

**Electronic Supporting information**  
**Of**  
**Structural, Spectroscopic and Functional Investigation into**  
**Fe-substituted MnSOD from Human Pathogen *Clostridium difficile***

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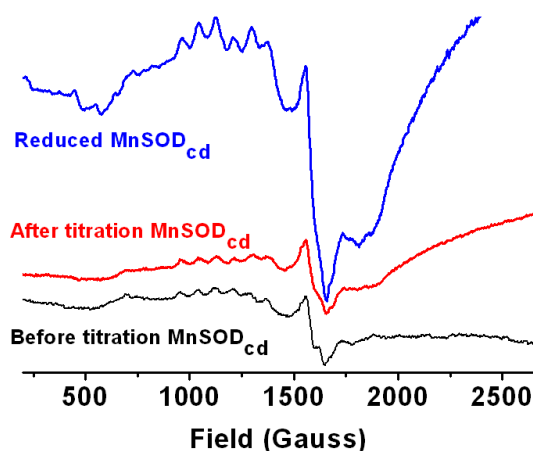
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## 1. The EPR spectra of MnSOD<sub>cd</sub>



**Figure S1. The EPR spectra of MnSOD<sub>cd</sub> before and after UV/Vis pH titrations.**

The Mn<sup>3+</sup> center is EPR silent and the Mn<sup>2+</sup> center exhibits a EPR spectrum characterized by six transitions at ~1000 G, which is due to the hyperfine structure arose from the magnetic interaction of the electron spin ( $S=5/2$ ) on Mn<sup>2+</sup> and the nuclear spin ( $I=5/2$ ) of <sup>55</sup>Mn. The fully reduced Mn<sup>2+</sup>SOD<sub>cd</sub> were obtained by H<sub>2</sub>O<sub>2</sub> reduction before EPR spectrum collection. The relative low intensity at ~1000 G in the EPR spectrum of the isolated MnSOD<sub>cd</sub> (before titration) indicated a small portion of Mn<sup>2+</sup> occupied into the Mn<sup>3+</sup>SOD<sub>cd</sub>, which is explained by our previous electrochemical experiment (1). After titration, the intensity of G=1000 almost didn't alter, indicating Mn<sup>3+</sup> has not been reduced by the pH titration.

## 2. Computationally-derived Coordinates for MnSOD<sub>cd</sub> and Fe-sub-MnSOD<sub>cd</sub>

Table S1a. Computationally-derived coordinates for the oxidized MnSOD<sub>cd</sub>

C	-5.266880	0.551262	2.308121
N	-4.059977	-0.391310	0.640633
C	7.606514	-1.818519	0.366405
C	4.926113	-0.976867	0.086194
O	3.597263	-0.595797	-0.053399
C	-2.061662	3.368950	-1.206773
N	-0.782245	2.896616	-0.946093
N	-2.128754	1.131963	-0.793681
C	2.978367	4.457323	-0.058005
C	2.789900	2.996390	0.070578
O	3.278555	1.886408	0.475837
C	-2.724810	-3.595685	-1.435369
O	-1.633443	-3.341348	-1.993077
O	-3.422299	-2.671879	-0.757569
C	0.611067	-0.736335	1.635814
C	-3.364617	-4.962709	-1.478622
H	-3.566793	-5.320903	-0.463455
H	-4.324230	-4.905135	-2.004852
H	-2.709348	-5.665362	-1.994850
C	-2.356260	4.800749	-1.511862
H	-2.052146	5.460992	-0.690345
H	-1.827756	5.137139	-2.412074
H	-3.427811	4.942857	-1.679281
C	-2.891525	2.265846	-1.117642
H	-3.959938	2.211290	-1.246927
C	-0.858305	1.566787	-0.712060
H	0.011950	0.978900	-0.495074
C	-5.847629	1.411424	3.380090
H	-6.882319	1.700931	3.157318
H	-5.843392	0.909500	4.355824
H	-5.262245	2.328957	3.478622
C	-4.183692	0.723053	1.480664
H	-3.502697	1.551324	1.414904
C	-5.055688	-1.233787	0.950446
H	-5.196721	-2.194273	0.486043
C	1.510941	-0.275452	2.733483
H	2.112289	-1.097970	3.137752

H	2.199889	0.496084	2.367663
H	0.922604	0.147846	3.552273
C	-0.748788	-0.639524	1.455936
H	-1.491995	-0.222606	2.111434
C	0.062777	-1.590224	-0.364299
H	0.124685	-2.067267	-1.326300
C	3.822197	5.094111	-1.138079
H	3.967300	4.402456	-1.974855
H	3.351166	6.006583	-1.528817
H	4.811844	5.370424	-0.749228
C	9.049111	-2.261802	0.485816
H	9.580749	-1.692778	1.257013
H	9.121731	-3.324401	0.743768
H	9.596427	-2.118818	-0.456737
C	7.233901	-0.485243	0.610744
H	7.991581	0.232157	0.915725
C	6.599177	-2.720389	-0.016896
H	6.857321	-3.758723	-0.208440
C	5.270972	-2.310670	-0.160646
H	4.500956	-3.012124	-0.464109
C	5.910786	-0.057234	0.475985
H	5.624297	0.970043	0.673824
N	1.747800	3.550026	-0.492901
H	0.177108	3.376121	-0.859340
N	1.099300	-1.332518	0.470309
N	-1.083508	-1.159897	0.198977
H	2.110044	-1.348658	0.226067
H	2.792442	5.086294	0.814687
H	-6.610479	-1.126080	2.372594
N	-5.802735	-0.693836	1.952582
O	-3.195321	-0.496517	-2.456397
H	-3.116265	0.380242	-2.880237
H	3.441131	0.409376	0.063024
Mn	-2.780816	-0.877096	-0.786628

**Table S1b. Computationally-derived coordinates for the reductive MnSOD<sub>cd</sub>**

C	4.839033	-2.413626	-0.158610
N	3.427790	-0.641572	-0.352418
C	-5.201683	-2.514458	-0.809612
C	-3.617939	-0.801316	0.810685
O	-2.792055	-0.025509	1.592660
C	-0.637707	-2.335206	-1.847671

N	-1.504597	-1.255364	-1.706145
N	0.455142	-0.552548	-0.955569
C	-4.066246	3.202921	0.167069
C	-2.623637	3.229187	0.225256
O	-1.920182	2.150094	0.598718
C	2.630502	2.998447	-2.015404
O	1.688660	3.758637	-1.637411
O	2.847980	1.787039	-1.540112
C	1.602195	-0.206503	3.937310
C	3.603809	3.473976	-3.073793
H	4.624309	3.468830	-2.673950
H	3.582077	2.793461	-3.932578
H	3.344138	4.482065	-3.398407
C	-1.071699	-3.656211	-2.389577
H	-1.918686	-4.060942	-1.821579
H	-1.380333	-3.587874	-3.440775
H	-0.251546	-4.377073	-2.330587
C	0.577203	-1.882607	-1.383941
H	1.512741	-2.409696	-1.326547
C	-0.821885	-0.200319	-1.171700
H	-1.274443	0.741143	-0.904406
C	5.555852	-3.673230	0.198269
H	5.659202	-4.345904	-0.662864
H	6.562539	-3.476794	0.589201
H	5.001512	-4.211138	0.971745
C	3.673937	-1.853559	0.310180
H	3.006686	-2.217922	1.070560
C	4.431342	-0.469672	-1.220865
H	4.510397	0.376025	-1.880524
C	2.034928	-0.259180	5.364693
H	1.537636	0.508882	5.970778
H	1.822487	-1.233131	5.824616
H	3.112302	-0.087172	5.436217
C	2.297949	0.014436	2.771202
H	3.350419	0.201771	2.642087
C	0.203616	-0.264819	2.172395
H	-0.732197	-0.321640	1.640518
C	-4.814508	4.294744	0.843082
H	-4.228648	5.208624	1.015182
H	-5.763731	4.529381	0.349436
H	-5.082746	3.874253	1.832628
C	-6.076545	-3.420405	-1.650263
H	-7.083106	-3.522202	-1.220551
H	-6.199706	-3.029428	-2.666702

H	-5.656408	-4.430215	-1.727145
C	-4.449054	-3.020398	0.266563
H	-4.476647	-4.086200	0.481470
C	-5.150611	-1.127506	-1.043253
H	-5.740533	-0.702705	-1.852294
C	-4.380118	-0.269032	-0.248008
H	-4.390587	0.808179	-0.416390
C	-3.668704	-2.182212	1.066482
H	-3.081711	-2.581228	1.886990
N	-2.202490	4.332873	-0.356968
H	-1.291985	4.261053	-0.833352
N	0.277201	-0.381788	3.532609
N	1.421647	-0.024487	1.676452
H	-0.522940	-0.516799	4.130569
H	-2.506040	-1.264753	-1.849853
H	6.139269	-1.633015	-1.681150
N	5.302044	-1.521202	-1.132151
H	0.892087	2.959027	-0.458042
O	0.638418	2.172094	0.111792
H	-0.330453	2.185238	0.420191
H	-2.584360	0.920215	1.211898
Mn	1.867163	0.654670	-0.202607

