	0.809830	5.419556
H	6.464539	1.642441	6.996414
H	4.725281	3.348022	6.895981
H	5.445160	3.477982	7.133804
H	2.050858	2.298065	5.536407
H	0.189346	2.387802	7.262756
H	-0.065750	2.876678	5.502594
H	1.276642	3.608139	2.791138
H	3.702026	3.994965	0.796280
H	4.900681	3.647049	0.989777
C	5.172592	0.580093	3.136429
C	4.118851	0.630814	1.708939
C	2.773804	0.043945	0.602753
O	2.514893	-0.346069	1.016724
O	1.908875	0.000000	2.152542
Fe	0.00000	0.00000	-0.000061
O	-0.547562	0.000015	0.00000
H	4.743088	0.971405	1.820877
H	6.070100	1.185272	2.638992
H	5.458466	-0.473328	1.447540
H	3.901047	1.667160	1.876114
H	4.446457	0.117523	0.299469
H	0.305847	-0.140091	-0.316574
C	0.283615	-5.991226	2.300903
C	-1.145874	-5.410233	-1.761047
C	-1.209702	-4.054703	-1.600494
N	-1.840942	-3.808624	-0.951874
C	-1.667877	-2.504654	0.261993
N	-0.967636	-1.886673	0.599808
C	-0.684814	-2.834595	-0.347946
H	0.206223	-6.929596	-1.315704
H	0.709991	-6.261169	-2.331741
H	0.933853	-5.291855	-0.768539
H	-1.602631	-5.343826	-2.375946
H	-1.770279	-6.116409	-2.598526
H	-2.327744	-4.489716	-1.031800
H	-2.007645	-2.043060	0.837311
H	-0.096954	-2.573349	1.519867
			-2.189178

Table S2. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Fe^{3+}SOD (starting coordinates based on PDB file 1ISB).[1]

Atom	x	y	z
C	-1.927597	-0.584091	-5.886459
C	-0.394424	-0.463196	-5.826584
C	0.103668	-0.188522	-4.449432
N	1.448059	-0.264374	-4.107941
C	1.567917	-0.118073	-2.765289
N	0.374405	0.049545	-2.215317
C	-0.539352	0.020218	-3.253281
H	-2.288269	-1.067932	-4.967209
H	-2.279251	-1.236252	-6.715912
H	-2.371872	0.424866	-5.929184
H	0.101364	-1.396240	-6.119888
H	-0.037460	0.291229	-6.544083
H	2.239349	-0.522202	-4.713837
H	2.506700	-0.134323	-2.227158
H	-1.598785	0.146912	-3.076218
C	-8.499268	4.451263	0.693985
C	-7.014130	4.532257	1.091385
C	-6.424835	3.204636	1.525986
C	-6.930313	2.511230	2.637329
C	-6.402222	1.284119	3.038025
C	-5.336411	0.721069	2.328873
O	-4.766571	-0.500519	2.671890
C	-4.807693	1.390472	1.225052
C	-5.349960	2.620500	0.848175
H	-9.054810	3.996552	1.529266
H	-8.741806	3.814926	-0.199249
H	-8.921600	5.469498	0.591293
H	-6.402176	4.954269	0.282013
H	-6.932693	5.226929	1.941940
H	-7.744095	2.933746	3.224319
H	-6.816010	0.766998	3.909729
H	-5.102585	-0.767441	3.552734
H	-3.959183	0.968872	0.684906
H	-4.895981	3.155014	0.015533
C	-2.920593	5.467178	4.050537
C	-3.897293	4.280685	4.014755
C	-3.525269	3.121811	4.975266
C	-2.201019	2.472214	4.599503
O	-1.121277	2.924988	5.024597
N	-2.261063	1.428055	3.731200
H	-1.894089	5.073593	4.147629
H	-3.039215	6.139221	4.933151
H	-2.958710	6.020782	3.078903
H	-4.927368	4.598587	4.238617
H	-3.953476	3.855255	2.999176
H	-3.403580	3.488571	5.999954
H	-4.335205	2.376282	4.965302
H	-1.424866	0.941177	3.373000
H	-3.154755	1.017853	3.477005
C	0.735336	6.040680	-0.945938
C	-0.560074	5.426254	-1.515625
C	-0.855103	4.069626	-0.965530
N	-1.479355	3.883926	0.255890
C	-1.445709	2.578979	0.588120
N	-0.862869	1.883728	-0.385620
C	-0.491409	2.805511	-1.360031
H	1.525787	5.275558	-0.994736
H	0.700531	6.387665	0.126190
H	1.057800	6.836853	-1.631073
H	-1.412781	6.091461	-1.327011
H	-0.463150	5.321472	-2.603745
H	-1.793076	4.643860	0.862595
H	-1.817688	2.180588	1.523788
H	0.035339	2.506516	-2.257767
C	5.759430	0.773529	6.205200
C	5.207260	2.213379	6.040802
C	3.824142	2.349442	5.486374
C	2.622528	2.165771	6.169312
N	1.565536	2.358292	5.323456
C	2.042740	2.702057	4.071716
C	1.353180	3.006744	2.900360
C	2.113266	3.379639	1.789139
C	3.516571	3.446548	1.856094
C	4.204453	3.110092	3.019775
C	3.463989	2.720947	4.150009
H	5.900375	0.295792	5.228210
H	5.053818	0.144257	6.801132
H	6.755447	0.855300	6.718323
H	5.215973	2.698471	7.022385
H	5.896332	2.793671	5.409119
H	2.458069	1.935074	7.218277
H	0.567490	2.339400	5.549194
H	0.266754	2.968369	2.864975
H	1.615982	3.624649	0.849167
H	4.076340	3.742096	0.971741
H	5.295990	3.135208	3.046021
C	5.301758	0.190048	1.505554
C	4.190842	0.389862	0.479675
C	2.837570	-0.151459	0.938660
O	2.630783	-0.677582	2.029297
O	1.903488	0.000000	0.000015
Fe	0.000000	0.000000	0.000000
O	-0.472397	0.000000	1.856766
H	4.955048	0.533340	2.488266
H	6.236618	0.736633	1.251190
H	5.523834	-0.884460	1.574081
H	4.023666	1.456131	0.263687
H	4.429489	-0.077957	-0.489944
H	0.361267	-0.285156	2.301895
C	-0.261856	-5.932205	-2.007813
C	-1.607330	-5.173050	-1.896713
C	-1.533844	-3.883804	-1.129410
N	-2.066269	-3.698486	0.142776
C	-1.756424	-2.450226	0.575775
N	-1.033432	-1.821335	-0.348419
C	-0.900757	-2.697495	-1.412582
H	-0.428436	-6.841217	-2.606781
H	0.111115	-6.272690	-1.006073
H	0.491531	-5.308365	-2.575623
H	-1.973251	-4.954041	-2.911667
H	-2.370010	-5.824921	-1.445007
H	-2.682297	-4.350357	0.615646
H	-2.018036	-2.033325	1.541229
H	-0.361465	-2.419586	-2.310944

Table S3. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of $Fe^{2+}SOD^{HOH}$ (starting coordinates based on PDB file 1ISA).[1]

Atom	x	Y	z
C	-1.722977	-5.977570	-0.285675
C	-0.225143	-5.756119	-0.544800
C	0.168182	-4.318573	-0.628036
N	1.487152	-3.915421	-0.762848
C	1.544662	-2.560577	-0.697006
N	0.330795	-2.063416	-0.501572
C	-0.533218	-3.144700	-0.471756
H	-2.036514	-5.281982	0.503922
H	-1.911530	-6.995422	0.122971
H	-2.340302	-5.759430	-1.183868
H	0.355118	-6.156570	0.300964
H	0.100266	-6.306473	-1.438614
H	2.334763	-4.493423	-0.848984
H	2.451019	-1.977386	-0.791168
H	-1.599106	-3.002960	-0.365555
C	-9.840317	1.467056	-2.264023
C	-8.426193	2.005219	-2.529419
C	-7.527161	2.032288	-1.312088
C	-7.903625	2.687637	-0.130157
C	-7.015350	2.818802	0.938416
C	-5.739502	2.261459	0.841766
O	-4.779205	2.428604	1.844254
C	-5.374466	1.516632	-0.277939
C	-6.265656	1.426071	-1.347778
H	-10.375900	2.129883	-1.567474
H	-9.801620	0.459824	-1.784622
H	-10.437012	1.489212	-3.191895
H	-7.927551	1.416779	-3.313187
H	-8.501770	3.032745	-2.923279
H	-8.903839	3.108276	-0.026093
H	-7.310135	3.367554	1.835526
H	-5.117477	3.119919	2.479019
H	-4.389465	1.055649	-0.333038
H	-5.959518	0.916321	-2.262054
C	-4.490143	5.166092	-3.440826
C	-5.176102	4.811615	-2.114639
C	-4.710526	5.640991	-0.889923
C	-3.246613	5.440796	-0.539368
O	-2.374496	6.196198	-0.993042
N	-2.921707	4.380295	0.263550
H	-3.404297	5.260971	-3.264709
H	-4.787231	6.150757	-3.869049
H	-4.629227	4.327759	-4.177307
H	-6.269882	4.903046	-2.193909
H	-5.002762	3.751709	-1.870926
H	-4.800339	6.718277	-1.070541
H	-5.343658	5.378662	-0.027573
H	-1.953979	4.295212	0.571533
H	-3.624695	3.820755	0.742935
C	-0.870392	0.823868	-5.923752
C	-1.995270	0.066010	-5.187927
C	-1.946167	0.216064	-3.701370
N	-2.482468	1.312653	-3.053482
C	-2.152298	1.274704	-1.747726
N	-1.448090	0.173630	-1.491669
C	-1.318451	-0.494431	-2.705032
H	0.074112	0.658798	-5.383789
H	-1.002365	1.937180	-6.010406
H	-0.737228	0.342636	-6.903000
H	-2.973251	0.403519	-5.553833
H	-1.921906	-1.006836	-5.405975
H	-2.963730	2.077652	-3.531662
H	-2.414215	2.056595	-1.046249
H	-0.747574	-1.412140	-2.789978
C	4.892853	7.098083	-0.623749
C	3.952454	7.265442	-1.845000
C	2.585632	6.649963	-1.742096
C	1.461639	7.217422	-1.174408
N	0.389450	6.350784	-1.254486
C	0.793076	5.204193	-1.891312
C	0.065048	4.061417	-2.255859
C	0.729736	3.077194	-2.992661
C	2.081680	3.236938	-3.364944
C	2.808273	4.363449	-2.987503
C	2.173843	5.363251	-2.228668
H	5.173935	6.053986	-0.457031
H	4.381409	7.472610	0.287598
H	5.811340	7.727142	-0.803986
H	3.818039	8.335556	-2.031113
H	4.456940	6.866241	-2.742065
H	1.338333	8.197876	-0.718079
H	-0.569855	6.521133	-0.937622
H	-1.006729	3.999710	-2.056152
H	0.193359	2.190414	-3.329880
H	2.552628	2.473038	-3.986771
H	3.851349	4.473526	-3.294968
C	4.910034	2.328323	-0.949417
C	3.906143	1.198975	-1.166931
C	2.691574	1.255432	-0.254318
O	2.492600	2.189240	0.549286
O	1.872498	0.241653	-0.416977
Fe	0.000000	0.000000	0.000000
H	4.394608	3.294296	-0.984253
H	5.703873	2.315292	-1.725723
H	5.367783	2.207825	0.049103
H	3.490219	1.224426	-2.187744
H	4.360260	0.202576	-1.057495
C	1.225220	-2.782288	5.403290
C	-0.272583	-2.541489	5.073898
C	-0.549820	-1.588257	3.943298
N	-1.262466	-0.402618	4.076660
C	-1.305573	0.232986	2.876144
N	-0.661453	-0.486160	1.960846
C	-0.199509	-1.618332	2.612259
H	1.276291	-3.552490	6.187180
H	1.685165	-1.865448	5.833832
H	1.779861	-3.198730	4.505707
H	-0.722168	-3.514297	4.819870
H	-0.793091	-2.191193	5.979095
H	-1.740463	-0.060043	4.920944
H	-1.774384	1.196396	2.719345
H	0.368469	-2.367950	2.070114
O	-0.117950	2.182892	0.380753
H	0.868454	2.261261	0.666763
H	-0.071747	2.644379	-0.495956

Table S4. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of $Fe^{2+}SOD^{OH-}$ (starting coordinates based on PDB file 1ISA).[1]

Atom	x	y	z
C	-2.698685	-5.871689	-0.808838
C	-1.225983	-5.846893	-1.250305
C	-0.622147	-4.480652	-1.253876
N	0.732635	-4.270844	-1.485916
C	0.996109	-2.940933	-1.333115
N	-0.099472	-2.287415	-0.992600
C	-1.108704	-3.228226	-0.951248
H	-2.805588	-5.199921	0.053192
H	-2.994232	-6.884628	-0.443298
H	-3.375824	-5.487350	-1.600342
H	-0.625153	-6.430800	-0.534637
H	-1.112930	-6.336639	-2.227844
H	1.457458	-4.965805	-1.713730
H	1.969100	-2.482590	-1.465912
H	-2.126587	-2.933548	-0.732849
C	-9.488495	2.720291	-0.980591
C	-8.036545	3.002380	-1.393280
C	-7.024551	2.736938	-0.298248
C	-7.183792	3.264877	0.992325
C	-6.205139	3.093246	1.970963
C	-5.056564	2.355209	1.673691
O	-4.034714	2.163513	2.596664
C	-4.900833	1.764862	0.418839
C	-5.875534	1.981125	-0.555222
H	-9.784180	3.392487	-0.160782
H	-9.597153	1.686752	-0.581207
H	-10.196411	2.945053	-1.801620
H	-7.757172	2.411331	-2.277924
H	-7.948486	4.057861	-1.700958
H	-8.089005	3.810410	1.257263
H	-6.335510	3.536026	2.961578
H	-4.084641	2.899078	3.270432
H	-4.000626	1.195877	0.192841
H	-5.712570	1.601471	-1.564163
C	-3.914047	5.713364	-2.544922
C	-4.454727	5.315125	-1.162903
C	-3.620132	5.838425	0.033722
C	-2.224991	5.216049	0.107361
O	-1.258377	5.772995	-0.445679
N	-2.120621	4.046783	0.786560
H	-2.817000	5.588669	-2.537338
H	-4.067078	6.787384	-2.815292
H	-4.309464	5.015762	-3.333145
H	-5.500595	5.636581	-1.031967
H	-4.489975	4.217392	-1.074707
H	-3.455719	6.920288	-0.033081
H	-4.168594	5.630264	0.967010
H	-1.291763	3.412354	0.766205
H	-2.955627	3.627869	1.183945
C	-1.448090	1.132965	-5.929916
C	-2.557953	0.467148	-5.092758
C	-2.293381	0.487259	-3.619934
N	-2.606674	1.587800	-2.846130
C	-2.099197	1.417877	-1.603638
N	-1.504500	0.233139	-1.507004
C	-1.620911	-0.354202	-2.763092
H	-0.475952	0.759277	-5.575104
H	-1.393143	2.255402	-5.867889
H	-1.543182	0.773331	-6.965652
H	-3.515366	0.965820	-5.291733
H	-2.672363	-0.581604	-5.396988
H	-3.020447	2.447540	-3.211761
H	-2.124344	2.168427	-0.826630
H	-1.173706	-1.316940	-2.980728
C	6.044159	5.735977	-0.819763
C	5.027786	6.086166	-1.937607
C	3.600891	5.667023	-1.733063
C	2.639816	6.291702	-0.957672
N	1.453537	5.590134	-1.011215
C	1.611511	4.514389	-1.853348
C	0.692657	3.538132	-2.251541
C	1.121613	2.592346	-3.178619
C	2.435150	2.618225	-3.691162
C	3.357132	3.572372	-3.273926
C	2.952835	4.539169	-2.336273
H	6.156891	4.653351	-0.685776
H	5.686630	6.170059	0.137421
H	7.035782	6.202133	-1.097763
H	5.035950	7.174179	-2.067017
H	5.382828	5.666473	-2.891968
H	2.711319	7.212800	-0.384583
H	0.560211	5.831055	-0.573715
H	-0.320618	3.527802	-1.855133
H	0.437622	1.811600	-3.516815
H	2.738373	1.862808	-4.414932
H	4.380402	3.558990	-3.658463
C	5.136475	1.178543	-1.462280
C	3.917877	0.260193	-1.593033
C	2.828995	0.465195	-0.529251
O	2.926880	1.296707	0.380463
O	1.807663	-0.351273	-0.702515
Fe	0.000000	0.000000	0.000000
O	-0.476456	1.713776	0.842422
H	4.803223	2.221893	-1.396133
H	5.809784	1.076645	-2.352127
H	5.679611	0.927994	-0.533829
H	3.414978	0.412415	-2.560394
H	4.206909	-0.804749	-1.574387
H	0.420486	2.083710	0.990509
C	1.395294	-4.113419	4.600342
C	-0.087387	-3.668137	4.488068
C	-0.362091	-2.518829	3.554565
N	-0.894012	-1.302139	3.967758
C	-0.971176	-0.468628	2.888794
N	-0.518097	-1.083527	1.802567
C	-0.148880	-2.354889	2.204437
H	1.435043	-4.960129	5.303940
H	2.004303	-3.306396	5.052643
H	1.798645	-4.478439	3.598831
H	-0.665161	-4.543427	4.155777
H	-0.463348	-3.416031	5.491898
H	-1.244995	-1.067917	4.903564
H	-1.286102	0.568436	2.913162
H	0.265579	-3.056885	1.486862