**Table S1c. Computationally-derived coordinates for the oxidized Fe-sub-MnSOD<sub>cd</sub>**

C	-5.021631	0.162687	2.610680
N	-3.900912	-0.547534	0.779818
C	7.551275	-1.846170	0.403940
C	4.884824	-0.936321	0.200230
O	3.564399	-0.520507	0.099015
C	-2.056792	3.268523	-0.940156
N	-0.785924	2.724095	-1.077106
N	-2.183058	1.006042	-0.936167
C	2.876483	4.467305	-0.288000
C	2.794928	3.013787	-0.031718
O	3.364940	1.986880	0.470750
C	-2.524263	-2.899700	-2.069105
O	-1.835896	-1.827997	-2.342626
O	-3.261263	-2.831459	-0.999783
C	0.526798	-0.792074	1.768521
C	-2.493465	-4.107647	-2.941636
H	-2.695652	-5.007475	-2.356783
H	-3.272813	-4.012300	-3.707679

H	-1.529394	-4.189224	-3.448165
C	-2.310139	4.739559	-0.903074
H	-1.744241	5.225792	-0.099253
H	-2.018202	5.221641	-1.843929
H	-3.372684	4.940902	-0.738949
C	-2.921587	2.193487	-0.861544
H	-3.992686	2.195498	-0.750191
C	-0.899321	1.378218	-1.081497
H	-0.056194	0.720178	-1.167729
C	-5.563822	0.885016	3.798479
H	-6.627329	1.127919	3.679927
H	-5.455757	0.298736	4.719732
H	-5.024895	1.825071	3.941139
C	-4.016434	0.475413	1.725029
H	-3.388141	1.347309	1.691269
C	-4.817923	-1.471855	1.074500
H	-4.971302	-2.380614	0.518676
C	1.377677	-0.325783	2.902995
H	1.977956	-1.140483	3.325252
H	2.069672	0.456960	2.568640
H	0.754878	0.084578	3.702588
C	-0.835676	-0.781875	1.566945
H	-1.611267	-0.463653	2.238828
C	0.064670	-1.570243	-0.274417
H	0.196084	-1.921379	-1.281463
C	3.699919	5.067856	-1.403932
H	3.910349	4.319714	-2.175668
H	3.177820	5.909385	-1.879604
H	4.659546	5.443285	-1.023015
C	8.984469	-2.327443	0.483134
H	9.564742	-1.742070	1.205654
H	9.037404	-3.379444	0.785260
H	9.495377	-2.241990	-0.486454
C	7.231911	-0.486703	0.567244
H	8.026048	0.224977	0.778559
C	6.498387	-2.738734	0.141326
H	6.714635	-3.796545	0.015434
C	5.177133	-2.295608	0.036530
H	4.371417	-2.992124	-0.170928
C	5.917232	-0.024902	0.469144
H	5.673469	1.023326	0.604159
N	1.728494	3.434917	-0.661522
H	0.194949	3.178944	-1.011191
N	1.072708	-1.298524	0.592414

N	-1.120047	-1.251488	0.279976
H	2.088376	-1.251116	0.365052
H	2.624112	5.154044	0.522201
H	-6.262278	-1.592463	2.610429
N	-5.512863	-1.075226	2.178804
O	-4.180388	-0.564574	-1.946182
H	-4.430732	0.371388	-2.075592
H	3.439138	0.499693	0.177449
Fe	-2.791287	-0.870151	-0.819165

**Table S1d. Computationally-derived coordinates for the reductive Fe-sub-MnSOD<sub>cd</sub>**

C	3.942025	-3.205194	-0.198779
N	2.949925	-1.222926	-0.701717
C	-5.392627	-2.187161	0.574541
C	-3.565708	-0.145784	1.319634
O	-2.631115	0.794598	1.699661
C	-1.177693	-2.530979	-1.917728
N	-1.961208	-1.462359	-1.487686
N	0.136134	-0.830810	-1.163418
C	-3.934847	3.353341	-0.783626
C	-2.496209	3.242264	-0.900138
O	-1.812119	2.377646	-0.131836
C	3.575407	2.690301	-0.822418
O	2.654569	3.557031	-0.711263
O	3.375901	1.391139	-0.863593
Fe	1.710624	0.313092	-0.712128
C	2.215297	0.572962	3.366249
C	5.018720	3.138331	-0.939624
H	5.638242	2.616675	-0.202467
H	5.406613	2.885300	-1.933734
H	5.090260	4.216453	-0.791339
C	-1.752391	-3.795410	-2.463856
H	-2.421319	-4.282062	-1.742761
H	-2.327885	-3.620334	-3.381851
H	-0.951792	-4.500303	-2.704495
C	0.120930	-2.123022	-1.717186
H	1.027340	-2.660224	-1.928282
C	-1.148201	-0.460036	-1.050587
H	-1.511431	0.496569	-0.706157
C	4.317904	-4.560288	0.301538
H	4.493587	-5.268340	-0.518735
H	5.225826	-4.534174	0.917839



H	3.512576	-4.965602	0.919672
C	2.815265	-2.437657	-0.016409
H	1.931339	-2.659749	0.554143
C	4.149298	-1.246722	-1.291989
H	4.579269	-0.428407	-1.838567
C	2.941215	0.730911	4.660643
H	2.721134	1.694355	5.138253
H	2.685076	-0.060757	5.376890
H	4.020468	0.687332	4.491440
C	2.662562	0.411538	2.076331
H	3.669102	0.376367	1.700735
C	0.462809	0.435892	1.953993
H	-0.566388	0.436658	1.630622
C	-4.504568	4.716189	-0.628464
H	-3.854454	5.522014	-0.998081
H	-5.515617	4.807913	-1.039112
H	-4.606417	4.847838	0.467509
C	-6.394598	-3.259660	0.202375
H	-7.327498	-3.156901	0.774463
H	-6.662381	-3.208643	-0.859235
H	-6.003800	-4.264267	0.403029
C	-4.506151	-2.361160	1.652949
H	-4.521191	-3.295460	2.209174
C	-5.345859	-0.960975	-0.114350
H	-6.036514	-0.785716	-0.936436
C	-4.454095	0.058542	0.245819
H	-4.463351	1.017752	-0.273961
C	-3.605206	-1.360820	2.023386
H	-2.918391	-1.505921	2.850544
N	-2.075693	3.902090	-1.957472
H	-1.210070	3.523782	-2.369791
N	0.822342	0.581830	3.266020
N	1.567409	0.326727	1.206791
H	0.167674	0.715327	4.020026
H	-2.970897	-1.430634	-1.423685
H	5.692140	-2.699429	-1.336547
N	4.776161	-2.433478	-1.013137
H	1.261956	2.746004	-0.859757
O	0.644595	1.954025	-0.958475
H	-0.291508	2.141777	-0.611851
H	-2.457718	1.538958	1.002380

**3. The DFT computationally-derived coordinates for the reactants, products and transition states in MnSOD<sub>cd</sub> and Fe-sub-MnSOD<sub>cd</sub>.**

**Table S2a. Computationally-derived Coordinates for the reactant of oxidized**

**MnSOD<sub>cd</sub> and OOH**

C	2.678099	-3.177473	-2.237248
N	2.957154	-1.331362	-0.958198
C	-7.038567	-2.516333	-0.095993
C	-4.737637	-0.972118	0.462422
O	-3.591394	-0.241921	0.746682
C	0.128504	1.966366	-2.617588
N	-0.095171	2.709920	-1.457997
N	1.593182	1.340028	-1.017367
C	-3.624148	4.629496	-0.564657
C	-3.511160	3.216798	-0.140220
O	-4.060602	2.239411	0.462133
C	3.516854	0.776021	2.452646
O	2.721117	1.584943	1.812389
O	3.762729	-0.363263	1.857795
C	-0.391858	-1.645192	2.409445
C	4.142832	1.132075	3.755110
H	4.115603	0.276688	4.435535
H	5.197108	1.382824	3.584990
H	3.639182	1.990568	4.201146
C	-0.694924	2.151927	-3.849248
H	-1.763988	2.145321	-3.609267
H	-0.477708	3.109600	-4.338273
H	-0.496886	1.353901	-4.570280
C	1.184274	1.123077	-2.338075
H	1.663091	0.392528	-2.966350
C	0.803405	2.323531	-0.528090
H	0.850422	2.699000	0.479543
C	2.181746	-4.320246	-3.058452
H	2.602761	-4.311278	-4.071819
H	2.428217	-5.288097	-2.603816
H	1.094015	-4.268030	-3.152343
C	2.023638	-2.142492	-1.613578
H	0.969069	-1.936210	-1.576034

C	4.168628	-1.857642	-1.173946
H	5.114419	-1.468615	-0.811902
C	-1.030523	-2.444162	3.496572
H	-1.671770	-1.820889	4.131517
H	-1.653124	-3.253237	3.095613
H	-0.264576	-2.894789	4.133277
C	0.933121	-1.396023	2.120394
H	1.822018	-1.738010	2.619905
C	-0.259419	-0.327773	0.613663
H	-0.579639	0.266646	-0.220234
C	-3.439999	5.792792	0.382273
H	-2.881056	5.485677	1.272797
H	-2.892858	6.615427	-0.097427
H	-4.412189	6.184627	0.710052
C	-8.279120	-3.339565	-0.369864
H	-8.886163	-2.898221	-1.169115
H	-8.021945	-4.361026	-0.670857
H	-8.921188	-3.413184	0.519051
C	-7.090858	-1.110876	-0.077375
H	-8.033897	-0.610531	-0.282436
C	-5.802005	-3.127381	0.167535
H	-5.729288	-4.211870	0.154029
C	-4.659890	-2.370010	0.444223
H	-3.707992	-2.855257	0.635651
C	-5.961867	-0.337219	0.199966
H	-6.009209	0.746098	0.214490
N	-2.428683	3.612259	-0.764630
H	-1.032685	3.251908	-1.220987
N	-1.121605	-0.961101	1.440120
N	1.008782	-0.558436	1.000091
H	-2.153723	-0.839223	1.328312
H	-4.179660	4.857105	-1.475687
H	4.794978	-3.557329	-2.250328
N	4.031692	-2.973419	-1.946667
O	4.276648	1.069300	-0.429664
H	4.141784	1.867802	-0.968579
H	-3.711411	0.781099	0.636450
Mn	2.706705	0.271904	0.227865
O	6.611983	0.608760	0.297401
H	5.605923	0.822498	-0.005808
O	6.869835	-0.688704	-0.108538

**Table S2b. Computationally-derived coordinates for the transition state of oxidized MnSOD<sub>cd</sub> and OOH**

C	4.096945	2.239135	-2.516476
N	3.165867	0.613035	-1.249898
C	-7.325338	-1.691536	-0.260530
C	-4.681648	-0.730573	-0.530887
O	-3.371398	-0.292458	-0.674250
C	0.568115	1.898890	2.858043
N	0.353451	2.482581	1.610663
N	1.852697	0.874293	1.305941
C	-2.776105	4.684372	0.029956
C	-2.766055	3.228794	-0.234162
O	-3.323000	2.252509	-0.833493
C	2.447579	-2.988691	2.028969
O	2.687290	-1.663613	1.943191
O	2.326677	-3.746672	1.049941
C	-0.316762	-2.413165	-1.769040
C	2.336378	-3.474548	3.459819
H	1.493765	-2.981742	3.957527
H	2.187473	-4.554975	3.472405
H	3.242814	-3.218754	4.018554
C	-0.153760	2.345884	4.086066
H	0.152666	3.353989	4.391907
H	-1.237261	2.370431	3.921637
H	0.049846	1.665877	4.917861
C	1.508393	0.907665	2.661588
H	1.916670	0.190871	3.350549
C	1.142155	1.854132	0.711557
H	1.146195	2.083096	-0.337700
C	4.875006	3.379381	-3.082511
H	5.506838	3.066888	-3.923370
H	4.221555	4.187006	-3.435550
H	5.530652	3.797292	-2.314696
C	4.081345	1.670260	-1.265039
H	4.657138	1.898736	-0.386653
C	2.630459	0.530126	-2.471149
H	1.898098	-0.189764	-2.790934
C	-0.997693	-3.322836	-2.736931
H	-1.679909	-4.014058	-2.227212
H	-1.586477	-2.765904	-3.476113
H	-0.258342	-3.922710	-3.274149

C	1.012276	-2.272489	-1.430687
H	1.870871	-2.833635	-1.754773
C	-0.118321	-0.855133	-0.183064
H	-0.403274	-0.107736	0.531915
C	-3.718715	5.340204	1.012609
H	-4.105818	4.606414	1.727879
H	-3.215991	6.136016	1.578960
H	-4.574231	5.790900	0.491587
C	-8.741777	-2.197747	-0.089617
H	-9.430061	-1.711111	-0.790813
H	-8.802561	-3.278570	-0.257573
H	-9.122107	-2.003136	0.923011
C	-7.065836	-0.328860	-0.491979
H	-7.898458	0.365656	-0.571248
C	-6.225451	-2.560428	-0.171500
H	-6.395021	-3.619541	0.004381
C	-4.914860	-2.091780	-0.301619
H	-4.073200	-2.772084	-0.220073
C	-5.763904	0.157874	-0.628437
H	-5.569712	1.208928	-0.811791
N	-1.780605	3.572063	0.559081
H	-0.491060	3.096177	1.287572
N	-1.007100	-1.503168	-0.968344
N	1.129801	-1.280618	-0.447316
H	-2.015325	-1.235426	-0.965066
H	-2.351782	5.354160	-0.720288
H	2.936618	1.659257	-4.230824
N	3.168677	1.502354	-3.262492
O	4.581057	-0.026887	1.046958
H	4.626810	-0.020683	2.021005
H	-3.281210	0.734716	-0.717641
O	5.215475	-2.037803	-0.388417
H	5.306917	-1.072972	0.466681
O	3.864517	-1.962974	-0.661681
Mn	2.837114	-0.604712	0.373669

**Table S2c. Computationally-derived coordinates for the product of reductive**

**MnSOD<sub>cd</sub> and O<sub>2</sub>**

C	4.848432	-2.559659	-0.434364
N	3.535455	-0.737656	-0.100469
C	-4.873272	-2.298668	-1.581531

C	-3.650869	-1.162044	0.714130
O	-3.015887	-0.650299	1.830884
C	-0.528057	-1.563805	-2.746220
N	-1.415555	-0.683609	-2.127359
N	0.583884	-0.202717	-1.301499
C	-4.062503	2.824605	1.249796
C	-2.621612	2.794856	1.261616
O	-1.935319	1.647876	1.367059
C	2.930409	3.269125	-0.559313
O	1.904770	3.875627	-0.119386
O	3.143015	1.976501	-0.440963
C	0.764354	-1.958842	3.649307
C	4.009511	4.050555	-1.279608
H	4.975583	3.901768	-0.784297
H	4.105676	3.687079	-2.309120
H	3.762051	5.112463	-1.290008
C	-0.963727	-2.589549	-3.739004
H	-1.736280	-3.248725	-3.323459
H	-1.373658	-2.132663	-4.648976
H	-0.114804	-3.212279	-4.034602
C	0.708190	-1.245601	-2.225920
H	1.663865	-1.690586	-2.444997
C	-0.715581	0.120282	-1.273185
H	-1.171021	0.866375	-0.641394
C	5.460571	-3.917460	-0.530310
H	5.708741	-4.185035	-1.565471
H	6.380395	-3.996857	0.063301
H	4.760769	-4.668609	-0.154894
C	3.625053	-2.130330	0.024032
H	2.814330	-2.706702	0.433156
C	4.689454	-0.320832	-0.630695
H	4.901432	0.708983	-0.858777
C	0.789344	-2.749061	4.915188
H	0.262985	-2.233104	5.728176
H	0.323408	-3.735423	4.793656
H	1.821816	-2.906956	5.238728
C	1.777968	-1.428279	2.878176
H	2.841403	-1.477847	3.039227
C	-0.095483	-0.868955	1.893025
H	-0.833629	-0.449513	1.245469
C	-4.765060	3.753609	2.172833
H	-4.148383	4.588098	2.534933
H	-5.712561	4.122007	1.764949
H	-5.033890	3.127436	3.046349

C	-5.568864	-2.908198	-2.780763
H	-6.618001	-3.148210	-2.558133
H	-5.571993	-2.223325	-3.636514
H	-5.085934	-3.840302	-3.096502
C	-4.225220	-3.104521	-0.627827
H	-4.194006	-4.181743	-0.772731
C	-4.900002	-0.909405	-1.350394
H	-5.419962	-0.262955	-2.054132
C	-4.306922	-0.335906	-0.218336
H	-4.375066	0.735663	-0.029657
C	-3.621418	-2.549638	0.503563
H	-3.113568	-3.178643	1.227249
N	-2.196894	3.992354	0.910224
H	-1.320849	4.012982	0.369280
N	-0.414181	-1.595759	2.994679
N	1.228881	-0.744678	1.782611
H	-1.376623	-1.753782	3.262508
H	-2.425774	-0.695701	-2.201414
H	6.437697	-1.350671	-1.230077
N	5.508816	-1.393448	-0.841954
H	0.953796	2.796171	0.610975
O	0.665443	1.879066	0.910147
H	-0.292374	1.801969	1.222598
H	-2.723643	0.337869	1.715166
Mn	1.983388	0.510040	0.336567
O	-0.543903	3.353419	-2.149620
O	0.444675	3.544647	-2.897312

**Table S2d. Computationally-derived coordinates for the reactant of reductive**

**MnSOD<sub>cd</sub> and OOH**

C	4.104933	2.074906	-2.537362
N	3.506188	0.508054	-1.014539
C	-7.635633	-2.254022	-0.217102
C	-5.048523	-1.119585	-0.196941
O	-3.766288	-0.589275	-0.183956
C	0.826968	2.258274	2.836068
N	0.096715	2.403933	1.661979
N	1.718268	0.957524	1.209315
C	-3.165337	4.377055	0.094162
C	-3.183880	2.908527	-0.064682