Table S5. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Fe^{3+}(Mn)SOD (starting coordinates based on PDB file 1VEW).[2]

Atom	x	y	z
C	-2.005539	-0.606537	-5.903351
C	-0.474884	-0.577515	-5.765244
C	-0.005936	-0.255142	-4.392990
N	1.343170	-0.178253	-4.087875
C	1.488510	-0.005508	-2.753265
N	0.291870	0.035355	-2.175888
C	-0.642761	-0.108154	-3.185364
H	-2.444977	-1.190200	-5.082565
H	-2.275024	-1.123184	-6.844528
H	-2.433777	0.414871	-5.868668
H	-0.067871	-1.579636	-5.977127
H	-0.023407	0.108994	-6.499725
H	2.120895	-0.258255	-4.762466
H	2.436111	0.077606	-2.236053
H	-1.703995	-0.092117	-2.979630
C	-8.816391	4.337265	0.809021
C	-7.299423	4.458755	1.049286
C	-6.624115	3.160965	1.433945
C	-7.154694	2.364822	2.457611
C	-6.564758	1.159332	2.828842
C	-5.429413	0.708664	2.153503
O	-4.848663	-0.530396	2.416245
C	-4.854050	1.498932	1.156357
C	-5.446518	2.718689	0.818268
H	-9.294708	3.868256	1.682007
H	-9.058502	3.682663	-0.058167
H	-9.245895	5.364182	0.725113
H	-6.799988	4.881805	0.165298
H	-7.147339	5.187943	1.862991
H	-8.049300	2.691162	2.982071
H	-6.982422	0.569778	3.650772
H	-5.442184	-1.035080	3.047684
H	-3.951600	1.157913	0.651443
H	-4.971878	3.341858	0.058670
C	0.230530	6.219177	-0.853348
C	-1.007141	5.480637	-1.414368
C	-1.146713	4.092606	-0.864944
N	-1.742981	3.838516	0.363388
C	-1.576965	2.536758	0.683960
N	-0.903885	1.916946	-0.284058
C	-0.630417	2.877533	-1.252075
H	1.112442	5.575104	-0.979813
H	0.139206	6.430176	0.246140
H	0.422989	7.131592	-1.454865
H	-1.913071	6.051025	-1.169373
H	-0.960648	5.420456	-2.507690
H	-2.323853	4.504807	0.880890
H	-1.926834	2.093231	1.607727
H	-0.065414	2.639587	-2.146576
C	5.294540	1.080139	6.490829
C	4.728424	2.512405	6.304291
C	3.513504	2.612946	5.436951
C	2.205429	2.218979	5.728867
N	1.414902	2.349838	4.623215
C	2.173462	2.868637	3.584167
C	1.818329	3.166382	2.269897
C	2.801498	3.745529	1.456924
C	4.096054	4.012604	1.944595
C	4.452011	3.670990	3.247772
C	3.490005	3.074600	4.081253
H	5.495453	0.601318	5.525406
H	4.570847	0.431870	7.046219
H	6.256256	1.200684	7.047043
H	4.507706	2.925858	7.296921
H	5.501694	3.161850	5.868881
H	1.794067	1.848938	6.663910
H	0.389572	2.276550	4.602875
H	0.823212	2.950043	1.889771
H	2.566513	3.970673	0.416702
H	4.846298	4.448685	1.284729
H	5.468887	3.847382	3.610138
C	-1.828232	2.697311	7.522720
C	-3.102371	2.977432	6.716888
C	-3.355438	1.986450	5.574112
C	-2.233047	1.935700	4.536621
O	-1.360062	2.827454	4.449921
N	-2.269700	0.885345	3.683075
H	-0.987045	2.698318	6.816162
H	-1.854691	1.704529	8.041092
H	-1.611664	3.542694	8.215683
H	-3.976364	2.970749	7.381210
H	-3.035492	3.975784	6.267258
H	-3.519775	0.967560	5.962173
H	-4.276215	2.254517	5.029114
H	-1.460648	0.619171	3.073746
H	-2.983673	0.170334	3.805603
C	5.101624	0.430222	1.903824
C	4.132767	0.443222	0.718155
C	2.753510	-0.119080	1.030090
O	2.430038	-0.611282	2.113373
O	1.915375	0.000000	0.000015
Fe	0.000000	0.000000	0.000000
O	-0.386719	0.000015	1.860016
H	4.581650	0.774750	2.805969
H	5.952500	1.120010	1.707306
H	5.448471	-0.605377	2.067734
H	3.945389	1.471954	0.368454
H	4.523849	-0.098312	-0.160278
H	0.482590	-0.301041	2.239471
C	-0.092773	-6.158615	-1.769882
C	-1.430359	-5.405243	-1.570190
C	-1.350769	-4.053146	-0.913925
N	-2.024368	-3.743118	0.263397
C	-1.759613	-2.457733	0.605011
N	-0.977982	-1.897003	-0.315277
C	-0.718094	-2.878189	-1.261078
H	-0.304474	-7.068771	-2.353317
H	0.342361	-6.501251	-0.803802
H	0.635132	-5.571182	-2.398682
H	-1.887238	-5.276047	-2.564194
H	-2.118668	-6.045364	-0.999313
H	-2.513107	-4.398087	0.867279
H	-2.109314	-1.976547	1.510544
H	-0.079666	-2.670853	-2.114349

Table S6. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Fe^{2+}(Mn)SOD^{HOH} (starting coordinates based on PDB file 1VEW).[2]

Atom	x	y	z
C	-5.817032	0.236893	-2.126648
C	-5.700333	0.218369	-0.595261
C	-4.319672	0.003922	-0.094574
N	-4.047012	-0.049988	1.260208
C	-2.706818	-0.143372	1.441772
N	-2.098587	-0.146530	0.259537
C	-3.090271	-0.068420	-0.701340
H	-5.043747	0.890686	-2.551529
H	-6.798996	0.672089	-2.398285
H	-5.688538	-0.772766	-2.559555
H	-5.992310	1.203857	-0.198120
H	-6.388870	-0.519958	-0.153152
H	-4.747986	-0.037613	2.017807
H	-2.211243	-0.193527	2.403046
H	-2.854874	-0.079651	-1.756714
C	1.365768	-3.833847	-8.965332
C	1.563309	-3.957993	-7.438919
C	1.887726	-2.645279	-6.754410
C	2.898422	-1.813751	-7.252853
C	3.197952	-0.584305	-6.671188
C	2.457855	-0.140518	-5.573730
O	2.650162	1.113785	-4.994812
C	1.470993	-0.963776	-5.028458
C	1.209686	-2.207993	-5.609300
H	2.240952	-3.335434	-9.407486
H	0.490128	-3.193588	-9.209015
H	1.318893	-4.850113	-9.434464
H	0.679123	-4.403381	-6.964355
H	2.383636	-4.664108	-7.252853
H	3.467972	-2.123337	-8.124283
H	4.017715	0.021591	-7.072784
H	3.299820	1.622406	-5.569183
H	0.910934	-0.628448	-4.156937
H	0.462357	-2.853668	-5.148926
C	-0.115631	-6.166595	-0.120941
C	-0.766281	-5.444702	-1.321533
C	-0.345062	-4.010620	-1.419998
N	0.801346	-3.610931	-2.088318
C	1.017319	-2.294464	-1.867844
N	0.051376	-1.802826	-1.090637
C	-0.802400	-2.865356	-0.809845
H	-0.285370	-5.561340	0.781723
H	1.001282	-6.291763	-0.216492
H	-0.643784	-7.122345	0.049667
H	-0.520782	-5.964890	-2.258331
H	-1.858261	-5.472733	-1.229584
H	1.366821	-4.221603	-2.685242
H	1.865646	-1.752258	-2.268707
H	-1.667175	-2.741165	-0.167664
C	6.699280	-0.660568	5.200455
C	6.592926	-2.063904	4.558151
C	5.747574	-2.152542	3.319580
C	6.036789	-1.725296	2.040344
N	4.947769	-1.924500	1.208527
C	3.944046	-2.533508	1.929703
C	2.672882	-2.979065	1.539291
C	1.886566	-3.620590	2.497437
C	2.359009	-3.823090	3.811874
C	3.614563	-3.368668	4.199982
C	4.420303	-2.700394	3.263535
H	5.708557	-0.237930	5.408585
H	7.237259	0.035919	4.513306
H	7.254395	-0.791290	6.162567
H	7.607803	-2.422119	4.334518
H	6.181137	-2.773148	5.292374
H	6.947830	-1.285507	1.643127
H	4.972244	-1.865555	0.188446
H	2.328354	-2.902206	0.504639
H	0.890106	-3.972427	2.228760
H	1.728012	-4.324402	4.547913
H	3.966141	-3.525253	5.223053
C	7.982178	-2.081802	-2.062759
C	7.124847	-2.398911	-3.293381
C	5.961000	-1.426086	-3.537460
C	4.929825	-1.415848	-2.415222
O	4.834900	-2.340103	-1.586456
N	4.054138	-0.368042	-2.406906
H	7.320404	-2.130569	-1.185272
H	8.434555	-1.057266	-2.084473
H	8.742081	-2.881851	-1.863800
H	7.730911	-2.451797	-4.206619
H	6.677521	-3.387268	-3.143951
H	6.316193	-0.397873	-3.717514
H	5.406250	-1.722549	-4.443481
H	3.524261	-0.163254	-1.550385
H	4.200394	0.412247	-3.045029
C	2.049744	-0.324402	5.077225
C	0.856995	-0.413452	4.124100
C	1.074722	0.205475	2.759338
O	2.124481	0.807678	2.438858
O	0.080627	0.000015	1.926819
Fe	0.000000	0.000000	0.000000
H	2.970047	-0.598923	4.546906
H	1.903320	-1.045181	5.906921
H	2.143417	0.711288	5.444855
H	0.612946	-1.466202	3.901047
H	-0.066223	0.017471	4.547684
C	-1.969391	6.003647	-0.052567
C	-1.651291	5.296341	-1.393967
C	-0.893616	3.996765	-1.318893
N	0.318665	3.784393	-1.964523
C	0.734512	2.513062	-1.728653
N	-0.162613	1.870987	-0.985275
C	-1.176819	2.783371	-0.728165
H	-2.616653	6.865509	-0.276886
H	-1.049408	6.419540	0.415466
H	-2.571808	5.355896	0.650543
H	-2.611526	5.094742	-1.896286
H	-1.106857	5.994781	-2.045822
H	0.889145	4.480743	-2.436966
H	1.670685	2.109619	-2.096176
H	-2.032928	2.500412	-0.123077
O	2.248291	0.000000	0.000015
H	2.305954	0.518295	0.905090
H	2.440384	-0.901443	0.331543

Table S7. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Fe^{2+}(Mn)SOD^{OH-} (starting coordinates based on PDB file 1VEW).[2]

Atom	x	y	z
C	-2.595734	-5.336212	-2.208145
C	-1.107100	-5.478943	-1.853683
C	-0.465836	-4.194016	-1.465530
N	0.866028	-4.150223	-1.086670
C	1.173492	-2.884750	-0.700729
N	0.102524	-2.112000	-0.805557
C	-0.916900	-2.907990	-1.289474
H	-3.086426	-4.679749	-1.477783
H	-3.088089	-6.324768	-2.127991
H	-2.729767	-4.893875	-3.214035
H	-1.003738	-6.134750	-0.974335
H	-0.553085	-5.961380	-2.675064
H	1.523636	-4.944717	-1.114105
H	2.141602	-2.546326	-0.349991
H	-1.897629	-2.497589	-1.489685
C	-7.350250	3.688751	-5.346710
C	-5.843079	3.667618	-5.022552
C	-5.532211	3.467804	-3.552368
C	-6.163147	4.261490	-2.585526
C	-5.906555	4.101349	-1.225845
C	-5.004227	3.124542	-0.801437
O	-4.757202	2.872421	0.542252
C	-4.329041	2.344666	-1.743591
C	-4.593658	2.528275	-3.102768
H	-7.851776	4.413193	-4.687286
H	-7.827789	2.709427	-5.126129
H	-7.515213	4.034225	-6.405060
H	-5.327515	2.896255	-5.613647
H	-5.418091	4.632996	-5.343857
H	-6.869308	5.028717	-2.897034
H	-6.393112	4.750122	-0.490402
H	-5.375549	3.433640	1.097717
H	-3.592529	1.614944	-1.410797
H	-4.039291	1.931427	-3.828583
C	1.690170	1.221146	-5.983749
C	0.276855	0.646240	-5.741562
C	-0.166229	0.712479	-4.310837
N	-0.769424	1.841385	-3.776520
C	-0.932480	1.665314	-2.439728
N	-0.467987	0.475769	-2.073334
C	0.011078	-0.123413	-3.231155
H	2.396347	0.731705	-5.300079
H	1.733383	2.316559	-5.750793
H	2.016327	0.974380	-7.017883
H	-0.437820	1.214661	-6.349640
H	0.218613	-0.394043	-6.081390
H	-1.155914	2.616318	-4.322159
H	-1.338287	2.421173	-1.779968
H	0.478745	-1.102417	-3.208679
C	5.880035	5.453200	2.277283
C	5.580704	5.841461	0.806931
C	4.356033	5.218765	0.199463
C	3.025284	5.493546	0.448868
N	2.214447	4.604111	-0.228287
C	3.008148	3.757782	-0.970000
C	2.663696	2.699097	-1.819580
C	3.697250	2.049911	-2.489685
C	5.045700	2.437485	-2.314194
C	5.386139	3.462158	-1.438431
C	4.364395	4.133667	-0.742447
H	5.893387	4.363235	2.400162
H	5.093582	5.865067	2.955276
H	6.895386	5.863205	2.523560
H	5.514633	6.937286	0.741776
H	6.438019	5.556931	0.177704
H	2.588669	6.262558	1.080536
H	1.205154	4.709641	-0.357697
H	1.629227	2.377441	-1.926422
H	3.467209	1.192398	-3.123352
H	5.842087	1.889800	-2.822403
H	6.435760	3.724426	-1.274216
C	-0.527328	8.125610	-0.000702
C	-1.775269	7.725647	-0.795227
C	-2.379547	6.377533	-0.385422
C	-1.424667	5.185333	-0.546280
O	-0.398117	5.252747	-1.257538
N	-1.798141	4.053421	0.085266
H	0.203979	7.312439	-0.108307
H	-0.741333	8.268478	1.093445
H	-0.040863	9.015778	-0.464355
H	-2.547714	8.499435	-0.688522
H	-1.518250	7.647583	-1.858841
H	-2.739471	6.405807	0.656403
H	-3.263016	6.150787	-1.005173
H	-1.164551	3.199417	0.231583
H	-2.623383	4.086655	0.680283
C	5.222656	0.993088	1.175690
C	4.189148	0.043610	0.561905
C	2.743591	0.282242	1.006851
O	2.432281	1.104935	1.878967
O	1.888916	-0.476776	0.351196
Fe	0.000000	0.000000	0.000000
O	-0.446289	1.818298	0.550247
H	4.857254	2.025604	1.106796
H	6.184250	0.929459	0.613098
H	5.352402	0.732925	2.239624
H	4.169769	0.147446	-0.535004
H	4.425323	-1.017334	0.756592
H	0.268127	2.002335	1.199219
C	-1.739868	-3.754349	4.906097
C	-2.853683	-3.083023	4.060135
C	-2.424942	-2.036667	3.068192
N	-2.859207	-0.716888	3.128235
C	-2.290665	-0.024124	2.097916
N	-1.555084	-0.832642	1.346878
C	-1.633835	-2.083862	1.939377
H	-2.216217	-4.559494	5.489944
H	-1.306351	-3.055695	5.651398
H	-0.944748	-4.256744	4.269638
H	-3.365372	-3.890671	3.514938
H	-3.600769	-2.653625	4.744766
H	-3.323135	-0.269241	3.913559
H	-2.383881	1.044708	1.943695
H	-1.092453	-2.928406	1.522049