O	-3.733604	1.903044	-0.632501
C	2.703548	-3.030250	0.943501
O	2.012061	-2.168929	1.623992
O	3.345894	-2.524986	-0.077804
C	-0.809375	-0.575884	-2.026727
C	2.755821	-4.477142	1.291450
H	3.425754	-5.010647	0.616648
H	3.106253	-4.595048	2.321631
H	1.752349	-4.912315	1.230484
C	0.485836	2.975754	4.099882
H	0.578826	4.063013	3.987627
H	-0.543841	2.766479	4.413181
H	1.153849	2.662398	4.906896
C	1.835934	1.361370	2.543954
H	2.598199	0.955864	3.186387
C	0.653316	1.617941	0.714279
H	0.241113	1.507131	-0.272482
C	4.212307	3.237341	-3.466833
H	5.082600	3.864872	-3.237510
H	4.296883	2.918753	-4.513469
H	3.321932	3.865610	-3.383540
C	3.120753	1.689658	-1.658082
H	2.190816	2.179284	-1.435525
C	4.717099	0.175825	-1.487323
H	5.319691	-0.661245	-1.148900
C	-1.748200	-0.147032	-3.105732
H	-2.307941	-0.995706	-3.516372
H	-2.477795	0.574942	-2.718638
H	-1.198071	0.322042	-3.925969
C	0.562575	-0.503779	-1.906100
H	1.287454	-0.150682	-2.617244
C	-0.194278	-1.377128	-0.033839
H	-0.248205	-1.764605	0.967263
C	-4.135659	5.128049	0.976240
H	-4.579914	4.458788	1.720713
H	-3.637624	5.948818	1.510106
H	-4.949741	5.562607	0.380383
C	-9.024778	-2.855288	-0.196995
H	-9.699358	-2.327990	-0.881066
H	-9.008634	-3.910966	-0.490359
H	-9.474366	-2.803652	0.804768
C	-7.441862	-0.880989	-0.448467
H	-8.303228	-0.246599	-0.641408
C	-6.498225	-3.044929	0.018569



H	-6.617081	-4.110836	0.195339
C	-5.215663	-2.490346	0.032846
H	-4.344248	-3.108568	0.221757
C	-6.167293	-0.309003	-0.441796
H	-6.022898	0.749520	-0.630128
N	-2.236259	3.272717	0.760072
H	-0.841913	2.895109	1.456330
N	-1.260486	-1.129443	-0.830536
N	0.941426	-0.994371	-0.649153
H	-2.266629	-1.153003	-0.546675
H	-2.679162	4.978766	-0.676115
H	5.977855	1.085864	-2.910563
N	5.103090	1.102225	-2.409743
O	4.122243	-0.397737	1.472281
H	4.460520	0.516670	1.546388
H	-3.732909	0.442255	-0.282533
O	6.019958	-2.323533	-0.173754
H	5.156488	-2.779792	-0.362866
O	5.975620	-2.317916	1.345386
H	5.345188	-1.543798	1.511563
Mn	2.659433	-0.646764	0.422206

**Table S2e. Computationally-derived coordinates for the transition state of reductive MnSOD<sub>cd</sub> and OOH**

C	4.348901	2.068225	-2.755767
N	3.470664	0.416615	-1.479289
C	-7.613716	-2.024979	-0.387581
C	-4.998796	-0.973078	-0.201132
O	-3.701773	-0.485260	-0.113525
C	1.019832	1.676674	2.863750
N	0.383336	2.184191	1.727073
N	1.904149	0.744477	1.007225
C	-2.958989	4.416734	0.726057
C	-3.005752	2.979485	0.385391
O	-3.626398	2.048388	-0.234164
C	2.843000	-3.115963	0.371741
O	2.235252	-2.308519	1.193263
O	3.237620	-2.552549	-0.741412
C	-0.903306	-0.249058	-2.135865
C	3.125530	-4.535196	0.705001
H	3.440259	-5.088314	-0.180720

H	3.931261	-4.539002	1.450138
H	2.247618	-5.006806	1.155646
C	0.645308	2.092769	4.247236
H	0.839798	3.158967	4.417103
H	-0.419874	1.919784	4.442146
H	1.222472	1.523668	4.980600
C	1.965552	0.782191	2.410851
H	2.667431	0.161691	2.954616
C	0.938575	1.616212	0.639779
H	0.587480	1.778648	-0.363841
C	4.813327	3.350371	-3.361603
H	5.902639	3.371164	-3.490158
H	4.356773	3.528959	-4.343100
H	4.541488	4.187551	-2.714088
C	3.671530	1.796483	-1.588674
H	3.310708	2.476645	-0.837458
C	4.019284	-0.151653	-2.558611
H	4.048382	-1.210599	-2.752140
C	-1.918886	0.369009	-3.038751
H	-2.552722	-0.388704	-3.514410
H	-2.575449	1.044972	-2.477199
H	-1.426954	0.942015	-3.829567
C	0.474103	-0.217548	-2.131966
H	1.140089	0.251178	-2.833466
C	-0.138802	-1.374845	-0.363079
H	-0.114599	-1.918776	0.564205
C	-3.813389	5.040003	1.805426
H	-4.169396	4.277251	2.506106
H	-3.251054	5.791200	2.376484
H	-4.690306	5.538780	1.370828
C	-9.017945	-2.586517	-0.455987
H	-9.673904	-1.952832	-1.063676
H	-9.026353	-3.592074	-0.891391
H	-9.473433	-2.660893	0.541624
C	-7.383745	-0.638409	-0.416671
H	-8.227912	0.039283	-0.515609
C	-6.498146	-2.871073	-0.268034
H	-6.645026	-3.947858	-0.247337
C	-5.201931	-2.357802	-0.171994
H	-4.347440	-3.019098	-0.073005
C	-6.095075	-0.106433	-0.325879
H	-5.922435	0.964023	-0.358292
N	-1.963997	3.246238	1.129778
H	-0.536798	2.745400	1.636747

N	-1.263068	-0.985099	-1.008156
N	0.948361	-0.911375	-1.011834
H	-2.242386	-1.032573	-0.644367
H	-2.563699	5.115916	-0.013165
H	5.041275	0.660143	-4.223122
N	4.558673	0.819927	-3.352586
O	4.339514	-0.632728	0.913555
H	4.929379	0.112465	0.702906
H	-3.640469	0.547204	-0.072437
O	4.445907	-2.669425	3.170543
H	3.533700	-2.791520	3.515045
O	4.518508	-1.153531	3.134034
H	4.460716	-0.942307	1.902569
Mn	2.701764	-0.741400	-0.028154

**Table S2f. Computationally-derived Coordinates for the product of oxidized MnSOD<sub>cd</sub> and H<sub>2</sub>O<sub>2</sub>**

C	-3.906412	-4.165304	-1.788298
N	-3.391678	-2.107180	-0.997779
C	7.089521	3.267525	-1.292793
C	4.746154	1.804679	-0.708485
O	3.575838	1.107406	-0.436140
C	-0.910759	-3.220801	2.765158
N	0.215064	-2.547149	2.310400
N	-1.486689	-1.783870	1.097283
C	4.358176	-2.880111	2.632225
C	3.814733	-1.931452	1.636512
O	4.063355	-1.156521	0.650398
C	-3.455450	1.930517	-1.248091
O	-2.481612	2.434664	-0.644783
O	-3.709739	0.613276	-1.238540
C	1.123669	-0.790978	-1.915559
C	-4.442764	2.756076	-2.037965
H	-4.527624	2.373073	-3.060509
H	-5.434371	2.686276	-1.576319
H	-4.125660	3.799490	-2.057850
C	-0.866363	-4.239761	3.855893
H	-0.209379	-5.079921	3.599326
H	-0.492920	-3.809681	4.793153
H	-1.866543	-4.639861	4.045707
C	-1.965070	-2.735598	2.012499

H	-3.007010	-3.007046	2.054822
C	-0.163867	-1.699534	1.327128
H	0.537143	-1.060634	0.826513
C	-3.985058	-5.612301	-2.143520
H	-4.923282	-6.067482	-1.802058
H	-3.910007	-5.773058	-3.226332
H	-3.163298	-6.156485	-1.671458
C	-3.021910	-3.458439	-1.010060
H	-2.171043	-3.810789	-0.456772
C	-4.488811	-1.989481	-1.759003
H	-4.983704	-1.055240	-1.960020
C	2.336939	-1.442187	-2.490794
H	2.768698	-0.849055	-3.305266
H	3.107800	-1.566205	-1.720052
H	2.084449	-2.429259	-2.887867
C	-0.164036	-1.237252	-1.732977
H	-0.601007	-2.180045	-2.008724
C	-0.067558	0.787604	-0.857338
H	-0.354254	1.710622	-0.385160
C	5.064873	-2.444945	3.895262
H	4.812839	-1.408209	4.142953
H	4.784117	-3.076516	4.749334
H	6.155020	-2.511151	3.776213
C	8.348006	4.056073	-1.586775
H	9.095192	3.445220	-2.108709
H	8.133630	4.927713	-2.214427
H	8.820211	4.423556	-0.665353
C	7.155658	1.999387	-0.687386
H	8.126356	1.575525	-0.442183
C	5.818873	3.780221	-1.600471
H	5.737610	4.757121	-2.069759
C	4.653651	3.063064	-1.312050
H	3.676117	3.471480	-1.545748
C	6.003895	1.266373	-0.395069
H	6.057796	0.285092	0.063931
N	2.860826	-2.401950	2.397123
H	1.261926	-2.617384	2.550304
N	1.159409	0.485215	-1.347672
N	-0.899107	-0.254121	-1.057841
H	2.046375	0.990093	-1.149066
H	4.561216	-3.905920	2.318724
H	-5.611100	-3.401765	-2.853114
N	-4.825900	-3.213894	-2.249895
O	-3.282111	0.009313	1.427364

H	-3.064345	-0.384798	2.294446
H	3.724592	0.236083	0.080052
Mn	-2.632878	-0.501107	-0.129240
O	-6.335977	10.279428	3.277603
H	-5.706885	9.751556	3.818948
O	-5.943268	9.728944	1.904242
H	-6.488619	10.333608	1.352581

**Table S2g. Computationally-derived coordinates for the reactant of oxidized**

**Fe-sub-MnSOD<sub>cd</sub> and OOH**

C	-4.371833	1.364220	2.65686
N	-3.435752	-0.044001	1.154136
C	7.803923	-1.885898	-0.049001
C	5.149390	-0.917890	0.00522
O	3.837005	-0.471835	0.02729
C	-1.158055	2.518226	-2.449261
N	-0.307746	2.484456	-1.349921
N	-1.777243	0.844985	-1.048907
C	2.928555	4.456746	0.30841
C	3.036345	2.983949	0.28969
O	3.664764	1.955805	0.72020
C	-2.541227	-3.211960	-1.036375
O	-1.996942	-2.297996	-1.790818
O	-3.130357	-2.779631	0.039005
C	0.927439	-0.858749	1.91484
C	-2.458036	-4.665087	-1.364455
H	-1.560993	-5.093163	-0.899559
H	-3.328711	-5.193546	-0.970583
H	-2.381443	-4.807736	-2.444230
C	-1.006199	3.498644	-3.565109
H	-1.103611	4.533314	-3.213620
H	-0.025478	3.409559	-4.048043
H	-1.772315	3.328598	-4.326953
C	-2.072549	1.502698	-2.248224
H	-2.909906	1.209137	-2.855364
C	-0.705135	1.480169	-0.535954
H	-0.201935	1.241177	0.38230
C	-4.823414	2.521069	3.48451
H	-5.915403	2.630402	3.47808
H	-4.503984	2.427890	4.53033
H	-4.396696	3.447460	3.09177

C	-3.548346	1.288173	1.55715
H	-3.039361	2.076020	1.03230
C	-4.179793	-0.776973	1.985629
H	-4.316325	-1.841740	1.914597
C	1.871445	-0.512195	3.018711
H	2.486304	-1.371057	3.31344
H	2.551227	0.290651	2.70798
H	1.319128	-0.174645	3.90002
C	-0.449658	-0.844620	1.832075
H	-1.171200	-0.603558	2.591636
C	0.296204	-1.425043	-0.152415
H	0.341371	-1.681689	-1.195255
C	3.819999	5.364452	-0.50727
H	4.272330	4.815186	-1.33993
H	3.255887	6.210165	-0.92395
H	4.630619	5.775689	0.10979
C	9.229207	-2.393517	-0.103566
H	9.826953	-2.005306	0.72974
H	9.265065	-3.487599	-0.059125
H	9.733323	-2.088151	-1.031295
C	7.521980	-0.554665	0.30622
H	8.340454	0.111765	0.56687
C	6.720777	-2.720116	-0.371458
H	6.908514	-3.754974	-0.646096
C	5.405339	-2.247677	-0.349587
H	4.575820	-2.898290	-0.606215
C	6.214366	-0.065288	0.33726
H	6.001390	0.959903	0.62073
N	2.039825	3.382940	-0.45749
H	0.602480	3.007544	-1.13406
N	1.373016	-1.234136	0.64975
N	-0.836056	-1.184420	0.531044
H	2.369042	-1.169726	0.34550
H	2.437448	4.933168	1.15919
H	-5.376037	-0.255755	3.650217
N	-4.759503	0.043559	2.91173
O	-3.998385	-0.547662	-1.484648
H	-4.041640	-1.140757	-2.267942
H	3.734719	0.541508	0.22817
Fe	-2.566823	-0.875176	-0.38896
O	-6.577958	-0.305185	-1.737623
H	-6.622173	0.532630	-1.217499
O	-5.671577	-1.129144	-0.970408

**Table S2h. Computationally-derived coordinates for the transition state of oxidized Fe-sub-MnSOD<sub>cd</sub> and OOH**

C	4.358131	1.986399	-2.070751
N	3.466320	0.197618	-1.012087
C	-7.625868	-1.727157	-0.180675
C	-4.968620	-0.766729	-0.223490
O	-3.655476	-0.321517	-0.240907
C	1.033807	1.977977	2.799490
N	0.408863	2.207227	1.574425
N	1.884578	0.586810	1.234324
C	-2.574745	4.540614	-0.055897
C	-2.777551	3.083731	-0.191611
O	-3.456114	2.146890	-0.735502
C	2.092809	-3.340658	1.076558
O	2.005271	-2.253878	1.810633
O	2.511844	-3.159841	-0.121560
C	-0.688983	-0.738152	-2.057986
C	1.691167	-4.673387	1.613086
H	0.598116	-4.732420	1.679904
H	2.049221	-5.467515	0.956462
H	2.091800	-4.809854	2.621536
C	0.685068	2.731643	4.040006
H	0.884136	3.805107	3.932703
H	-0.376246	2.620201	4.292714
H	1.273369	2.363311	4.885033
C	1.956449	0.977940	2.574834
H	2.669686	0.538351	3.243640
C	0.939572	1.367706	0.664152
H	0.620478	1.334172	-0.360768
C	4.852107	3.327128	-2.499956
H	5.938471	3.332182	-2.654500
H	4.378964	3.661706	-3.431953
H	4.625514	4.069491	-1.730542
C	3.702523	1.572383	-0.935542
H	3.408578	2.148694	-0.079124
C	3.979831	-0.228343	-2.168001
H	4.043627	-1.255511	-2.476180
C	-1.579265	-0.369838	-3.198551
H	-2.187758	-1.219542	-3.530408
H	-2.265409	0.434829	-2.907964
H	-0.986533	-0.026618	-4.050718

C	0.684536	-0.771114	-1.926524
H	1.434703	-0.564928	-2.666333
C	-0.155900	-1.315467	0.030614
H	-0.252418	-1.546828	1.075603
C	-3.434670	5.418592	0.823477
H	-3.941448	4.821128	1.588823
H	-2.834649	6.185605	1.331762
H	-4.202187	5.934101	0.230362
C	-9.052219	-2.232312	-0.133489
H	-9.657928	-1.804181	-0.941187
H	-9.092368	-3.322907	-0.228227
H	-9.544686	-1.968286	0.812855
C	-7.345574	-0.373097	-0.438017
C	-8.166423	0.314377	-0.626283
C	-6.539816	-2.587461	0.049545
H	-6.726187	-3.639938	0.246954
C	-5.222638	-2.119163	0.032345
H	-4.391050	-2.791508	0.216105
C	-6.036654	0.112756	-0.462234
H	-5.826350	1.156601	-0.669384
N	-1.781756	3.340100	0.617203
H	-0.460481	2.799942	1.319982
N	-1.193088	-1.091591	-0.810638
N	1.007939	-1.116905	-0.612827
H	-2.200496	-1.002366	-0.540835
H	-2.027408	5.065764	-0.840880
H	4.994146	0.771829	-3.724443
N	4.513423	0.829594	-2.840849
O	4.062666	-0.653177	1.831042
H	3.925748	-1.314774	2.540039
H	-3.551736	0.705524	-0.374310
Fe	2.742310	-1.022228	0.407743
O	5.680896	-1.190224	0.025871
H	5.303017	-0.823966	1.206343
O	4.496811	-1.941724	-0.189985