Table S8. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Fe^{3+}(Mn)SOD (starting coordinates based on PDB file 1MMM).[3]

Atom	x	y	z
C	-2.383987	-5.657013	-1.638763
C	-0.919342	-5.635513	-1.175079
C	-0.326752	-4.281418	-0.986755
N	1.004730	-4.156600	-0.629181
C	1.268326	-2.862976	-0.328979
N	0.166229	-2.137300	-0.488876
C	-0.828812	-3.006622	-0.904892
H	-2.965225	-4.908173	-1.083145
H	-2.815598	-6.642258	-1.371048
H	-2.479660	-5.438980	-2.722870
H	-0.852158	-6.096558	-0.176010
H	-0.289566	-6.243668	-1.843200
H	1.652267	-4.955933	-0.565414
H	2.230057	-2.481598	-0.011063
H	-1.830414	-2.663956	-1.124771
C	-7.237488	2.526886	-6.257645
C	-5.718460	2.635590	-6.033508
C	-5.304855	2.574997	-4.579391
C	-5.903458	3.398972	-3.613495
C	-5.572968	3.289825	-2.262924
C	-4.642960	2.332779	-1.847672
O	-4.327988	2.142242	-0.508942
C	-4.007370	1.525742	-2.790756
C	-4.332275	1.668137	-4.140808
H	-7.748245	3.353882	-5.741440
H	-7.652039	1.585938	-5.823196
H	-7.464005	2.639969	-7.349411
H	-5.191483	1.843857	-6.586411
H	-5.381104	3.589203	-6.462814
H	-6.660095	4.130020	-3.905579
H	-6.056259	3.937561	-1.524139
H	-4.930176	2.731995	0.014252
H	-3.282425	0.781265	-2.465164
H	-3.829269	1.033829	-4.867920
C	1.849792	0.408569	-6.037613
C	0.476700	-0.231140	-5.740479
C	0.006271	0.072220	-4.348190
N	-0.555573	1.293213	-3.997162
C	-0.716827	1.347794	-2.658096
N	-0.298294	0.210373	-2.108124
C	0.154541	-0.589722	-3.152512
H	2.551773	0.101944	-5.246521
H	1.828186	1.529617	-6.028717
H	2.274445	0.009064	-6.975876
H	-0.266525	0.135132	-6.461670
H	0.523438	-1.319687	-5.861633
H	-0.869400	2.006866	-4.658295
H	-1.112686	2.204224	-2.128281
H	0.569809	-1.576248	-2.978165
C	5.530762	6.238129	1.678818
C	5.346817	6.314713	0.139709
C	4.199005	5.538239	-0.432739
C	2.833800	5.792435	-0.292938
N	2.101654	4.805176	-0.891281
C	2.966614	3.890671	-1.469254
C	2.699463	2.715134	-2.169388
C	3.792480	2.008469	-2.684616
C	5.112747	2.460861	-2.495361
C	5.373734	3.617767	-1.761490
C	4.294220	4.342484	-1.222885
H	5.600342	5.193573	2.010651
H	4.680222	6.720795	2.230148
H	6.504181	6.738251	1.902802
H	5.247391	7.371948	-0.146866
H	6.262604	5.954712	-0.352112
H	2.339233	6.620102	0.207504
H	1.089615	4.840988	-1.073288
H	1.680374	2.355591	-2.299835
H	3.618408	1.075333	-3.221207
H	5.946655	1.876434	-2.885056
H	6.401031	3.945068	-1.586166
C	-0.826630	8.098160	-1.317520
C	-2.023804	7.480240	-2.048355
C	-2.538498	6.175674	-1.428024
C	-1.482880	5.072144	-1.324890
O	-0.471664	5.030350	-2.062515
N	-1.746002	4.105988	-0.417480
H	-0.045975	7.326080	-1.248032
H	-1.085159	8.437469	-0.276688
H	-0.367355	8.902191	-1.946671
H	-2.859314	8.192245	-2.089554
H	-1.737411	7.245438	-3.079727
H	-2.974579	6.349884	-0.429398
H	-3.352219	5.766235	-2.051346
H	-1.093400	3.322693	-0.179718
H	-2.531723	4.231552	0.211609
C	5.046585	1.621262	1.200928
C	4.084442	0.553085	0.675552
C	2.621552	0.795868	0.999634
O	2.200363	1.784698	1.606750
O	1.833893	-0.169998	0.527206
O	-0.318298	1.849762	0.318924
Fe	0.000000	0.000000	0.000000
H	4.667007	2.620987	0.958298
H	6.039520	1.490265	0.718200
H	5.118332	1.520279	2.297623
H	4.118393	0.499374	-0.426300
H	4.341553	-0.461273	1.024948
H	0.458115	2.074203	0.902908
C	-1.619125	-3.123184	5.411758
C	-2.698761	-2.617661	4.422546
C	-2.259400	-1.683151	3.326721
N	-2.864685	-0.447464	3.124130
C	-2.299088	0.161346	2.052979
N	-1.353302	-0.619965	1.541672
C	-1.319519	-1.766266	2.320908
H	-2.099930	-3.855316	6.077850
H	-1.247116	-2.307129	6.065796
H	-0.774002	-3.669846	4.891647
H	-3.166992	-3.498566	3.947906
H	-3.512726	-2.138458	4.987793
H	-3.692017	-0.119293	3.614090
H	-2.545120	1.156403	1.704208
H	-0.619904	-2.566437	2.100739

Table S9. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Fe^{2+}(Mn)SOD^{HOH} (starting coordinates based on PDB file 1MMM).[3]

Atom	x	y	z
C	-2.802643	-0.520050	-5.585861
C	-1.267900	-0.579208	-5.568542
C	-0.615800	-0.261765	-4.267990
N	0.763458	-0.256424	-4.181335
C	1.131424	-0.141144	-2.881485
N	0.044662	-0.059998	-2.119232
C	-1.047318	-0.126602	-2.971634
H	-3.210144	-0.992462	-4.681717
H	-3.149536	-1.130615	-6.446503
H	-3.179153	0.519348	-5.629913
H	-0.950531	-1.615204	-5.770737
H	-0.843613	0.041519	-6.373900
H	1.386292	-0.374756	-4.992966
H	2.155472	-0.115936	-2.531693
H	-2.062805	-0.061874	-2.605347
C	-8.648575	4.728027	1.491806
C	-7.120453	4.899124	1.561737
C	-6.375778	3.612732	1.849472
C	-6.728821	2.794220	2.934433
C	-6.094269	1.572479	3.157959
C	-5.095306	1.136475	2.283264
O	-4.475861	-0.101273	2.428406
C	-4.701935	1.944260	1.217331
C	-5.333405	3.174698	1.023300
H	-9.019638	4.339905	2.452637
H	-8.940643	3.976883	0.718658
H	-9.139633	5.725143	1.342300
H	-6.736908	5.332642	0.626190
H	-6.898132	5.626587	2.354919
H	-7.528809	3.095840	3.613739
H	-6.390610	0.946350	4.006058
H	-4.922546	-0.554900	3.189606
H	-3.922333	1.603867	0.537415
H	-5.016632	3.794571	0.186462
C	0.214890	6.208450	-1.023209
C	-1.005127	5.382889	-1.485245
C	-1.104660	4.052704	-0.796570
N	-1.632568	3.893234	0.478104
C	-1.466766	2.612122	0.877869
N	-0.860229	1.913635	-0.080002
C	-0.632904	2.804535	-1.126328
H	1.117798	5.592896	-1.157974
H	0.187073	6.492844	0.061646
H	0.359604	7.084763	-1.684555
H	-1.928421	5.950943	-1.309052
H	-0.951630	5.201157	-2.565979
H	-2.144363	4.611465	0.996628
H	-1.788162	2.237228	1.841049
H	-0.136749	2.493408	-2.038986
C	5.663849	1.622314	6.333344
C	5.042160	3.013000	6.046616
C	3.807175	3.029053	5.188278
C	2.531616	2.611649	5.508820
N	1.694885	2.725098	4.411362
C	2.410324	3.260086	3.362442
C	2.016098	3.572769	2.055145
C	2.962448	4.158142	1.215866
C	4.277344	4.422700	1.663132
C	4.673264	4.083374	2.953537
C	3.742432	3.482620	3.822861
H	5.825104	1.070511	5.397293
H	4.998138	1.000153	6.987137
H	6.663940	1.799393	6.806015
H	4.831528	3.510422	7.004425
H	5.791534	3.644745	5.545776
H	2.149277	2.219162	6.448380
H	0.675522	2.669632	4.454010
H	1.003387	3.370987	1.704926
H	2.685364	4.398331	0.188614
H	5.003189	4.863159	0.978134
H	5.699585	4.262543	3.284286
C	-1.235825	3.257950	7.801407
C	-2.585709	3.467636	7.107239
C	-2.922700	2.400146	6.059433
C	-1.885529	2.300858	4.943100
O	-1.134918	3.239304	4.621460
N	-1.874344	1.119736	4.258881
H	-0.460205	3.181732	7.024750
H	-1.211609	2.317108	8.418700
H	-0.955032	4.175003	8.374741
H	-3.398483	3.494766	7.845184
H	-2.580902	4.430695	6.583954
H	-3.053482	1.406982	6.522964
H	-3.883408	2.640137	5.572388
H	-1.098953	0.895111	3.619553
H	-2.354431	0.320618	4.662140
C	5.158737	0.729980	1.741043
C	4.110062	0.728073	0.625320
C	2.767136	0.154770	0.999069
O	2.459213	-0.095184	2.193649
O	1.933838	0.000000	-0.000015
Fe	0.000000	0.000000	0.000000
H	4.724762	1.121200	2.668411
H	5.992400	1.391296	1.433441
H	5.503052	-0.306290	1.906800
H	3.868042	1.765152	0.326263
H	4.454895	0.227249	-0.294266
C	-0.140717	-6.197083	-1.331818
C	-1.454147	-5.443512	-1.012146
C	-1.354630	-4.063202	-0.416794
N	-2.133087	-3.679367	0.667465
C	-1.914215	-2.365219	0.935043
N	-1.018723	-1.871811	0.082870
C	-0.668091	-2.917068	-0.759567
H	-0.419891	-7.139221	-1.827011
H	0.397049	-6.490402	-0.407333
H	0.523544	-5.630966	-2.056625
H	-2.039658	-5.361267	-1.945633
H	-2.071487	-6.065445	-0.345078
H	-2.880920	-4.241180	1.067932
H	-2.426422	-1.814880	1.715897
H	0.040085	-2.753265	-1.564865
O	-0.036453	0.000015	2.232483
H	-0.236938	-0.912613	2.525986
H	1.049454	-0.024292	2.296829

Table S10. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Fe^{2+}(Mn)SOD^{OH-} (starting coordinates based on PDB file 1MMM).[3]

Atom	x	y	z
C	-2.728378	-5.722290	1.029709
C	-1.190094	-5.691742	1.067581
C	-0.563339	-4.401642	0.656433
N	0.817917	-4.285873	0.658585
C	1.151443	-2.986832	0.432846
N	0.054000	-2.264023	0.270172
C	-1.016449	-3.129913	0.401291
H	-3.130188	-4.778397	1.422760
H	-3.080963	-6.520950	1.716949
H	-3.114487	-5.868088	-0.000137
H	-0.856506	-5.838348	2.107834
H	-0.775238	-6.529251	0.482605
H	1.450729	-5.071213	0.866608
H	2.159805	-2.592163	0.390182
H	-2.037506	-2.783966	0.304230
C	-8.613953	0.641754	-4.880142
C	-7.075745	0.693817	-5.005219
C	-6.358261	1.170166	-3.754883
C	-6.761551	2.336731	-3.086655
C	-6.129990	2.757004	-1.916702
C	-5.090027	2.001968	-1.365173
O	-4.529373	2.318481	-0.140930
C	-4.637939	0.862137	-2.033737
C	-5.264984	0.471924	-3.220459
H	-8.985687	1.622070	-4.548431
H	-8.933700	-0.090042	-4.099930
H	-9.095383	0.426712	-5.879654
H	-6.678619	-0.289276	-5.296982
H	-6.831009	1.378357	-5.832077
H	-7.592361	2.936400	-3.469971
H	-6.453522	3.678116	-1.413742
H	-5.103149	3.013123	0.277435
H	-3.815200	0.281174	-1.615936
H	-4.887680	-0.414139	-3.731384
C	0.348526	-1.837402	-6.153793
C	-0.858719	-2.260086	-5.289261
C	-1.000061	-1.476242	-4.016174
N	-1.512695	-0.187195	-3.990280
C	-1.396698	0.311569	-2.733505
N	-0.855179	-0.593811	-1.928055
C	-0.603638	-1.709946	-2.718246
H	1.259491	-1.918488	-5.542694
H	0.300598	-0.772644	-6.502441
H	0.485992	-2.549133	-6.993500
H	-1.777573	-2.146866	-5.877823
H	-0.780991	-3.322311	-5.030350
H	-1.948883	0.288788	-4.780197
H	-1.672836	1.319702	-2.454224
H	-0.139236	-2.601685	-2.310150
C	5.553421	5.982071	-2.022812
C	4.943924	5.513687	-3.367172
C	3.734268	4.623200	-3.287003
C	2.446335	4.949371	-2.907593
N	1.642410	3.827698	-2.908371
C	2.386108	2.750671	-3.333588
C	2.023529	1.410202	-3.518555
C	2.988388	0.542465	-4.022202
C	4.295166	0.990341	-4.322632
C	4.662888	2.312927	-4.098709
C	3.708221	3.218323	-3.596436
H	5.722504	5.123825	-1.357941
H	4.868454	6.694626	-1.496689
H	6.549271	6.443924	-2.246628
H	4.711594	6.401978	-3.975739
H	5.710907	4.961304	-3.931686
H	2.039185	5.914505	-2.616409
H	0.619186	3.849777	-2.847153
H	1.030975	1.053635	-3.249359
H	2.743851	-0.514038	-4.142044
H	5.040543	0.278778	-4.683151
H	5.686325	2.645477	-4.295120
C	-1.323822	7.224747	-3.750412
C	-2.660568	6.487839	-3.896042
C	-2.980713	5.519882	-2.751678
C	-1.947403	4.395996	-2.564041
O	-1.145538	4.074982	-3.470856
N	-2.008789	3.747513	-1.385162
H	-0.545532	6.463028	-3.598038
H	-1.308762	7.929672	-2.868454
H	-1.044540	7.713882	-4.717651
H	-3.491638	7.202164	-3.983475
H	-2.639252	5.885437	-4.810867
H	-3.102539	6.056335	-1.795853
H	-3.946152	5.023788	-2.950607
H	-1.304672	3.015717	-1.032303
H	-2.642822	4.111313	-0.679062
C	5.142853	1.513504	-0.637878
C	4.144806	0.362091	-0.473572
C	2.786194	0.729752	0.117371
O	2.505478	1.880707	0.489532
O	1.961960	-0.297546	0.154755
O	-0.436615	1.882614	-0.321121
Fe	0.000000	0.000000	0.000000
H	4.657959	2.367447	-1.125671
H	5.976303	1.162445	-1.286423
H	5.512512	1.827286	0.353027
H	3.908722	-0.079971	-1.455902
H	4.556503	-0.466080	0.129013
H	0.430344	2.273117	-0.059448
C	-0.271973	-0.981705	6.390488
C	-1.570847	-0.747910	5.573273
C	-1.423050	-0.288177	4.147842
N	-1.934830	0.923325	3.700439
C	-1.658188	1.056473	2.372070
N	-0.994064	-0.003571	1.933319
C	-0.845779	-0.845108	3.024551
H	-0.567245	-1.375351	7.376038
H	0.262222	-0.030304	6.589996
H	0.411972	-1.752151	5.912308
H	-2.142807	-1.692429	5.576736
H	-2.208405	-0.031006	6.114883
H	-2.530700	1.554688	4.229645
H	-1.876648	1.935928	1.776993
H	-0.320496	-1.790634	2.928406