**Table S2i. Computationally-derived coordinates for the product of reductive**

**Fe-sub-MnSOD<sub>cd</sub> and O<sub>2</sub>**

C	4.967181	-2.336642	-1.442255
N	3.776761	-0.661691	-0.469816
C	-5.567353	-1.920802	-1.383067



C	-3.684344	-1.515455	0.680508
O	-2.759016	-1.378292	1.721485
C	-0.329351	-0.105736	-2.623988
N	-0.727986	1.086402	-2.031124
N	1.128802	0.454591	-0.984226
C	-3.461034	2.830835	1.325101
C	-2.390262	2.125755	1.880849
O	-1.640376	1.137696	2.050661
C	3.185348	3.259975	0.258224
O	2.178619	3.679441	0.922429
O	3.466825	1.996531	0.062487
C	0.926671	-2.816600	2.769088
C	4.137651	4.262434	-0.355341
H	5.165649	4.040923	-0.049028
H	4.096258	4.191091	-1.448589
H	3.869832	5.273926	-0.048518
C	-1.100736	-0.761830	-3.721907
H	-2.121877	-1.005611	-3.402717
H	-1.178304	-0.116994	-4.606174
H	-0.612712	-1.692517	-4.026670
C	0.828825	-0.486988	-1.974008
H	1.447112	-1.352099	-2.138760
C	0.170773	1.399139	-1.063503
H	0.081850	2.269267	-0.443814
C	5.510866	-3.626712	-1.959786
H	5.586726	-3.631056	-3.054803
H	6.508322	-3.844638	-1.556564
H	4.852207	-4.450528	-1.672576
C	3.844940	-2.042848	-0.703365
H	3.092132	-2.710442	-0.324469
C	4.846018	-0.119883	-1.063154
H	5.058715	0.933425	-1.068672
C	0.856428	-3.859561	3.834579
H	0.207247	-3.550380	4.663376
H	0.470572	-4.812484	3.450679
H	1.852312	-4.044890	4.246193
C	1.990296	-2.103676	2.253847
H	3.030895	-2.158562	2.526594
C	0.209319	-1.407659	1.184735
H	-0.458975	-0.881683	0.533358
C	-4.678566	2.999587	0.544411
H	-5.088904	4.007918	0.648792
H	-4.401912	2.778026	-0.512388
H	-5.430505	2.260424	0.847712

C	-6.602496	-2.121003	-2.469122
H	-7.574436	-1.694476	-2.183708
H	-6.299900	-1.636792	-3.404062
H	-6.764754	-3.184486	-2.677880
C	-5.395136	-2.871037	-0.360785
H	-5.998070	-3.775349	-0.364521
C	-4.764722	-0.768417	-1.347441
H	-4.862145	-0.010332	-2.119546
C	-3.824021	-0.557830	-0.332640
H	-3.217627	0.342390	-0.371445
C	-4.467510	-2.674518	0.665145
H	-4.345078	-3.404160	1.458375
N	-2.662411	3.448505	2.255616
H	-2.169501	4.138405	-1.134377
N	-0.189044	-2.358241	2.073548
N	1.530233	-1.218763	1.267904
H	-1.177209	-2.546676	2.222155
H	-1.670908	1.611393	-2.116523
H	6.441640	-0.957776	-2.174305
N	5.588964	-1.103729	-1.658529
H	1.490087	2.454298	1.562641
O	1.300109	1.461918	1.727652
H	0.383186	1.261231	2.011072
H	-2.397934	-0.453756	1.810451
O	-2.147722	3.238967	-0.741938
O	-2.956292	2.430991	-1.778521
Fe	2.393420	0.369318	0.479011

**Table S2j. Computationally-derived coordinates for the reactant of reductive**

**Fe-sub-MnSOD<sub>cd</sub> and OOH**

C	-5.307698	-2.750461	0.229226
N	-4.064630	-0.972677	-0.443016
C	7.306844	-1.111443	-1.897400
C	4.624393	-1.174946	-1.005332
O	3.302407	-1.187541	-0.593399
C	-0.880855	1.070684	3.030961
N	-0.561271	-0.238296	2.698587
N	-2.024254	0.452260	1.166377
C	2.137685	-3.161522	3.865331
C	2.338457	-2.613383	2.507503
O	2.957937	-2.723057	1.395545

C	-2.765134	2.191112	-2.457358
O	-2.146648	2.413960	-1.325964
O	-3.505157	1.131273	-2.522762
C	0.102217	-2.121959	-1.740942
C	-2.590777	3.106319	-3.629243
H	-3.426573	3.001773	-4.323720
H	-2.499207	4.142878	-3.294826
H	-1.666301	2.846036	-4.159754
C	-0.275485	1.781872	4.196146
H	-0.558865	1.317862	5.149211
H	0.819642	1.772416	4.143418
H	-0.603060	2.825338	4.219392
C	-1.794094	1.487941	2.080861
H	-2.247598	2.458690	1.971381
C	-1.260885	-0.574589	1.586575
H	-1.152052	-1.518702	1.083296
C	-5.940622	-3.897732	0.944208
H	-7.015023	-3.740848	1.105193
H	-5.820577	-4.840608	0.395389
H	-5.475563	-4.027157	1.924884
C	-4.300401	-1.885475	0.592422
H	-3.733476	-1.855780	1.505896
C	-4.919597	-1.273415	-1.426415
H	-4.992842	-0.743286	-2.360002
C	0.802588	-3.423383	-1.956220
H	1.389863	-3.423592	-2.882769
H	1.492182	-3.634369	-1.129722
H	0.078513	-4.240796	-2.016946
C	-1.234426	-1.787326	-1.663404
H	-2.097649	-2.417130	-1.785003
C	-0.104698	0.054826	-1.286658
H	0.149806	1.070455	-1.042478
C	3.090772	-2.906723	5.010510
H	3.701157	-2.018564	4.814473
H	2.550168	-2.746862	5.953682
H	3.767833	-3.759873	5.154641
C	8.749098	-1.057784	-2.354849
H	9.223194	-2.045469	-2.307956
H	8.827394	-0.698539	-3.386965
H	9.349241	-0.382506	-1.728538
C	6.922022	-1.907264	-0.803633
H	7.669743	-2.510834	-0.294865
C	6.311475	-0.352959	-2.535634
H	6.578212	0.267892	-3.387218

C	4.984002	-0.377341	-2.098852
H	4.223108	0.214842	-2.596475
C	5.600451	-1.946822	-0.354004
H	5.307923	-2.569252	0.484870
N	1.447401	-1.915253	3.164221
H	0.232925	-0.868602	3.062795
N	0.796824	-0.939318	-1.508299
N	-1.355678	-0.426513	-1.361136
H	1.820178	-0.892870	-1.334659
H	1.492091	-4.033520	3.986788
H	-6.408289	-2.770568	-1.613913
N	-5.686809	-2.346435	-1.053438
O	-4.296810	1.833556	0.163955
H	-4.557143	1.714949	1.093659
H	3.129678	-1.753295	0.258225
O	2.647112	12.237554	1.338648
H	3.577043	11.902102	1.264317
O	1.823914	11.136249	1.110008
H	-3.985753	2.742129	-0.016099
Fe	-2.878270	0.575922	-0.618604

**Table S2k. Computationally-derived coordinates for the transition state of reductive Fe-sub-MnSOD<sub>cd</sub> and OOH**

C	4.157426	2.131253	-2.772036
N	3.403239	0.433530	-1.483240
C	-7.630128	-2.012237	-0.352254
C	-5.008771	-0.978185	-0.155148
O	-3.709143	-0.498726	-0.062077
C	1.078027	1.617645	2.907499
N	0.377286	2.109506	1.805233
N	1.878885	0.693652	1.015758
C	-2.896400	4.392514	0.710591
C	-2.978817	2.949857	0.404306
O	-3.603126	2.025218	-0.222889
C	2.923707	-3.060380	0.287877
O	2.243449	-2.298148	1.093978
O	3.321790	-2.459079	-0.808720
C	-0.929973	-0.319207	-2.115674
C	3.284325	-4.458026	0.621202
H	3.633144	-4.995401	-0.261371

H	4.085844	-4.401969	1.370418
H	2.435393	-4.976622	1.075037
C	0.775320	2.033922	4.308601
H	0.955192	3.105163	4.461987
H	-0.271757	1.837164	4.568672
H	1.408622	1.482544	5.008399
C	2.014770	0.734161	2.410704
H	2.753340	0.125219	2.920552
C	0.881930	1.541853	0.691244
H	0.476176	1.696845	-0.292738
C	4.518675	3.438568	-3.393981
H	5.604784	3.559693	-3.489354
H	4.079535	3.552355	-4.392879
H	4.148393	4.259440	-2.775114
C	3.471254	1.822356	-1.619559
H	3.032633	2.480305	-0.890807
C	4.037717	-0.106017	-2.529344
H	4.167805	-1.162080	-2.694287
C	-1.955573	0.253971	-3.036704
H	-2.595508	-0.525678	-3.466102
H	-2.604318	0.957361	-2.500224
H	-1.473231	0.786760	-3.860775
C	0.447286	-0.278384	-2.121818
H	1.106707	0.161141	-2.847567
C	-0.150832	-1.353367	-0.293966
H	-0.116532	-1.852964	0.657242
C	-3.777647	5.075348	1.730585
H	-4.193906	4.345616	2.433248
H	-3.216001	5.822028	2.308209
H	-4.614426	5.592266	1.241334
C	-9.037969	-2.563952	-0.426141
H	-9.686845	-1.925796	-1.036643
H	-9.051912	-3.569653	-0.861197
H	-9.497882	-2.634843	0.569688
C	-7.388699	-0.628229	-0.400951
H	-8.226341	0.054397	-0.519370
C	-6.522669	-2.865167	-0.207612
H	-6.678449	-3.940296	-0.171275
C	-5.223462	-2.360718	-0.106095
H	-4.375407	-3.027004	0.012837
C	-6.096712	-0.105096	-0.305235
H	-5.915269	0.963323	-0.352862
N	-1.965221	3.197612	1.192668
H	-0.536341	2.673660	1.744190

N	-1.278805	-1.006409	-0.954406
N	0.927832	-0.916171	-0.971701
H	-2.257787	-1.049054	-0.585096
H	-2.440457	5.057119	-0.025764
H	5.026426	0.763780	-4.182898
N	4.504462	0.895779	-3.330558
O	4.300756	-0.579577	0.882654
H	4.972859	0.031270	0.538497
H	-3.638390	0.536133	-0.034079
Fe	2.671505	-0.722257	-0.069704
O	4.505620	-2.648470	3.067672
H	3.679533	-2.788567	3.578160
O	4.568362	-1.118309	3.094002
H	4.453126	-0.865619	1.874441

**Table S2l. Computationally-derived coordinates for the product of oxidized Fe-sub-MnSOD<sub>cd</sub> and H<sub>2</sub>O<sub>2</sub>**

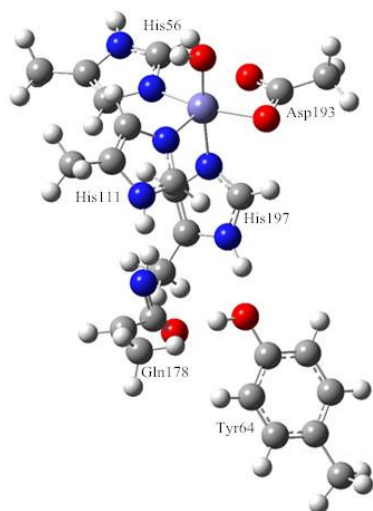
C	-4.456163	-3.887413	-0.807252
N	-3.614042	-1.790105	-0.874831
C	7.606675	0.728110	-1.880230
C	4.983565	0.161501	-0.997713
O	3.683522	-0.105098	-0.590803
C	-1.841029	-1.169770	3.295626
N	-0.628544	-0.675188	2.831372
N	-2.069508	-0.450109	1.159360
C	3.172381	-1.482393	4.234812
C	3.067628	-1.257320	2.777586
O	3.656419	-1.316460	1.645119
C	-2.724130	1.828367	-2.163174
O	-2.031995	1.832481	-1.059721
O	-3.313645	0.704581	-2.448149
C	0.895393	-2.021493	-1.405363
C	-2.856924	3.039235	-3.022139
H	-2.969449	2.752796	-4.070253
H	-3.754512	3.592993	-2.720086
H	-1.993303	3.695271	-2.894857
C	-2.018271	-1.724462	4.670546
H	-1.319549	-2.546812	4.866091
H	-1.844501	-0.960428	5.437974
H	-3.035208	-2.105517	4.801484
C	-2.734837	-1.018178	2.252651

H	-3.778340	-1.281351	2.213896
C	-0.803291	-0.246401	1.562492
H	-0.012444	0.173726	0.971382
C	-4.805630	-5.308804	-0.517388
H	-5.865033	-5.425278	-0.256295
H	-4.598179	-5.964915	-1.372170
H	-4.215817	-5.672377	0.327833
C	-3.559712	-3.024035	-0.220970
H	-2.901016	-3.191609	0.612260
C	-4.527378	-1.888829	-1.843315
H	-4.792894	-1.092585	-2.516945
C	1.910364	-3.113231	-1.323444
H	2.528567	-3.164993	-2.227609
H	2.581849	-2.950739	-0.471330
H	1.418790	-4.081351	-1.194140
C	-0.480229	-2.027563	-1.335432
H	-1.144106	-2.868218	-1.251899
C	0.130669	0.076354	-1.488038
H	0.110746	1.150714	-1.496120
C	3.867769	-0.525161	5.174936
H	3.951796	0.469056	4.723255
H	3.318852	-0.423357	6.121145
H	4.880585	-0.877778	5.413179
C	9.013029	1.053728	-2.336424
H	9.697581	0.215179	-2.160829
H	9.040887	1.289335	-3.405894
H	9.422203	1.921353	-1.800093
C	7.376525	0.054869	-0.666963
H	8.223916	-0.254308	-0.060059
C	6.488047	1.105032	-2.641380
H	6.635596	1.623492	-3.585218
C	5.186848	0.830255	-2.210055
H	4.329250	1.131213	-2.802739
C	6.084664	-0.231305	-0.220726
H	5.911035	-0.756879	0.712086
N	1.946800	-0.948005	3.376673
H	0.371250	-0.745804	3.241444
N	1.256513	-0.680931	-1.506252
N	-0.954505	-0.711384	-1.367749
H	2.232777	-0.338785	-1.383081
H	3.052062	-2.498813	4.614516
H	-5.767103	-3.482895	-2.461654
N	-5.055805	-3.146017	-1.832387
O	-4.247175	0.728209	0.002764

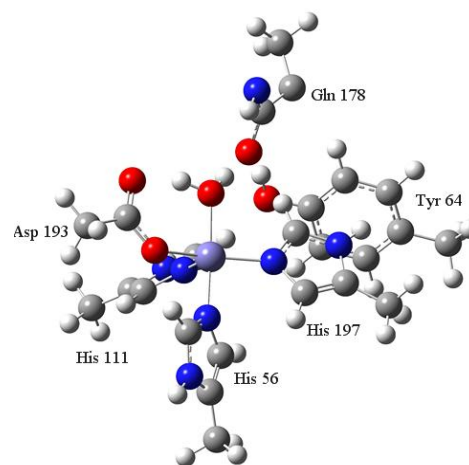
H	-4.473966	0.503873	0.926826
H	3.618107	-0.537214	0.343176
O	-2.928689	11.339116	1.974056
H	-2.654194	10.607993	2.572112
O	-2.594095	10.658858	0.643653
H	-2.835574	11.402008	0.046253
Fe	-2.737982	-0.035957	-0.653237



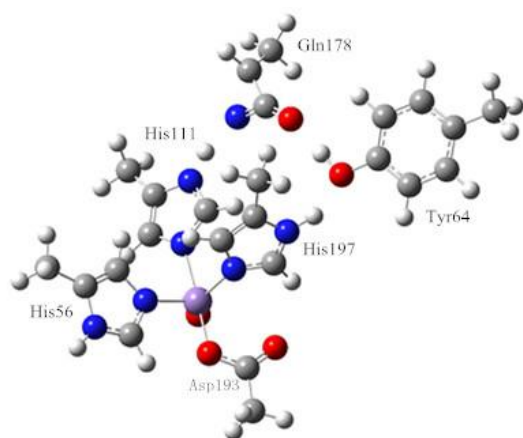
#### 4. The chemical models of MnSOD<sub>cd</sub> and Fe-sub-MnSOD<sub>cd</sub>



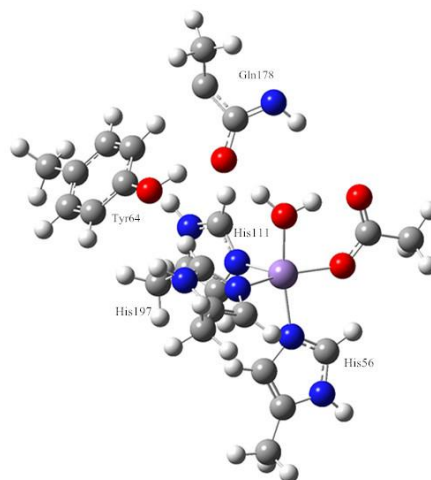
The oxidative Fe-sub-MnSOD<sub>cd</sub>



The reductive Fe-sub-MnSOD<sub>cd</sub>



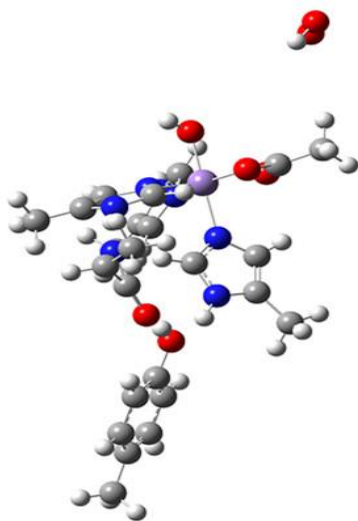
The oxidative MnSOD<sub>cd</sub>



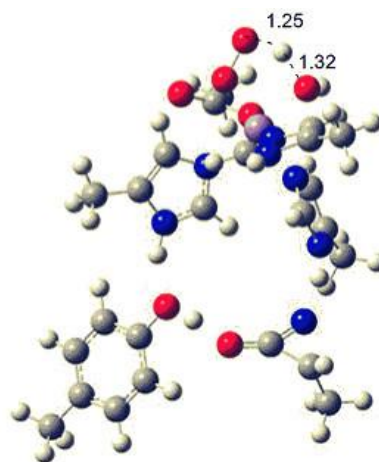
The reductive MnSOD<sub>cd</sub>

Fig. S2. The chemical models of MnSOD<sub>cd</sub> and Fe-sub-MnSOD<sub>cd</sub>

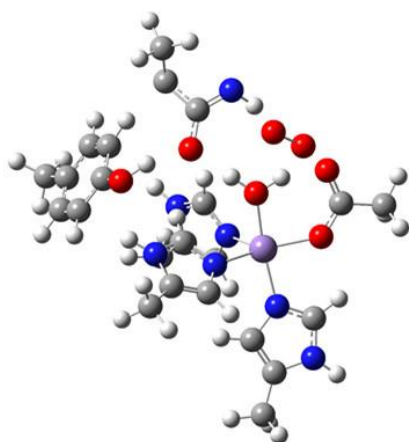
**5. The chemical configurations for the reactants, products and transition states in MnSOD<sub>cd</sub> and Fe-sub-MnSOD<sub>cd</sub>**