Table S11. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Q69E $Fe^{3+}SOD^{HOH}$ with Glu69 deprotonated (starting coordinates based on PDB file 1ISA).[1]

Atom	x	y	z
C	-2.424316	-0.567902	-5.722229
C	-0.888245	-0.613129	-5.716217
C	-0.291260	-0.335602	-4.374069
N	1.073593	-0.418533	-4.136230
C	1.308884	-0.228745	-2.815643
N	0.160812	-0.044586	-2.175339
C	-0.835342	-0.093094	-3.133270
H	-2.778763	-1.050079	-4.803787
H	-2.865463	-1.157135	-6.560837
H	-2.792358	0.472046	-5.679123
H	-0.539322	-1.624710	-5.971954
H	-0.477859	0.060898	-6.479034
H	1.829010	-0.638900	-4.802078
H	2.291382	-0.221878	-2.361588
H	-1.867035	0.089432	-2.868378
C	-8.737228	4.752335	1.976685
C	-7.231323	4.789810	2.308975
C	-6.577942	3.425278	2.280365
C	-7.069412	2.333862	3.014084
C	-6.512787	1.062012	2.864655
C	-5.452300	0.874100	1.974442
O	-4.908249	-0.403778	1.769150
C	-4.948288	1.942764	1.238464
C	-5.511139	3.207489	1.402908
H	-9.311325	4.398514	2.846481
H	-8.925644	4.032852	1.152267
H	-9.105362	5.768570	1.745132
H	-6.699509	5.405685	1.571609
H	-7.081512	5.275711	3.283768
H	-7.910706	2.472763	3.697632
H	-6.892853	0.216187	3.439285
H	-4.312500	-0.576889	2.548843
H	-4.118347	1.774078	0.553238
H	-5.119873	4.065384	0.850586
C	-2.396194	5.283493	4.285034
C	-3.372787	4.090988	4.248993
C	-2.985657	2.879303	5.126358
C	-1.745422	2.095200	4.654709
O	-0.710159	2.157974	5.370865
O	-1.856628	1.376694	3.581039
H	-1.362717	4.892548	4.316833
H	-2.462433	5.958267	5.179276
H	-2.494598	5.885788	3.336121
H	-4.386032	4.409500	4.533432
H	-3.476929	3.715652	3.218231
H	-2.798660	3.188873	6.162735
H	-3.831284	2.174393	5.122360
C	0.775330	5.978745	-0.898529
C	-0.583282	5.376465	-1.315247
C	-0.867126	4.016342	-0.766205
N	-1.499466	3.823685	0.448883
C	-1.505463	2.517334	0.768250
N	-0.946594	1.821777	-0.225677
C	-0.548600	2.750336	-1.187500
H	1.558151	5.218979	-1.038956
H	0.848755	6.330688	0.166794
H	0.995438	6.783646	-1.619019
H	-1.392731	6.054321	-1.018021
H	-0.618958	5.295273	-2.409225
H	-1.746735	4.588943	1.080124
H	-1.881012	2.130493	1.718460
H	-0.034729	2.454041	-2.093842
C	6.181458	1.145523	5.929077
C	5.570800	2.558304	5.725891
C	4.166504	2.608688	5.216705
C	2.995056	2.354630	5.956772
N	1.901428	2.471954	5.168365
C	2.309372	2.819489	3.887726
C	1.542664	3.061630	2.756348
C	2.224396	3.469131	1.600693
C	3.619263	3.629761	1.593445
C	4.385834	3.355576	2.727737
C	3.726913	2.933929	3.894653
H	6.251434	0.601898	4.980057
H	5.580170	0.531876	6.641678
H	7.206100	1.288528	6.351746
H	5.584442	3.085968	6.687561
H	6.215027	3.134979	5.046921
H	2.914536	2.120392	7.015091
H	0.890350	2.277435	5.388092
H	0.459320	2.953857	2.774719
H	1.663498	3.678772	0.689835
H	4.108017	3.979645	0.686432
H	5.471771	3.466721	2.705338
C	5.330872	0.255951	1.433975
C	4.178360	0.423325	0.443115
C	2.823792	-0.054276	0.947800
O	2.596130	-0.434647	2.099335
O	1.888885	0.000000	0.000046
Fe	0.000000	0.000000	0.000000
H	5.034439	0.645813	2.415756
H	6.238861	0.805496	1.089417
H	5.559067	-0.821045	1.535828
H	4.020355	1.484680	0.191040
H	4.376007	-0.078354	-0.518082
C	-0.165894	-6.030975	-1.529053
C	-1.533554	-5.361954	-1.212357
C	-1.452957	-3.993347	-0.589539
N	-1.959030	-3.668213	0.666519
C	-1.660538	-2.379135	0.949753
N	-0.987854	-1.837708	-0.061417
C	-0.861633	-2.826828	-1.023071
H	-0.367966	-6.958740	-2.085739
H	0.352798	-6.338486	-0.592087
H	0.459915	-5.372147	-2.210403
H	-2.101624	-5.282242	-2.150818
H	-2.125092	-6.022217	-0.560425
H	-2.587891	-4.210388	1.262375
H	-1.890000	-1.888382	1.884766
H	-0.326080	-2.627930	-1.944824
O	-0.200241	-0.000015	2.125000
H	0.746582	-0.138947	2.409393
H	-0.698975	0.604309	2.808151

Table S12. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Q69E $Fe^{3+}SOD^{OH-}$ with Glu69 protonated (starting coordinates based on PDB file 1ISA).[1]

Atom	x	y	z
C	-1.949646	-0.490829	-5.885468
C	-0.416580	-0.387100	-5.850784
C	0.102432	-0.131027	-4.476440
N	1.450348	-0.181870	-4.148651
C	1.581207	-0.038467	-2.804581
N	0.388062	0.092072	-2.241500
C	-0.533279	0.053818	-3.270630
H	-2.289215	-1.019302	-4.985382
H	-2.290146	-1.102539	-6.742218
H	-2.422500	0.516449	-5.871521
H	0.035721	-1.340561	-6.166489
H	-0.065918	0.370865	-6.563950
H	2.251587	-0.374969	-4.765823
H	2.526810	-0.031326	-2.279282
H	-1.589035	0.184875	-3.077500
C	-8.830963	4.462982	0.900223
C	-7.334671	4.508438	1.256195
C	-6.704010	3.142136	1.433472
C	-7.265350	2.162613	2.268478
C	-6.675995	0.905594	2.409637
C	-5.514343	0.597794	1.693161
O	-4.932587	-0.665222	1.736755
C	-4.942291	1.550278	0.852661
C	-5.529114	2.811478	0.748077
H	-9.408676	4.052567	1.742294
H	-9.031097	3.786118	0.032181
H	-9.232452	5.483688	0.751282
H	-6.771194	5.046707	0.478700
H	-7.205811	5.090607	2.184479
H	-8.188751	2.364517	2.811752
H	-7.124832	0.158173	3.068207
H	-5.012207	-0.986877	2.677139
H	-4.023788	1.312073	0.318649
H	-5.041245	3.579147	0.146378
C	-3.324203	5.113922	4.186096
C	-4.252914	3.890060	4.113251
C	-3.841370	2.698914	5.019821
C	-2.566025	2.004471	4.584030
O	-1.471283	2.196442	5.101730
O	-2.738937	1.128098	3.559280
H	-2.278091	4.759674	4.234421
H	-3.432938	5.765686	5.091003
H	-3.411453	5.704285	3.233566
H	-5.289948	4.161652	4.359406
H	-4.308990	3.504242	3.083435
H	-3.670761	3.024826	6.051788
H	-4.654709	1.958405	5.010040
H	-1.855804	0.749405	3.267471
C	0.501129	6.140198	-0.739273
C	-0.757706	5.470856	-1.332016
C	-0.966049	4.065323	-0.873184
N	-1.662552	3.782181	0.285858
C	-1.579941	2.470322	0.562454
N	-0.888992	1.856842	-0.395721
C	-0.501053	2.843307	-1.297775
H	1.347366	5.448303	-0.860764
H	0.459793	6.407806	0.355362
H	0.734604	7.011963	-1.369278
H	-1.653290	6.055862	-1.084564
H	-0.680176	5.453003	-2.426834
H	-2.079025	4.489746	0.894089
H	-2.007217	2.004517	1.438889
H	0.103638	2.617584	-2.167587
C	5.527359	1.171036	6.437225
C	4.901108	2.572617	6.222580
C	3.526550	2.589508	5.630646
C	2.326600	2.302185	6.282532
N	1.286255	2.368668	5.399292
C	1.769852	2.716949	4.149551
C	1.093948	2.943024	2.953445
C	1.850052	3.379578	1.861053
C	3.238297	3.583115	1.967575
C	3.914581	3.328064	3.159424
C	3.178329	2.882523	4.272186
H	5.711945	0.665695	5.480835
H	4.851471	0.516678	7.041946
H	6.503265	1.326996	6.961884
H	4.855469	3.086472	7.189758
H	5.568176	3.173630	5.587402
H	2.148193	2.068192	7.328949
H	0.299500	2.190628	5.596146
H	0.017288	2.803070	2.879288
H	1.355972	3.584808	0.910248
H	3.790070	3.955551	1.104538
H	4.994858	3.478302	3.227142
C	5.194473	0.455400	1.695328
C	4.145111	0.569733	0.588058
C	2.796326	-0.011826	0.996567
O	2.561142	-0.445175	2.120407
O	1.906067	0.000000	0.000015
Fe	0.000000	0.000000	0.000000
O	-0.614563	0.000015	1.827713
H	4.765366	0.815384	2.637878
H	6.107956	1.048279	1.468460
H	5.462631	-0.608337	1.825272
H	3.946930	1.620956	0.325012
H	4.461533	0.085175	-0.350845
H	0.211472	-0.178711	2.335449
C	0.099838	-5.872726	-2.103912
C	-1.308243	-5.254349	-1.901428
C	-1.326630	-3.942841	-1.165771
N	-1.962662	-3.742477	0.054794
C	-1.739548	-2.469818	0.471573
N	-1.002900	-1.827423	-0.431046
C	-0.747223	-2.727783	-1.450882
H	-0.014832	-6.779373	-2.718323
H	0.533936	-6.203506	-1.130478
H	0.766037	-5.171814	-2.697968
H	-1.758682	-5.104248	-2.893997
H	-1.957108	-5.975281	-1.381531
H	-2.483734	-4.435120	0.583557
H	-2.073059	-2.046143	1.411789
H	-0.147476	-2.439300	-2.307220

Table S13. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Q69E $Fe^{3+}SOD^{OH-}$ with Glu69 deprotonated (starting coordinates based on PDB file 1ISA).[1]

Atom	x	y	z
C	-1.820251	-1.022995	-5.998291
C	-0.297684	-1.049911	-5.800461
C	0.152603	-0.626511	-4.443512
N	1.485413	-0.704636	-4.059891
C	1.583191	-0.363907	-2.748276
N	0.385681	-0.083710	-2.259796
C	-0.506836	-0.229691	-3.304672
H	-2.301636	-1.444702	-5.106293
H	-2.131363	-1.673019	-6.848831
H	-2.188736	0.016403	-6.118332
H	0.074829	-2.078766	-5.919098
H	0.189758	-0.441284	-6.572250
H	2.290344	-1.022675	-4.617508
H	2.506332	-0.330139	-2.183456
H	-1.558075	-0.015488	-3.170746
C	-8.826706	4.695465	-0.014526
C	-7.354462	4.768967	0.408096
C	-6.766037	3.492279	0.968246
C	-7.356354	2.830582	2.060913
C	-6.687988	1.822647	2.751465
C	-5.380127	1.448090	2.371933
O	-4.632935	0.654602	3.162308
C	-4.860489	1.986160	1.176529
C	-5.534119	3.007950	0.512238
H	-9.438858	4.397659	0.851791
H	-9.005234	3.933746	-0.813339
H	-9.191208	5.703186	-0.304092
H	-6.721786	5.113922	-0.423935
H	-7.266083	5.535278	1.196869
H	-8.324631	3.178619	2.440536
H	-7.115173	1.404388	3.666718
H	-3.877914	1.657562	0.839325
H	-5.043045	3.512833	-0.322021
H	-3.685791	1.191437	3.335022
C	-3.138794	5.906967	3.398056
C	-4.107544	4.713058	3.424805
C	-3.831680	3.678894	4.543304
C	-2.510071	2.943222	4.308395
O	-1.464584	3.452072	4.795837
O	-2.512207	1.874680	3.578522
H	-2.118317	5.530289	3.590103
H	-3.307129	6.662827	4.203812
H	-3.145721	6.372559	2.376724
H	-5.154694	5.049515	3.488510
H	-4.055283	4.165619	2.469772
H	-3.757019	4.166580	5.521240
H	-4.654739	2.950790	4.566986
C	0.572922	6.007065	-1.380981
C	-0.736176	5.331085	-1.840637
C	-0.976669	3.999863	-1.196030
N	-1.543991	3.858917	0.060959
C	-1.463623	2.571915	0.455338
N	-0.906265	1.844803	-0.513916
C	-0.597229	2.726349	-1.543396
H	1.372940	5.251434	-1.376877
H	0.540955	6.438431	-0.345474
H	0.878693	6.753891	-2.132294
H	-1.592651	5.991302	-1.647751
H	-0.700150	5.161118	-2.924500
H	-1.863800	4.642319	0.635208
H	-1.773300	2.199341	1.431381
H	-0.082520	2.402695	-2.440231
C	5.399826	1.655640	6.204208
C	4.772522	3.046097	5.923584
C	3.413361	3.061722	5.298264
C	2.181381	2.913132	5.933136
N	1.164719	2.963135	5.019974
C	1.706741	3.180481	3.772110
C	1.064697	3.341888	2.547073
C	1.864029	3.619110	1.437378
C	3.263504	3.732056	1.557175
C	3.904114	3.544922	2.779465
C	3.121094	3.258300	3.911362
H	5.546295	1.082520	5.280853
H	4.729950	1.081818	6.877930
H	6.382400	1.828644	6.722931
H	4.707184	3.588745	6.873611
H	5.457794	3.628723	5.287491
H	1.973236	2.801178	6.994736
H	0.132187	2.970490	5.165527
H	-0.017746	3.263245	2.488998
H	1.407486	3.755905	0.456300
H	3.855972	3.961975	0.673553
H	4.992920	3.615448	2.852219
C	5.224884	0.433670	1.659195
C	4.163513	0.497025	0.561676
C	2.797211	-0.037109	0.999832
O	2.557907	-0.458115	2.124863
O	1.910461	0.000000	0.000000
Fe	0.000000	0.000000	0.000000
O	-0.829422	0.000000	1.665436
H	4.832230	0.907745	2.568069
H	6.159866	0.964645	1.361420
H	5.447403	-0.624039	1.891739
H	3.988327	1.534531	0.236679
H	4.470108	-0.053497	-0.344131
H	-0.212585	0.062286	2.425461
C	0.128052	-6.165558	-1.403931
C	-1.273926	-5.496552	-1.405502
C	-1.315353	-4.094925	-0.861832
N	-1.995956	-3.737259	0.297195
C	-1.772018	-2.424988	0.558655
N	-0.974548	-1.910095	-0.370392
C	-0.694138	-2.931046	-1.259674
H	0.027039	-7.153152	-1.881638
H	0.478973	-6.360916	-0.365204
H	0.852676	-5.555359	-2.032425
H	-1.639496	-5.485443	-2.443893
H	-1.981766	-6.124008	-0.842500
H	-2.681290	-4.299454	0.812668
H	-2.139557	-1.882339	1.422485
H	-0.041382	-2.761566	-2.110718

Table S14. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Q69E $Fe^{2+}SOD^{HOH}$ with Glu69 and Tyr34 protonated (starting coordinates based on PDB file 2BKB) [4]

Atom	x	y	z
C	-2.660172	-1.389313	-5.318466
C	-1.130600	-1.385284	-5.404633
C	-0.458054	-0.942627	-4.140182
N	0.897797	-1.077087	-3.931610
C	1.203125	-0.624313	-2.727600
N	0.094635	-0.198669	-2.148727
C	-0.959579	-0.386398	-3.011261
H	-2.932358	-1.718307	-4.315445
H	-3.076355	-2.078766	-6.053009
H	-3.047806	-0.375961	-5.422974
H	-0.775970	-2.392044	-5.625595
H	-0.812561	-0.706741	-6.196136
H	1.564102	-1.459610	-4.587112
H	2.236313	-0.650574	-2.381271
H	-1.966644	-0.094955	-2.712692
C	-8.612579	4.532684	1.332397
C	-7.090012	4.697861	1.401703
C	-6.344879	3.507172	1.973618
C	-6.658813	3.003891	3.240875
C	-5.924057	1.964050	3.806244
C	-4.865860	1.413635	3.103745
O	-4.116898	0.407349	3.674377
C	-4.538284	1.885864	1.840164
C	-5.280151	2.930344	1.280167
H	-8.953491	4.115341	2.279800
H	-8.899765	3.868042	0.517654
H	-9.079849	5.505295	1.178284
H	-6.695800	4.861649	0.398773
H	-6.845047	5.552780	2.031967
H	-7.491150	3.425903	3.804108
H	-6.183731	1.588577	4.796066
H	-3.740250	-0.141205	2.953796
H	-3.707336	1.442749	1.291214
H	-5.029938	3.305588	0.287811
C	-2.660980	5.813156	3.835297
C	-3.528519	4.560547	3.961807
C	-2.967010	3.523026	4.931900
C	-1.700043	2.856018	4.409622
O	-0.614212	3.425110	4.414398
O	-1.758362	1.587357	3.934967
H	-1.621262	5.486343	3.853729
H	-2.842773	6.495239	4.665878
H	-2.815521	6.287537	2.866135
H	-4.519196	4.838928	4.321213
H	-3.617783	4.079865	2.987671
H	-2.724762	4.004410	5.879349
H	-3.709686	2.743225	5.100632
H	-2.668793	1.196365	4.030487
C	0.393326	5.994888	-1.380203
C	-0.915405	5.252335	-1.670914
C	-1.029297	3.954773	-0.935455
N	-1.398376	3.881912	0.391998
C	-1.309097	2.629974	0.804413
N	-0.900711	1.886780	-0.209366
C	-0.722183	2.689636	-1.309875
H	1.191116	5.255081	-1.446136
H	0.383621	6.431503	-0.381470
H	0.603973	6.721146	-2.165176
H	-1.760162	5.874527	-1.375183
H	-0.981018	5.034302	-2.736923
H	-1.692719	4.656357	0.969650
H	-1.558350	2.376434	1.834702
H	-0.389633	2.255707	-2.252823
C	6.515976	1.546814	5.515579
C	5.851929	2.908279	5.294540
C	4.441849	2.851730	4.806717
C	3.324936	2.540909	5.531403
N	2.214752	2.547836	4.715851
C	2.605103	2.870193	3.442932
C	1.849548	3.003143	2.271393
C	2.518845	3.342224	1.121521
C	3.913193	3.549820	1.114197
C	4.661423	3.416885	2.274933
C	4.003372	3.071411	3.466064
H	6.584213	1.005600	4.571960
H	5.931168	0.964462	6.227539
H	7.515411	1.729980	5.910187
H	5.834839	3.461411	6.233536
H	6.416214	3.471970	4.551620
H	3.407715	2.333481	6.598236
H	1.251404	2.501343	5.025955
H	0.772247	2.838745	2.296036
H	1.971466	3.456726	0.185883
H	4.419205	3.819138	0.187042
H	5.738907	3.580017	2.250519
C	5.482681	0.204620	1.039139
C	4.290268	0.329285	0.081604
C	2.983185	-0.208771	0.660568
O	1.938538	0.000000	-0.000107
O	2.984375	-0.826996	1.752197
Fe	0.000000	0.000000	0.000000
H	5.261093	0.698547	1.985153
H	6.349121	0.676941	0.576309
H	5.731552	-0.844711	1.197327
H	4.129440	1.378952	-0.164474
H	4.496429	-0.229858	-0.831024
C	-0.340302	-6.247131	-1.029510
C	-1.642380	-5.440277	-0.825714
C	-1.440033	-4.050705	-0.301178
N	-1.976563	-3.626633	0.895309
C	-1.675812	-2.354600	1.086502
N	-0.961166	-1.937439	0.057159
C	-0.798019	-2.978729	-0.824997
H	-0.623611	-7.196900	-1.483063
H	0.167526	-6.433060	-0.083084
H	0.300186	-5.738510	-1.750061
H	-2.164398	-5.345230	-1.777924
H	-2.282669	-5.957260	-0.110962
H	-2.517410	-4.189590	1.536026
H	-2.018677	-1.842682	1.985672
H	-0.230637	-2.830841	-1.743790
O	0.280319	0.000000	2.134430
H	0.522568	0.886078	2.476669
H	1.188812	-0.461304	2.142197

Table S15. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Q69E $Fe^{2+}SOD^{HOH}$ with Glu69 protonated and Tyr34 deprotonated (starting coordinates based on PDB file 2BKB).[4]

Atom	x	y	z
C	-2.337219	-5.639847	-0.150436
C	-0.829880	-5.616013	-0.423019
C	-0.253784	-4.234131	-0.497421
N	1.103241	-3.993011	-0.512314
C	1.316315	-2.689117	-0.559738
N	0.146393	-2.075851	-0.578644
C	-0.852707	-3.019730	-0.540543
H	-2.558533	-4.830231	0.545197
H	-2.623566	-6.591919	0.296402
H	-2.890457	-5.418030	-1.062973
H	-0.307343	-6.142960	0.375381
H	-0.624588	-6.104965	-1.375381
H	1.830811	-4.693146	-0.490800
H	2.335754	-2.303665	-0.576355
H	-1.897308	-2.708252	-0.548782
C	-9.269302	2.215469	-2.381256
C	-7.797577	2.439529	-2.747665
C	-6.866180	2.619476	-1.564392
C	-7.101471	3.614502	-0.609268
C	-6.205872	3.839066	0.433945
C	-5.063217	3.063965	0.533035
O	-4.159332	3.305939	1.544815
C	-4.809204	2.062729	-0.394241
C	-5.712692	1.844300	-1.438736
H	-9.542862	2.938141	-1.612610
H	-9.431946	1.205353	-2.005447
H	-9.893585	2.371460	-3.261017
H	-7.427872	1.581802	-3.309631
H	-7.707153	3.338791	-3.356979
H	-7.998489	4.230438	-0.673462
H	-6.406921	4.621384	1.165894
H	-3.292587	3.540421	1.047119
H	-3.910141	1.452881	-0.305374
H	-5.520859	1.058945	-2.169968
C	-3.644638	5.400604	-3.623856
C	-4.287842	5.033066	-2.286453
C	-3.566986	5.626160	-1.077560
C	-2.200470	4.994308	-0.840576
O	-1.198700	5.470764	-1.425629
O	-2.140793	3.961700	-0.026917
H	-2.564743	5.376495	-3.477737
H	-3.947205	6.399918	-3.937119
H	-3.868759	4.643661	-4.375458
H	-5.314575	5.398178	-2.263977
H	-4.285248	3.949692	-2.167038
H	-3.418655	6.695100	-1.230804
H	-4.167892	5.468018	-0.181946
C	-0.618561	0.779327	-6.083435
C	-1.779434	0.164993	-5.293762
C	-1.677841	0.403748	-3.820511
N	-2.041153	1.598404	-3.233765
C	-1.744141	1.563660	-1.946869
N	-1.206300	0.387100	-1.676331
C	-1.156876	-0.358475	-2.829285
H	0.293915	0.518723	-5.547104
H	-0.711426	1.864014	-6.138123
H	-0.527267	0.305573	-7.060776
H	-2.720245	0.597626	-5.634109
H	-1.797363	-0.913254	-5.452805
H	-2.468018	2.384552	-3.702713
H	-1.956055	2.426193	-1.315125
H	-0.746857	-1.368195	-2.808136
C	6.108185	6.138535	-0.528885
C	5.224487	6.351334	-1.760635
C	3.848969	5.779587	-1.657745
C	2.794632	6.277466	-0.943924
N	1.706848	5.440338	-1.060669
C	2.048218	4.383408	-1.862442
C	1.291702	3.279526	-2.274948
C	1.904068	2.362411	-3.092911
C	3.242828	2.520538	-3.505173
C	3.992218	3.613800	-3.095383
C	3.391708	4.568115	-2.258759
H	6.275955	5.073761	-0.367523
H	5.624420	6.567719	0.348450
H	7.058334	6.638504	-0.717056
H	5.105194	7.419312	-1.942612
H	5.691513	5.885391	-2.628342
H	2.901810	7.212387	-0.393921
H	0.734161	5.644958	-0.817276
H	0.257813	3.173813	-1.946060
H	1.353653	1.487427	-3.438812
H	3.704117	1.777466	-4.155762
H	5.026505	3.719330	-3.422958
C	5.358475	1.413971	-0.684097
C	4.171005	0.478409	-0.946182
C	2.969147	0.749268	-0.043228
O	1.910233	0.130707	-0.302841
O	3.065491	1.561691	0.907913
Fe	0.000000	0.000000	0.000000
H	5.047668	2.454559	-0.776932
H	6.136276	1.199800	-1.417053
H	5.780716	1.220795	0.302155
H	3.836395	0.595230	-1.977005
H	4.477371	-0.554169	-0.779007
C	0.735413	-3.121002	5.469986
C	-0.686569	-2.742264	4.998444
C	-0.728058	-1.762482	3.864761
N	-1.339645	-0.532211	3.972794
C	-1.261124	0.101593	2.816422
N	-0.618454	-0.672760	1.961044
C	-0.272797	-1.844208	2.591278
H	0.621719	-3.889542	6.234467
H	1.258896	-2.262924	5.891830
H	1.286667	-3.579605	4.649094
H	-1.208496	-3.637772	4.660843
H	-1.236145	-2.291900	5.825012
H	-1.782730	-0.160248	4.800644
H	-1.694122	1.096191	2.709610
H	0.269485	-2.616852	2.046234
O	-0.328354	2.106781	0.766571
H	-0.833710	2.908463	0.411179
H	0.590576	2.404922	0.950089

Table S16. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Q69E $Fe^{2+}SOD^{HOH}$ with Glu69 deprotonated and Tyr34 protonated (starting coordinates based on PDB file 2BKB).[4]

Atom	x	y	z
C	-1.878479	-5.800125	0.349731
C	-0.423431	-5.675827	-0.113297
C	0.026428	-4.259430	-0.309692
N	1.347397	-3.918228	-0.505859
C	1.447784	-2.605484	-0.626526
N	0.239258	-2.083221	-0.518173
C	-0.668564	-3.096588	-0.319473
H	-2.075882	-4.978607	1.038498
H	-2.029938	-6.749710	0.863068
H	-2.556732	-5.662155	-0.492294
H	0.234680	-6.125290	0.630386
H	-0.299530	-6.190781	-1.065964
H	2.125732	-4.560165	-0.552170
H	2.423080	-2.145889	-0.786514
H	-1.727631	-2.864975	-0.205719
C	-9.640594	1.403763	-1.259109
C	-8.248474	1.720688	-1.817703
C	-7.194824	2.023560	-0.769852
C	-7.388596	3.040573	0.171371
C	-6.391296	3.378830	1.083374
C	-5.186829	2.696915	1.063721
O	-4.186600	3.051743	1.942917
C	-4.970505	1.676392	0.147964
C	-5.976288	1.343521	-0.764496
H	-9.873627	2.138153	-0.488205
H	-9.673935	0.402496	-0.829880
H	-10.379791	1.472427	-2.057266
H	-7.883911	0.868423	-2.391190
H	-8.306763	2.595505	-2.465286
H	-8.333100	3.584015	0.200012
H	-6.561905	4.176315	1.806610
H	-3.415329	3.319504	1.322815
H	-4.021454	1.140350	0.143311
H	-5.814484	0.542358	-1.485687
C	-4.487091	4.941803	-3.320709
C	-4.927734	4.588303	-1.899994
C	-4.112198	5.288116	-0.814651
C	-2.680649	4.771927	-0.731171
O	-1.797882	5.313843	-1.441589
O	-2.432114	3.788300	0.106247
H	-3.398972	5.005356	-3.312485
H	-4.905273	5.900314	-3.628265
H	-4.741455	4.136749	-4.010100
H	-5.969681	4.876038	-1.759995
H	-4.823654	3.514664	-1.743300
H	-4.070160	6.357086	-1.023590
H	-4.582642	5.126251	0.155243
C	-1.429535	0.453262	-5.979065
C	-2.430374	-0.209839	-5.026566
C	-2.166107	0.102631	-3.587769
N	-2.548279	1.292175	-3.002472
C	-2.091965	1.338333	-1.763519
N	-1.432175	0.218933	-1.521835
C	-1.466705	-0.572479	-2.644333
H	-0.439575	0.286453	-5.554367
H	-1.614990	1.524307	-6.060150
H	-1.422653	-0.056305	-6.942581
H	-3.437759	0.135117	-5.259552
H	-2.381485	-1.292511	-5.143478
H	-3.091629	2.021957	-3.441086
H	-2.292145	2.210403	-1.141098
H	-0.977707	-1.546646	-2.639557
C	5.483856	6.548706	-1.521072
C	4.439896	6.638428	-2.637054
C	3.138016	5.970444	-2.339539
C	2.143997	6.419846	-1.515488
N	1.120712	5.499084	-1.462753
C	1.443466	4.435303	-2.263290
C	0.732422	3.260208	-2.536438
C	1.309952	2.355377	-3.392532
C	2.570190	2.594452	-3.977310
C	3.274689	3.758423	-3.705460
C	2.708191	4.702042	-2.833847
H	5.755112	5.507919	-1.344452
H	5.079956	6.979889	-0.605072
H	6.360168	7.109406	-1.846451
H	4.213700	7.685104	-2.840347
H	4.831329	6.169800	-3.539993
H	2.243408	7.384216	-1.017303
H	0.166077	5.639450	-1.118698
H	-0.240784	3.092407	-2.075073
H	0.792740	1.426743	-3.634018
H	3.005127	1.859207	-4.654358
H	4.248444	3.926117	-4.165665
C	5.101532	1.779083	-1.410858
C	3.969437	0.746185	-1.486084
C	2.871216	0.966995	-0.447632
O	1.841217	0.259628	-0.548111
O	3.019516	1.826782	0.453888
Fe	0.000000	0.000000	0.000000
H	4.699265	2.788162	-1.500427
H	5.796890	1.590698	-2.228760
H	5.657013	1.663147	-0.480194
H	3.501144	0.790604	-2.469376
H	4.375931	-0.251831	-1.322525
C	1.656555	-2.805008	5.439667
C	0.161255	-2.555862	5.139786
C	-0.098984	-1.634445	3.986389
N	-0.788986	-0.449860	4.127472
C	-0.905685	0.134781	2.948624
N	-0.314270	-0.627304	2.046585
C	0.199677	-1.739700	2.669052
H	1.700607	-3.544373	6.239319
H	2.157898	-1.891891	5.760513
H	2.136566	-3.257935	4.572144
H	-0.325134	-3.502350	4.903549
H	-0.315720	-2.110794	6.013016
H	-1.154266	-0.074890	4.991165
H	-1.426849	1.088257	2.862396
H	0.730225	-2.493469	2.087341
O	-0.407867	2.114059	0.707184
H	-1.033005	2.849700	0.397308
H	0.493134	2.502243	0.749649

Table S17. Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Q69E $Fe^{2+}SOD^{OH-}$ with Glu69 protonated and Tyr34 protonated (starting coordinates based on PDB file 2BKB).[4]

Atom	x	y	z
C	-2.659805	-1.187820	-5.367172
C	-1.130188	-1.180664	-5.453033
C	-0.457764	-0.785934	-4.172760
N	0.898087	-0.928177	-3.969330
C	1.203278	-0.521149	-2.749084
N	0.094757	-0.117554	-2.154602
C	-0.959351	-0.272583	-3.023727
H	-2.932068	-1.554474	-4.377380
H	-3.075912	-1.849228	-6.127228
H	-3.047394	-0.171280	-5.433472
H	-0.775543	-2.178391	-5.711746
H	-0.812103	-0.472717	-6.218475
H	1.564438	-1.285736	-4.638687
H	2.236481	-0.560364	-2.403946
H	-1.966446	0.007324	-2.714432
C	-8.612640	4.479385	1.501617
C	-7.090057	4.641754	1.577164
C	-6.345062	3.430359	2.103943
C	-6.659027	2.879700	3.351273
C	-5.924332	1.819275	3.877106
C	-4.866135	1.295715	3.154434
O	-4.117203	0.268616	3.686844
C	-4.538391	1.815247	1.909561
C	-5.280258	2.880081	1.389328
H	-8.953659	4.026627	2.432617
H	-8.899796	3.845932	0.662369
H	-9.079910	5.457123	1.384186
H	-6.695816	4.843292	0.581223
H	-6.845184	5.472351	2.239273
H	-7.491394	3.280243	3.929977
H	-6.184082	1.406784	4.852066
H	-3.173203	0.666870	3.729980
H	-3.707458	1.393112	1.344406
H	-5.029953	3.292465	0.411835
C	-2.661240	5.664505	4.051422
C	-3.528732	4.408020	4.130585
C	-2.967316	3.334702	5.060959
C	-1.700363	2.687866	4.514038
O	-0.587814	3.200928	4.782455
O	-1.835236	1.599380	3.785614
H	-1.621521	5.337234	4.057632
H	-2.843079	6.314850	4.907089
H	-2.815689	6.175034	3.100922
H	-4.519485	4.672700	4.500153
H	-3.617950	3.964447	3.139069
H	-2.725220	3.780029	6.025879
H	-3.710114	2.549103	5.200058
C	0.393463	6.042648	-1.153198
C	-0.915237	5.311569	-1.471848
C	-1.029175	3.987152	-0.785797
N	-1.398392	3.864410	0.537933
C	-1.309082	2.597778	0.902802
N	-0.900696	1.893311	-0.138168
C	-0.722107	2.737091	-1.207611
H	1.191315	5.305847	-1.246964
H	0.383667	6.441330	-0.138748
H	0.604218	6.797958	-1.910233
H	-1.759995	5.922195	-1.152969
H	-0.980789	5.133865	-2.545334
H	-1.692734	4.616562	1.144348
H	-1.558456	2.305618	1.922928
H	-0.389450	2.338989	-2.166245
C	6.515518	1.337738	5.570435
C	5.851517	2.706604	5.400803
C	4.441422	2.668488	4.911179
C	3.324509	2.330627	5.623520
N	2.214371	2.368271	4.808700
C	2.604828	2.738403	3.548874
C	1.849380	2.915390	2.383118
C	2.518784	3.297546	1.246887
C	3.913086	3.505280	1.247498
C	4.661209	3.328690	2.402466
C	4.003113	2.938553	3.579697
H	6.583893	0.832504	4.607178
H	5.930664	0.729050	6.259903
H	7.514954	1.505951	5.971771
H	5.834351	3.224000	6.360000
H	6.415863	3.297836	4.679749
H	3.407242	2.083115	6.681778
H	1.229752	2.379608	5.089966
H	0.772095	2.750198	2.401505
H	1.971481	3.447220	0.316193
H	4.419235	3.809326	0.331177
H	5.738754	3.492569	2.384323
C	5.482574	0.165237	1.046570
C	4.290222	0.325943	0.094315
C	2.983124	-0.233505	0.652512
O	1.938492	0.000000	0.000031
O	2.984161	-0.892487	1.720032
Fe	0.000000	0.000000	0.000000
H	5.260925	0.623123	2.010544
H	6.349060	0.654648	0.601898
H	5.731522	-0.889328	1.165039
H	4.129425	1.384125	-0.112045
H	4.496445	-0.198456	-0.838730
C	-0.340240	-6.203888	-1.264236
C	-1.642380	-5.405273	-1.030289
C	-1.440063	-4.036484	-0.453674
N	-1.976669	-3.657791	0.757858
C	-1.675980	-2.393890	0.996887
N	-0.961227	-1.938217	-0.015900
C	-0.797989	-2.945496	-0.936661
H	-0.623627	-7.135941	-1.753250
H	0.167450	-6.425369	-0.325424
H	0.300278	-5.668503	-1.964996
H	-2.164368	-5.274400	-1.978226
H	-2.282730	-5.948822	-0.335510
H	-2.517593	-4.244537	1.376892
H	-2.018860	-1.916200	1.914688
H	-0.230606	-2.763123	-1.849197
O	-0.322327	0.000000	2.246277
H	-0.729935	0.663147	2.895600
H	0.567169	-0.233200	2.589951

Table S18 Cartesian coordinates (Å) for QM/MM geometry-optimized active-site model of Q69E $Fe^{2+}SOD^{HOH}$ with Glu69 deprotonated and Tyr34 deprotonated (starting coordinates based on PDB file 2BKB).[4]

Atom	x	y	z
C	-3.263870	-4.963379	-1.415909
C	-1.754379	-5.224900	-1.424698
C	-0.929596	-3.996231	-1.185500
N	0.424835	-4.045975	-0.934830
C	0.880280	-2.819778	-0.742416
N	-0.129471	-1.976425	-0.861679
C	-1.273636	-2.686737	-1.139069
H	-3.463455	-4.213882	-0.650009
H	-3.802948	-5.880203	-1.177109
H	-3.577300	-4.523361	-2.362656
H	-1.504608	-5.941040	-0.641785
H	-1.460861	-5.629395	-2.393402
H	0.991959	-4.880920	-0.900772
H	1.936600	-2.658188	-0.527588
H	-2.220520	-2.163818	-1.273849
C	-8.052460	4.382248	-3.528625
C	-6.521973	4.333710	-3.603500
C	-5.823059	4.171875	-2.267395
C	-6.052536	5.073380	-1.222290
C	-5.352417	4.979019	-0.021545
C	-4.414505	3.974792	0.146057
O	-3.697098	3.899277	1.320236
C	-4.173615	3.059921	-0.869812
C	-4.879883	3.162064	-2.072113
H	-8.332718	5.049713	-2.713821
H	-8.469345	3.391602	-3.347229
H	-8.452927	4.769500	-4.465546
H	-6.214554	3.490433	-4.221985
H	-6.149582	5.259766	-4.041687
H	-6.790100	5.867371	-1.339462
H	-5.544586	5.693359	0.778946
H	-3.437759	2.268463	-0.727295
H	-4.697357	2.446533	-2.873900
C	-1.803665	6.437805	-3.299133
C	-2.752548	6.057510	-2.162262
C	-2.185104	6.337784	-0.772202
C	-1.032013	5.409042	-0.410492
O	0.145584	5.907181	-0.452957
O	-1.281326	4.199219	-0.086960
H	-0.796646	6.169922	-2.979462
H	-1.849167	7.508316	-3.499313
H	-2.012482	5.839645	-4.186096
H	-3.678406	6.625076	-2.255844
H	-2.973694	4.991470	-2.214096
H	-1.814697	7.362045	-0.730209
H	-2.968124	6.204269	-0.025818
C	0.737747	1.609192	-5.904633
C	-0.648270	1.163284	-5.426224
C	-0.794357	1.198593	-3.937897
N	-1.038223	2.364624	-3.241806
C	-1.010254	2.115463	-1.944656
N	-0.762527	0.828522	-1.774078
C	-0.627274	0.231598	-3.004074
H	1.463531	1.100677	-5.269989
H	0.859497	2.687744	-5.804703
H	0.929184	1.246384	-6.914459
H	-1.407913	1.821457	-5.848083
H	-0.833725	0.139694	-5.751800
H	-1.212372	3.272964	-3.647690
H	-1.178375	2.921997	-1.231003
H	-0.423111	-0.836945	-3.071793
C	7.120804	4.734955	1.464844
C	6.549850	5.273636	0.150574
C	5.099289	4.995850	-0.069000
C	4.036194	5.615952	0.526505
N	2.856689	5.046280	0.100189
C	3.146973	4.044052	-0.787521
C	2.294968	3.181000	-1.487700
C	2.875183	2.259491	-2.323944
C	4.274445	2.180344	-2.476105
C	5.118134	3.034958	-1.781296
C	4.552505	3.987885	-0.919220
H	7.054077	3.647202	1.484451
H	6.562637	5.148895	2.304520
H	8.165131	5.042618	1.518845
H	6.667892	6.356735	0.119553
H	7.083176	4.826385	-0.688217
H	4.204727	6.435303	1.225296
H	1.886932	5.410828	0.188019
H	1.215393	3.256775	-1.357483
H	2.250992	1.567261	-2.889100
H	4.708572	1.439560	-3.147568
H	6.197800	2.958755	-1.910263
C	5.555984	0.326385	0.453033
C	4.290619	-0.300537	-0.146881
C	3.006592	0.107788	0.572632
O	1.923187	-0.238983	0.046005
O	3.063538	0.762848	1.641068
Fe	0.000000	0.000000	0.000000
H	5.467087	1.412537	0.472366
H	6.408829	0.042053	-0.163315
H	5.734055	-0.067032	1.453873
H	4.191452	0.005630	-1.188324
H	4.362228	-1.386871	-0.093353
C	-0.937943	-3.833160	4.962814
C	-2.145370	-3.110626	4.324005
C	-1.782562	-2.016357	3.365875
N	-2.165359	-0.706741	3.559814
C	-1.746552	0.029160	2.545914
N	-1.103424	-0.755783	1.700562
C	-1.110245	-2.040161	2.189835
H	-1.338974	-4.645935	5.568359
H	-0.357727	-3.160767	5.594711
H	-0.331284	-4.296631	4.184784
H	-2.747528	-3.829681	3.768509
H	-2.753082	-2.656189	5.106522
H	-2.685242	-0.350983	4.349213
H	-1.958832	1.098038	2.524002
H	-0.624146	-2.839157	1.630081
O	-0.083800	2.051834	0.995804
H	-0.430756	2.946930	0.639175
H	0.824249	2.209076	1.322113

Table S19. Structural parameters (Å) of the QM/MM geometry-optimized active-site model of Fe^{3+}SOD derived from PDB file 1ISB.

	Fe^{3+}SOD
Bond lengths (Å)	
Fe–O (Sol)	1.92
Fe–O (Asp)	1.90
Fe–N (His26)	2.25
Fe–N (His160)	2.12
Fe–N (His73)	2.11
H–bond distances (Å)	
O(Sol)···N(Gln/Glu)	2.96
O(Sol)···O(Asp)	3.18
O(Tyr)···N(Gln/Glu)	3.34
O(Gln/Glu)···N(Trp)	2.76
Bond angle (deg)	
His–Fe–His	123

Table S20. INDO/S-CI computed electronic excitation energies (cm^{-1}) and zero-field splitting parameters for the Fe^{3+}SOD model derived from PDB file 1ISB.

	Fe^{3+}SOD
$d \rightarrow d$	5591.7
transitions	5672.4
	9877.8
	10 523.0
	16 849.2
	20 745.5
	21 197.7
	23 554.8
$Asp \rightarrow Fe^{3+}$	27 870 (f = 0.0028)
CT transitions	28 763 (f = 0.015)
	29 537 (f = 0.040)
	29 681 (f = 0.011)
	33 812 (f = 0.017)
D (cm^{-1})	-0.915
E/D	0.032

Table S21. Structural parameters (Å) of QM/MM geometry-optimized active-site models for the oxidized and reduced states of Fe(Mn)SOD derived from PDB file 1MMM.

	Fe^{3+}(Mn)SOD	Fe^{2+}(Mn)SOD^{HOH}	Fe^{2+}(Mn)SOD^{OH-}
Bond lengths (Å)			
Fe–O (Sol)	1.90	2.23	1.96
Fe–O (Asp)	1.92	1.93	1.99
Fe–N (His26)	2.20	2.12	2.28
Fe–N (His160)	2.14	2.13	2.17
Fe–N (His73)	2.14	2.10	2.19
H–bond distances (Å)			
O(Sol)···N(Gln/Glu)	2.77	2.96	2.66
O(Sol)···O(Asp)	2.83	2.50	3.05
O(Tyr)···N(Gln/Glu)	3.25	3.41	3.15
O(Gln/Glu)···N(Trp)	2.84	2.88	2.86
Bond angles (deg)			
His–Fe–His	131	127	127

Table S22. Structural parameters (Å) of QM/MM geometry-optimized active-site models for the oxidized and reduced states of Q69E FeSOD.

	Q69E Fe^{3+}SOD[a]	Q69E Fe^{3+}SOD[b]
Bond lengths (Å)		
Fe–O (Sol)	1.86	2.13
Fe–O (Asp)	1.91	1.89
Fe–N (His26)	2.29	2.18
Fe–N (His160)	2.18	2.09
Fe–N (His73)	2.12	2.07
H–bond distances (Å)		
O(Sol)···N(Gln/Glu)	3.16	2.60
O(Sol)···O(Asp)	3.45	2.83
O(Tyr)···N(Gln/Glu)	2.48	3.97
O(Gln/Glu)···N(Trp)	2.68	2.64
Bond angles (deg)		
His–Fe–His	122	124

[a] In this model the solvent ligand is OH^- and Glu69 is deprotonated.
[b] In this model the solvent ligand is HOH and Glu69 is deprotonated.

Table S23. Structural parameters (Å) derived from the partially QM/MM-optimized models of the Q69E Fe^{2+}SOD species based on the PDB files 2BKB.

	Q69E Fe^{2+}SOD[a]	Q69E Fe^{2+}SOD[b]	Q69E Fe^{2+}SOD[c]	Q69E Fe^{2+}SOD[d]	Q69E Fe^{2+}SOD[e]
Bond lengths (Å)					
Fe–O (Sol)	2.27	2.27	2.27	2.28	2.28
Fe–O (Asp)	1.94	1.94	1.94	1.94	1.94
Fe–N (His26)	2.16	2.16	2.16	2.16	2.16
Fe–N (His160)	2.10	2.10	2.10	2.10	2.10
Fe–N (His73)	2.16	2.16	2.16	2.16	2.16
C(Glu)–O(H-bonds W122)	1.26	1.25	1.25	1.25	1.28
C(Glu)–O(H-bonds sol/Y34)	1.32	1.32	1.32	1.32	1.28
H-bond distances (Å)					
O(Sol)···O(Glu)	2.70	2.71	2.69	2.69	2.69
O(Sol)···O(Asp)	3.45	3.44	3.47	3.48	3.46
O(Tyr)···O(Glu)	2.65	2.64	2.64	2.62	2.81
O(Glu)···N(Trp)	2.93	2.93	2.92	2.92	2.90
Bond angles (deg)					
His–Fe–His	128	128	128	128	128

[a] Initial protonation state: the solvent ligand and Tyr34 are protonated and Glu69 is deprotonated.
Final protonation state: the solvent ligand and Tyr34 are protonated and Glu69 is deprotonated.
[b] Initial protonation state: the solvent ligand and Glu69 are protonated and Tyr34 is deprotonated.
Final protonation state: the solvent ligand and Tyr34 are protonated and Glu69 is deprotonated.
[c] Initial protonation state: Glu69 and Tyr34 are protonated and the solvent ligand is deprotonated.
Final protonation state: the solvent ligand and Tyr34 are protonated and Glu69 is deprotonated.
[d] Initial protonation state: the solvent ligand, Glu69 and Tyr34 are protonated and a solvent molecule is OH^-.
Final protonation state: the solvent ligand and Tyr34 are protonated and Glu69 is deprotonated and the solvent molecule is HOH.
[e] Initial protonation state: Glu69 and Tyr34 are deprotonated and the solvent molecule is protonated.
Final protonation state: Glu69 and Tyr34 are deprotonated and the solvent molecule is protonated.

Table S24. INDO/S-CI computed electronic transition energies (cm^{-1}) and zero-field splitting parameters for the QM/MM geometry-optimized active-site models of the Fe^{2+}-bound SOD species.

	Fe^{2+}SOD	Fe^{2+}(Mn)SOD[a]	Fe^{2+}(Mn)SOD[b]	Q69E Fe^{2+}SOD
$3d_{yz} \rightarrow 3d_{x^2-y^2}$	814	722	592	729
$3d_{yz} \rightarrow 3d_{xz}$	2535	2506	2322	2638
$3d_{yz} \rightarrow 3d_{xy}$	3050	2874	3069	2984
$3d_{yz} \rightarrow 3d_{z^2}$	9187	8239	8724	7986
D (cm^{-1})	-4.630	-5.450	-4.231	-5.217
E/D (cm^{-1})	0.098	0.140	0.117	0.145

[a] This model is based upon the PDB file 1VEW.
[b] This model is based upon the PDB file 1MMM.

Table S25. INDO/S-CI computed electronic transition energies (cm^{-1}) and zero-field splitting parameters for the QM/MM geometry-optimized active-site model of Fe^{3+}(Mn)SOD derived from the PDB file 1MMM.

	Fe^{3+}(Mn)SOD
$d \rightarrow d$ transitions	4942
	5042
	8505
	10 109
	15 944
	21 178
	24 192
Asp $\rightarrow Fe^{3+}$ CT transitions	28 632 (f = 0.011)
	29 383 (f = 0.043)
	29 610 (f = 0.010)
	33 569 (f = 0.011)
	33 637 (f = 0.010)
D (cm^{-1})	-1.214
E/D	0.050

Table S26. TD-DFT and DFT/Slater computed transition energies (cm^{-1}) for the QM/MM geometry-optimized active-site model of Fe^{2+}(Mn)SOD derived from the PDB file 1MMM.

	Fe^{2+}(Mn)SOD
TD-DFT[a]	
1 ($3d_{yz} \rightarrow 3d_{x^2-y^2}$)	1875
2 ($3d_{yz} \rightarrow 3d_{xz}$)	4942
3 ($3d_{yz} \rightarrow 3d_{xy}$)	5305
4 ($3d_{yz} \rightarrow 3d_{z^2}$)	14 515
Slater method[b]	12 032

Table S27. Energies, occupations, and composition (%) of the Fe^{3+} 3d-, Asp-, and Sol-based spin-down MOs for the QM/MM geometry-optimized active-site model of Fe^{3+}SOD, obtained from a spin-unrestricted DFT/COSMO computation using ORCA 2.4 (B3LYP functional) and ε = 4.0.

			Fe^{3+} 3d-based MOs					O (Sol)	O/O (Asp)
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}		
194b	-9.0402	1	1.5	1.6	0.0	4.7	0.0	7.0	54.8
195b	-8.7236	1	0.2	0.0	0.1	0.4	4.0	1.6	70.0
196b	-8.5740	1	0.1	0.2	13.7	0.1	0.0	65.1	0.7
199b	-7.8290	1	0.2	1.0	0.0	0.1	0.0	0.5	57.3
200b	-7.7999	1	0.2	0.3	0.0	0.0	0.0	0.6	16.8
208b	-4.1230	0	5.8	38.9	14.9	19.1	5.6	2.9	4.2
209b	-4.0881	0	2.1	14.0	43.7	4.6	16.0	10.9	3.0
210b	-3.8362	0	0.1	1.0	19.3	1.7	57.3	2.6	5.2
211b	-3.7582	0	4.5	24.6	1.6	50.3	1.5	1.8	3.3
212b	-2.6040	0	58.5	9.9	0.0	0.0	0.0	9.7	3.7

Table S28. Energies, occupations, and composition (%) of the Fe^{3+} 3d-, Asp-, and Sol-based spin-down MOs for the QM/MM geometry-optimized active-site model of Fe^{3+}(Mn)SOD (derived from PDB file 1VEW), obtained from a spin-unrestricted DFT/COSMO computation using ORCA 2.4 (B3LYP functional) and ε = 4.0.

			Fe^{3+} 3d-based MOs					O (Sol)	O/O (Asp)
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}		
194b	-9.1011	1	1.3	0.7	0.0	2.4	0.0	6.2	30.0
195b	-8.8155	1	0.3	0.0	0.0	0.5	3.6	1.0	69.3
196b	-8.6665	1	0.4	0.9	12.6	0.4	0.0	67.9	1.1
197b	-7.9588	1	0.3	0.7	0.0	0.1	0.0	1.1	41.3
198b	-7.9525	1	0.0	0.8	0.0	0.0	0.0	0.9	36.9
208b	-4.1969	0	0.0	0.1	59.5	0.1	22.0	11.1	2.0
209b	-4.1898	0	5.2	58.1	0.5	21.1	0.0	0.9	5.1
210b	-3.9607	0	0.1	1.3	19.8	4.2	55.0	2.3	4.5
211b	-3.9007	0	1.8	23.6	1.0	50.6	3.6	3.3	4.0
212b	-2.6399	0	62.5	5.7	0.0	0.0	0.0	9.5	4.0

Table S29. Energies, occupations, and composition (%) of the Fe^{3+} 3d-, Asp-, and Sol-based spin-down MOs for the QM/MM geometry-optimized active-site model of Fe^{3+}(Mn)SOD (derived from PDB file 1MMM), obtained from a spin-unrestricted DFT/COSMO computation using ORCA 2.4 (B3LYP functional) and ε = 4.0.

			Fe^{3+} 3d-based MOs					O (Sol)	O/O (Asp)
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}		
193b	-9.1556	1	2.1	0.9	0.1	2.9	0.0	11.6	39.1
195b	-8.8079	1	0.3	0.0	0.3	0.7	3.7	3.1	65.7
196b	-8.5812	1	0.3	0.9	13.2	0.4	0.0	67.8	1.3
197b	-7.9777	1	0.4	1.6	0.1	0.1	0.1	2.6	76.2
208b	-4.1501	0	1.3	16.3	44.1	3.1	16.1	10.8	2.7
209b	-4.1431	0	2.5	50.6	11.9	11.3	10.3	1.6	4.3
210b	-3.9642	0	0.4	2.7	23.8	1.7	52.2	2.8	4.7
211b	-3.8167	0	2.0	14.8	0.5	58.7	2.6	2.6	5.0
212b	-2.6011	0	63.5	4.8	0.0	0.4	0.1	9.6	3.2

Table S30. Energies, occupations, and composition (%) of the Fe^{3+} 3d-, Asp-, and Sol-based spin-down MOs for the QM/MM geometry-optimized active-site model of Q69E Fe^{3+}SOD, obtained from a spin-unrestricted DFT/COSMO computation using ORCA 2.4 (B3LYP functional) and ε = 4.0.

			Fe^{3+} 3d-based MOs					O (Sol)	O/O (Asp)
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}		
195b	-9.0792	1	0.9	1.8	0.0	4.5	0.0	4.8	55.0
196b	-8.7679	1	0.0	0.0	0.4	0.2	3.9	2.1	68.0
197b	-8.6779	1	0.3	0.2	12.0	0.2	0.0	66.6	2.4
199b	-7.8421	1	0.4	1.0	0.0	0.0	0.0	0.6	65.7
208b	-4.2650	0	9.0	46.6	6.1	21.3	1.7	0.8	4.7
209b	-4.2512	0	1.4	4.6	56.4	1.4	17.5	12.1	2.2
210b	-3.9214	0	0.3	1.6	16.5	3.1	57.2	1.8	5.8
211b	-3.8887	0	5.0	22.3	2.1	49.8	3.1	1.4	3.3
212b	-2.8603	0	56.4	12.7	0.0	0.0	0.0	9.4	3.7

Table S31. Energies, occupations, and composition (%) of the Fe^{3+} 3d-, Asp-, and Sol-based spin-down MOs for the QM/MM geometry-optimized active-site model of Fe^{3+}SOD, obtained from a spin-unrestricted DFT computation using ADF 2006 (BP functional).

			Fe^{3+} 3d-based MOs					O (Sol)	O/O (Asp)
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}		
111b	-9.690	1	0.0	1.8	0.0	6.1	1.6	3.9	57.9
113b	-9.437	1	0.0	0.0	5.2	0.0	4.9	15.9	50.3
114b	-9.336	1	0.0	0.0	12.2	0.0	0.0	49.2	19.4
119b	-8.241	1	0.0	3.9	0.0	0.0	0.0	0.0	80.6
123b	-6.993	0	9.1	62.2	4.6	4.2	2.9	1.3	6.3
124b	-6.834	0	1.3	6.7	42.4	0.0	25.3	14.2	2.5
125b	-6.539	0	0.0	4.6	5.3	60.0	5.8	0.0	5.4
126b	-6.533	0	0.0	0.0	22.4	9.4	43.2	3.8	4.0
127b	-5.223	0	57.6	9.0	0.0	0.0	0.0	3.0	11.4

Table S32. Energies, occupations, and composition (%) of the Fe^{3+} 3d-, Asp-, and Sol-based spin-down MOs for the QM/MM geometry-optimized active-site model of Fe^{3+}(Mn)SOD (derived from PDB file 1VEW), obtained from a spin-unrestricted DFT computation using ADF 2006 (BP functional).

			Fe^{3+} 3d-based MOs					O (Sol)	O/O (Asp)
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}		
109b	-9.685	1	2.4	1.6	0.0	5.3	0.0	7.9	51.9
111b	-9.437	1	0.0	0.0	2.7	0.0	4.5	7.8	61.1
112b	-9.318	1	0.0	1.2	13.0	0.0	0.0	56.3	7.4
118b	-8.323	1	0.0	3.5	0.0	0.0	0.0	1.3	71.8
123b	-6.966	0	4.2	58.5	14.3	1.9	3.2	2.8	6.4
124b	-6.829	0	1.8	14.4	34.7	0.0	25.1	12.8	2.4
125b	-6.582	0	0.0	0.0	11.7	41.8	22.9	1.5	4.9
126b	-6.490	0	0.0	3.9	14.5	29.7	26.8	3.7	5.8
127b	-5.128	0	61.1	5.2	0.0	0.0	0.0	10.0	3.2

Table S33. Energies, occupations, and composition (%) of the Fe^{3+} 3d-, Asp-, and Sol-based spin-down MOs for the QM/MM geometry-optimized active-site model of Fe^{3+}(Mn)SOD (derived from PDB file 1MMM), obtained from a spin-unrestricted DFT computation using ADF 2006 (BP functional).

			Fe^{3+} 3d-based MOs					O (Sol)	O/O (Asp)
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}		
108b	-9.738	1	2.9	1.3	0.0	4.7	0.0	9.2	55.0
111b	-9.433	1	0.0	0.0	2.7	0.0	4.6	8.4	56.3
113b	-9.257	1	0.0	1.0	13.2	0.0	0.0	51.6	5.9
118b	-8.348	1	0.0	2.5	0.0	0.0	0.0	2.1	53.0
123b	-6.953	0	3.5	65.0	9.4	1.4	4.2	1.6	4.8
124b	-6.815	0	1.4	11.9	34.4	0.0	28.9	12.8	2.8
125b	-6.601	0	0.0	0.0	26.7	13.5	36.7	4.6	3.9
126b	-6.423	0	0.0	2.2	4.4	58.3	8.5	2.7	7.0
127b	-5.125	0	62.2	4.3	0.0	0.0	0.0	10.3	2.7

Table S34. Energies, occupations, and composition (%) of the Fe^{3+} 3d-, Asp-, and Sol-based spin-down MOs for the QM/MM geometry-optimized active-site model of Q69E Fe^{3+}SOD, obtained from a spin-unrestricted DFT computation using ADF 2006 (BP functional).

			Fe^{3+} 3d-based MOs					O (Sol)	O/O (Asp)
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}		
110b	-9.786	1	0.0	1.9	0.0	5.3	0.0	1.3	51.2
112b	-9.563	1	0.0	0.0	8.5	0.0	4.4	29.4	35.6
113b	-9.466	1	0.0	0.0	7.3	0.0	1.1	35.6	34.5
119b	-8.304	1	1.1	3.7	0.0	0.0	0.0	0.0	80.7
123b	-7.190	0	11.6	61.3	6.3	3.7	2.1	0.0	5.8
124b	-7.065	0	1.8	5.7	49.3	0.0	19.4	15.0	2.1
125b	-6.732	0	0.0	5.0	0.0	68.3	0.0	0.0	5.0
126b	-6.677	0	0.0	0.0	20.5	0.0	54.1	2.5	6.2
127b	-5.552	0	55.5	11.3	0.0	0.0	0.0	11.1	2.9

Table S35. Energies, occupations, and composition (%) of the Fe^{2+} 3d-based spin-down MOs for the QM/MM geometry-optimized active-site model of Fe^{2+}SOD, obtained from a spin-unrestricted DFT/COSMO computation using ORCA 2.4 (B3LYP functional) and ε = 4.0.

			Fe^{2+} 3d-based MOs				
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}
208b	-5.7668	1	0.1	0.1	91.4	0.0	0.1
209b	-1.8690	0	0.3	6.4	0.0	48.9	1.2
210b	-1.6164	0	0.7	83.7	0.0	7.9	0.0
211b	-1.3669	0	0.8	0.2	0.0	0.0	59.8
222b	-0.0070	0	15.6	0.2	0.7	0.2	1.1
225b	0.4528	0	12.9	0.2	0.1	8.4	1.5
227b	0.5397	0	13.4	0.1	0.1	1.2	0.0

Table S36. Energies, occupations, and composition (%) of the Fe^{2+} 3d-based spin-down MOs for the QM/MM geometry-optimized active-site model of Fe^{3+}(Mn)SOD (derived from PDB file 1VEW), obtained from a spin-unrestricted DFT/COSMO computation using ORCA 2.4 (B3LYP functional) and ε = 4.0.

			Fe^{2+} 3d-based MOs				
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}
208b	-5.8181	1	0.8	0.1	90.4	0.3	0.0
209b	-1.8834	0	0.8	10.5	0.0	47.7	1.7
210b	-1.7090	0	1.1	79.4	0.1	11.3	0.8
211b	-1.4765	0	0.4	0.2	0.0	0.9	62.4
219b	-0.0872	0	21.5	0.0	0.6	0.5	2.7
224b	0.3043	0	11.5	0.4	0.3	5.5	0.4

Table S37. Energies, occupations, and composition (%) of the Fe^{2+} 3d-based spin-down MOs for the QM/MM geometry-optimized active-site model of Fe^{3+}(Mn)SOD (derived from PDB file 1MMM), obtained from a spin-unrestricted DFT/COSMO computation using ORCA 2.4 (B3LYP functional) and ε = 4.0.

			Fe^{2+} 3d-based MOs				
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}
207b	-5.7873	1	0.1	1.0	88.4	0.4	0.0
209b	-1.8355	0	1.8	8.8	0.0	50.5	0.4
210b	-1.7191	0	1.0	78.1	1.2	8.1	2.8
211b	-1.5955	0	0.5	3.1	0.1	1.7	62.6
219b	-0.1130	0	11.7	0.2	0.2	0.2	2.9
222b	0.1545	0	17.5	0.1	0.2	0.7	4.0

Table S38. Energies, occupations, and composition (%) of the Fe^{2+} 3d-based spin-down MOs for the QM/MM geometry-optimized active-site model of Q69E Fe^{2+}SOD, obtained from a spin-unrestricted DFT/COSMO computation using ORCA 2.4 (B3LYP functional) and ε = 4.0.

			Fe^{2+} 3d-based MOs				
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}
208b	-4.6907	1	0.6	0.1	90.8	0.3	1.1
209b	-0.8047	0	0.5	13.0	0.6	43.2	3.2
210b	-0.5445	0	3.7	74.6	0.0	11.4	0.1
211b	-0.3208	0	0.4	0.0	0.8	1.8	62.2
220b	0.9027	0	12.5	0.8	0.3	1.4	0.9
227b	1.5336	0	13.5	0.0	0.3	6.1	0.2
228b	1.6094	0	10.3	0.0	0.1	0.4	0.2

Table S39. Energies, occupations, and composition (%) of the Fe^{2+} 3d-based spin-down MOs for the QM/MM geometry-optimized active-site model of Fe^{2+}SOD, obtained from a spin-unrestricted DFT computation using ADF 2006 (BP functional).

			Fe^{2+} 3d-based MOs				
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}
151b	-5.862	1	0.0	0.0	91.9	0.0	0.0
152b	-5.232	0	0.0	91.6	0.0	0.0	0.0
153b	-5.088	0	0.0	0.0	0.0	69.8	0.0
154b	-4.726	0	0.0	0.0	0.0	3.3	76.8
155b	-3.711	0	36.0	0.0	0.0	0.0	0.0
156b	-3.588	0	15.6	0.0	0.0	0.0	0.0

Table S40. Energies, occupations, and composition (%) of the Fe^{2+} 3d-based spin-down MOs for the QM/MM geometry-optimized active-site model of Fe^{3+}(Mn)SOD (derived from PDB file 1VEW), obtained from a spin-unrestricted DFT computation using ADF 2006 (BP functional).

			Fe^{2+} 3d-based MOs				
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}
151b	-6.007	1	0.0	0.0	90.7	0.0	0.0
152b	-5.169	0	5.0	87.2	0.0	0.0	0.0
153b	-5.169	0	8.9	2.8	0.0	55.8	7.4
154b	-4.875	0	1.6	0.0	0.0	5.4	71.9
155b	-3.657	0	44.8	1.6	0.0	13.0	0.0
159b	-3.159	0	17.2	0.0	0.0	0.0	0.0

Table S41. Energies, occupations, and composition (%) of the Fe^{2+} 3d-based spin-down MOs for the QM/MM geometry-optimized active-site model of Fe^{3+}(Mn)SOD (derived from PDB file 1MMM), obtained from a spin-unrestricted DFT computation using ADF 2006 (BP functional).

			Fe^{2+} 3d-based MOs				
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}
151b	-6.074	1	0.0	0.0	89.7	0.0	0.0
152b	-5.495	0	0.0	89.4	1.1	2.1	0.0
153b	-5.224	0	3.0	1.7	0.0	68.4	0.0
154b	-5.110	0	0.0	0.0	0.0	0.0	79.9
155b	-3.753	0	53.2	0.0	0.0	0.0	0.0
156b	-3.547	0	11.4	0.0	1.2	1.8	0.0

Table S42. Energies, occupations, and composition (%) of the Fe^{2+} 3d-based spin-down MOs for the QM/MM geometry-optimized active-site model of Q69E Fe^{2+}SOD, obtained from a spin-unrestricted DFT computation using ADF 2006 (BP functional).

			Fe^{2+} 3d-based MOs				
MO	E (eV)	Occ	d_{z2}	d_{xz}	d_{yz}	d_{x2-y2}	d_{xy}
151b	-3.481	1	0.0	0.0	90.4	0.0	1.4
152b	-2.923	0	0.0	85.3	0.0	1.1	1.0
153b	-2.701	0	7.7	2.4	0.0	60.7	8.8
154b	-2.467	0	0.0	0.0	1.0	9.6	70.3
155b	-1.455	0	28.1	2.2	0.0	1.1	0.0
156b	-1.152	0	34.6	0.0	0.0	1.4	0.0

Table S43. DFT/COSMO (ε = 4.0) computed total energies (kcal/mol), ε_{PT}, ε_{ET}, pK, and $E°$ values for Fe(Mn)SOD obtained with the QM/MM geometry-optimized active-site models derived from the PDB file 1MMM.

	Fe(Mn)SOD
Fe^{3+}/OH^-	-2281808
Fe^{2+}/HOH	-2282198
Fe^{2+}/OH^-	-2281900
IP	92.0
ε_{ET} (eV)	-0.44
ε_{deprot}	298
pK[$Fe^{2+}SOD^{HOH}$]	18.3
ε_{PT} (eV)	0.67
$E°$ (V)	0.23

Table S44. DFT/COSMO (ε = 10.0) computed total energies (kcal/mol), ε_{PT}, ε_{ET}, p*K*, and *E*° values for the QM/MM geometry-optimized FeSOD, Fe(Mn)SOD, and Q69E FeSOD active-site models.

	FeSOD	Fe(Mn)SOD[a]	Fe(Mn)SOD[b]	Q69E FeSOD
Fe^{3+}/OH^-	-2281813	-2281820	-2281819	-2294266
Fe^{2+}/HOH	-2282207	-2282204	-2282209	-2294634
Fe^{2+}/OH^-	-2281898	-2281907	-2281907	-2294363
IP	85.1	86.8	87.6	96.8
ε_{ET} (eV)	-0.74	-0.66	-0.63	-0.23
ε_{deprot}	309	298	302	271
p*K*[$Fe^{2+}SOD^{HOH}$]	25.9	17.9	21.2	-1.96
ε_{PT} (eV)	1.12	0.65	0.85	-0.53
E° (V)	0.38	-0.02	0.22	-0.77

[a] This model is derived from the PDB file 1VEW.
[b] This model is derived from the PDB file 1MMM.

Table S45. DFT/COSMO computed solvation energies (kcal/mol) for the QM/MM geometry-optimized FeSOD, Fe(Mn)SOD, and Q69E FeSOD active-site models.

	ε = 4.0	ε = 10.0	1st sphere model
WT FeSOD			
Fe^{3+}/OH^-	-38.429	-39.361	-34.234
Fe^{2+}/HOH	-35.446	-36.546	-34.317
Fe^{2+}/OH^-	-23.352	-24.420	-21.190
Fe(Mn)SOD[a]			
Fe^{3+}/OH^-	-39.361	-52.6909	-34.593
Fe^{2+}/HOH	-36.546	-48.7216	-33.556
Fe^{2+}/OH^-	-24.420	-33.7103	-21.819
Fe(Mn)SOD[b]			
Fe^{3+}/OH^-	-39.894	-53.510	-34.912
Fe^{2+}/HOH	-38.743	-51.882	-33.211
Fe^{2+}/OH^-	-24.739	-34.204	-22.832
Q69E FeSOD			
Fe^{3+}/OH^-	-36.668	-48.843	-34.392
Fe^{2+}/HOH	-38.472	-51.319	-36.265
Fe^{2+}/OH^-	-25.419	-35.011	-39.321

[a] This model is derived from the PDB file 1VEW.
[b] This model is derived from the PDB file 1MMM.

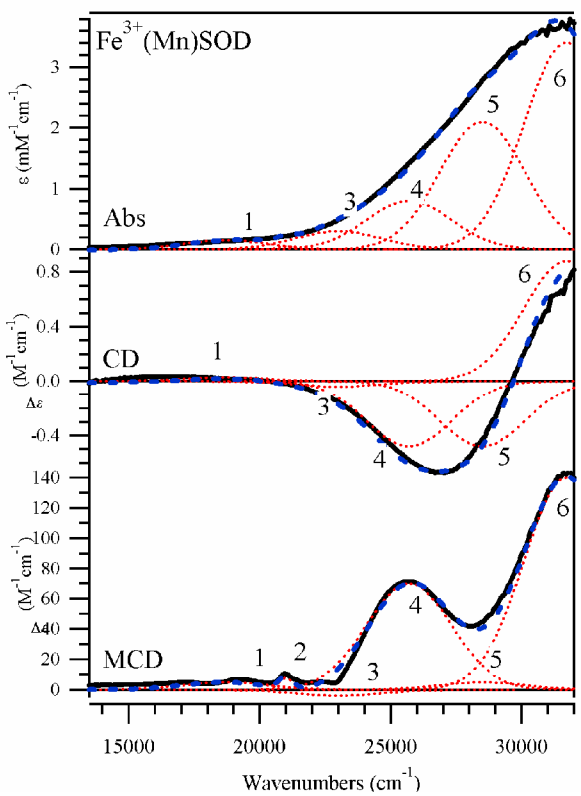


Figure S1. Absorption (top), CD (middle), and MCD (bottom) spectra at 4.5 K (solid lines) of Fe^{3+}(Mn)SOD. Individual Gaussian bands (···) and their sums (---) obtained from an iterative fit are shown for each spectrum. Sample conditions: [Fe^{3+}(Mn)SOD] = 1.1 mM in 55% (v/v) glycerol and 50 mM MES buffer (pH 7.0).

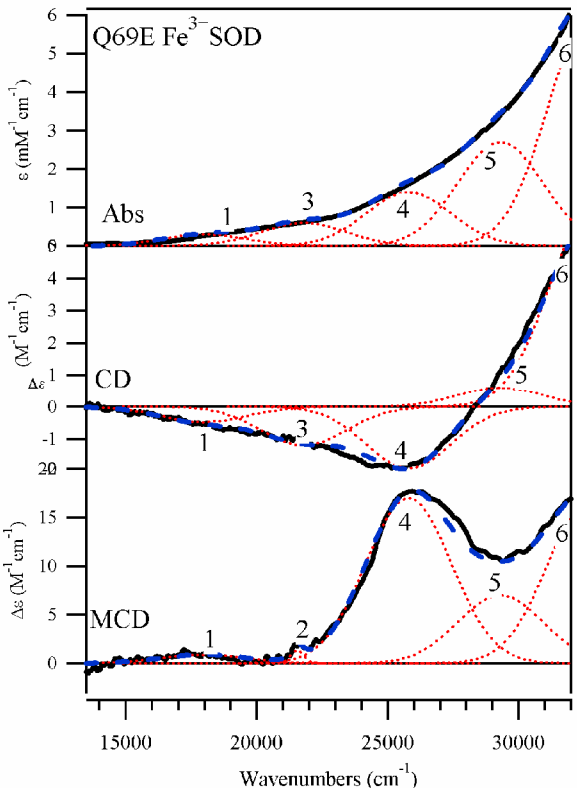
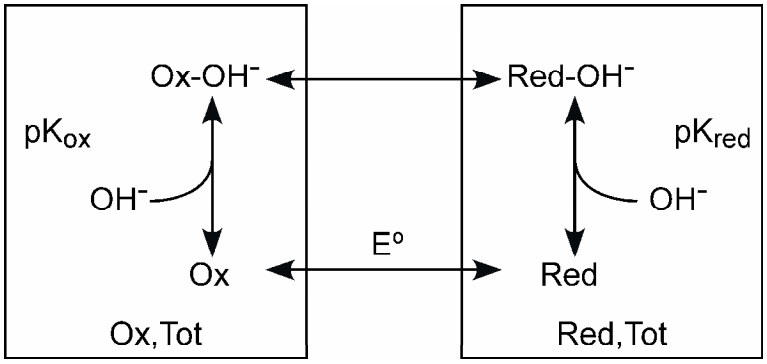


Figure S2. Absorption (top), CD (middle), and MCD (bottom) spectra at 4.5 K (solid lines) of Q69E Fe^{3+}SOD. Individual Gaussian bands (···) and their sums (---) obtained from an iterative fit are shown for each spectrum. Sample conditions: [Q69E Fe^{3+}SOD] = 0.85 mM in 55% (v/v) glycerol and 50 mM phosphate buffer (pH 7.0).

Supplementary Calculations. Effect of OH^- binding to Fe^{3+}(Mn)SOD and Q69E Fe^{3+}SOD on experimental E^o values.

The following scheme was used to estimate how coordination of an exogenous OH^- ion to the putative substrate-binding site of Fe^{3+}(Mn)SOD and Q69E Fe^{3+}SOD under physiological conditions (i.e., at pH 7.0) affects the measured reduction potential E_m. In this scheme, E^o corresponds to the proton-coupled metal ion reduction potential of the wild type-like 5-coordinate state; this is the quantity of interest that we computed using the DFT/COSMO methodology as outlined in the manuscript.



$$\mathrm{Ox,Tot} + e^- \xleftrightarrow[E_m]{} \mathrm{Red,Tot}$$

$$[\mathrm{OxOH}] = [\mathrm{Ox}]10^{pH-pK_{ox}} \qquad [\mathrm{RedOH}] = [\mathrm{Red}]10^{pH-pK_{red}}$$

$$-nFE_m = \Delta G = -RT\ln K = -RT\ln\left(\frac{[\mathrm{Red}]+[\mathrm{RedOH}]}{[\mathrm{Ox}]+[\mathrm{OxOH}]}\right)$$

$$E_m = \frac{RT}{F}\ln\left(\frac{[\mathrm{Red}]\left(1+10^{pH-pK_{red}}\right)}{[\mathrm{Ox}]\left(1+10^{pH-pK_{ox}}\right)}\right)$$

$$E_m = \frac{RT}{F}\left[\ln\left(\frac{[\mathrm{Red}]}{[\mathrm{Ox}]}\right)+\ln\left(\frac{1+10^{pH}\times10^{-pK_{red}}}{1+10^{pH}\times10^{-pK_{ox}}}\right)\right]$$

$$E_m = E^\circ + \frac{RT}{F}\ln\left(\frac{10^{-pH}+10^{-pK_{red}}}{10^{-pH}+10^{-pK_{ox}}}\right)$$

Fe(Mn)SOD

$$E_m = E^\circ + \frac{RT}{F}\ln\left(\frac{[H^+] + [H^+]_{\text{at 50\% OH free Red}}}{[H^+] + [H^+]_{\text{at 50\% OH free Ox}}}\right)$$

$$E_m = E^\circ + \frac{RT}{F}\ln\left(\frac{10^{-7} + (<10^{-12})}{10^{-7} + 10^{-6.5}}\right)$$ where the pK of OH^- binding to Ox is 6.5[5]

$$E_m = E^\circ + \frac{RT}{F}\ln\left(\frac{10^{-7}}{4.2\times10^{-7}}\right) = E^\circ - \frac{RT}{F}\times 1.4 = E^\circ - 38\,\text{mV}$$

Q69E FeSOD

$$E_m = E^\circ + \frac{RT}{F}\ln\left(\frac{[H^+] + [H^+]_{\text{at 50\% OH free Red}}}{[H^+] + [H^+]_{\text{at 50\% OH free Ox}}}\right)$$

$$E_m = E^\circ + \frac{RT}{F}\ln\left(\frac{10^{-7} + (<10^{-12})}{10^{-7} + 10^{-5}}\right)$$ where the pK of OH^- binding to Ox is estimated to be 5

$$E_m = E^\circ + \frac{RT}{F}\ln\left(\frac{10^{-7}}{10^{-5}}\right) = E^\circ - \frac{2.3RT}{F}\log 10^2 = E^\circ - 120\,\text{mV}$$

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