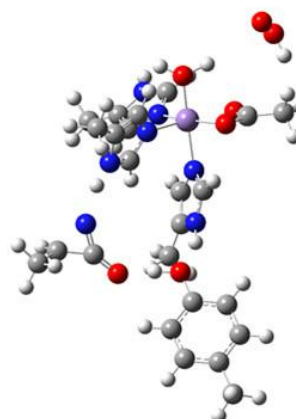
**The reactant of oxidized MnSOD<sub>cd</sub> and OOH**



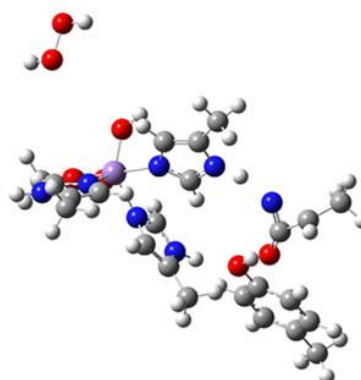
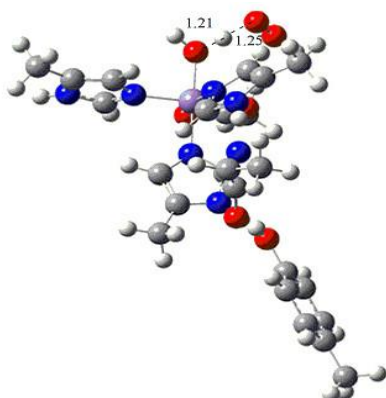
**The transition state of oxidized MnSOD<sub>cd</sub> and OOH**



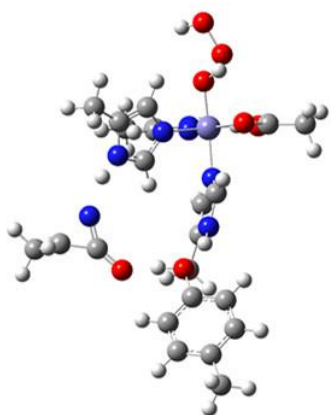
**The product of reductive MnSOD<sub>cd</sub> and O<sub>2</sub>**



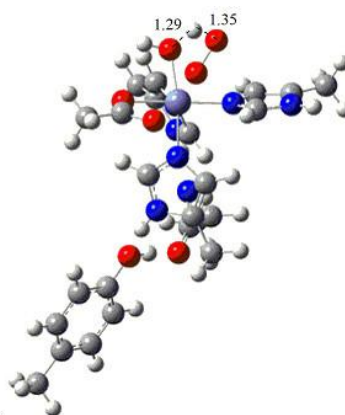
**The reactant of reductive MnSOD<sub>cd</sub> and OOH**



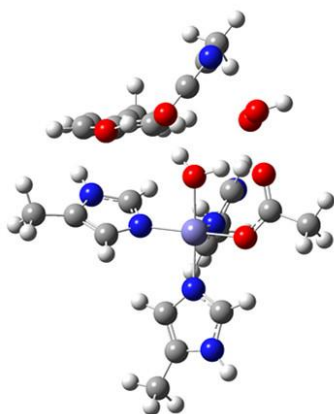
The transition state of reductive MnSOD<sub>cd</sub> and OOH



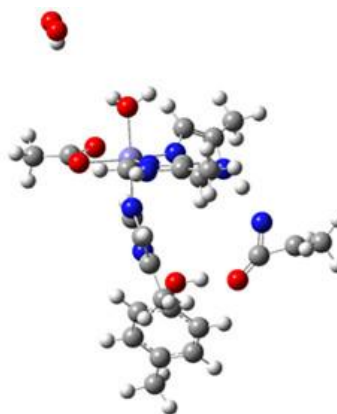
The product of oxidized MnSOD<sub>cd</sub> and H<sub>2</sub>O<sub>2</sub>



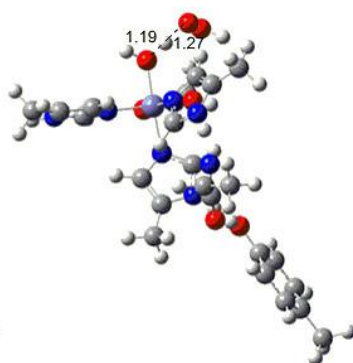
The reactant of oxidized Fe-sub-MnSOD<sub>cd</sub> and OOH



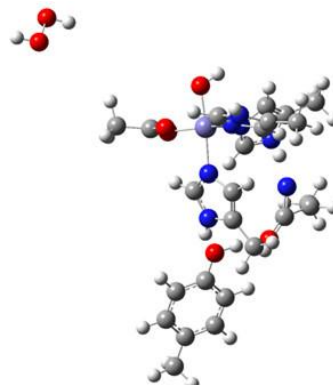
The transition state of oxidized Fe-sub-MnSOD<sub>cd</sub> and OOH



The product of reductive Fe-sub-MnSOD<sub>cd</sub> and O<sub>2</sub>



The reactant of reductive Fe-sub-MnSOD<sub>cd</sub> and OOH



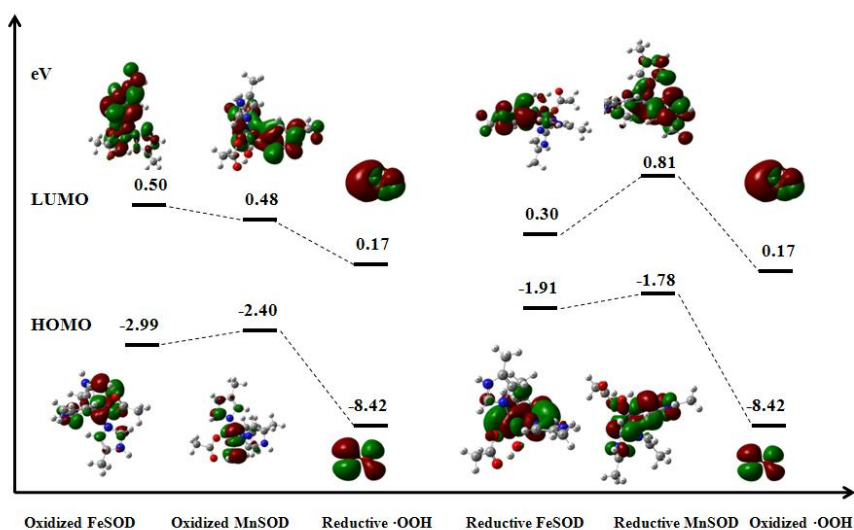
The transition state of reductive Fe-sub-MnSOD<sub>cd</sub> and OOH

The product of oxidized Fe-sub-MnSOD<sub>cd</sub> and H<sub>2</sub>O<sub>2</sub>

**Fig. S3.** The configurations of the reactants, products and transition states

## 6. The HUMO and LUMO energy gap between $\cdot\text{OOH}$ and $\text{MnSOD}_{\text{cd}}$

### /Fe-sub- $\text{MnSOD}_{\text{cd}}$



**Fig. S4.** The frontier molecular orbitals of Fe-sub- $\text{MnSOD}_{\text{cd}}$ ,  $\text{MnSOD}_{\text{cd}}$  and  $\cdot\text{OOH}$ . Solid values are orbital energies (in eV). According to symmetry principle, for the two pairs of frontier molecular orbital interactions between the reactants ( $\text{LUMO}_{\text{Fe-sub-MnSOD}}$  with  $\text{HOMO}_{\text{OOH}}$  and  $\text{LUMO}_{\text{MnSOD}}$  with  $\text{HOMO}_{\text{OOH}}$ ), the order of the LUMO orbital energies in the oxidized states is:  $\text{Fe-sub-MnSOD}_{\text{cd}} > \text{MnSOD}_{\text{cd}}$ . Therefore, the gap between  $\text{HOMO}_{\text{OOH}}$  and  $\text{LUMO}_{\text{Fe-sub-MnSOD}}$  is bigger than the corresponding gap between  $\text{HOMO}_{\text{OOH}}$  and  $\text{LUMO}_{\text{MnSOD}}$ . Meanwhile, the order of the HOMO orbital energies of the reductive states is:  $\text{Fe-sub-MnSOD}_{\text{cd}} < \text{MnSOD}_{\text{cd}}$ . Therefore, the gap between  $\text{LUMO}_{\text{OOH}}$  and  $\text{HOMO}_{\text{Fe-sub-MnSOD}}$  is also bigger than the corresponding gap between  $\text{LUMO}_{\text{OOH}}$  and  $\text{HOMO}_{\text{MnSOD}}$ . Thus the results indicated

that the catalytic activity of MnSOD<sub>cd</sub> was stronger than that of Fe-sub-MnSOD<sub>cd</sub> during the whole catalytic process.

## **Reference**

1. Li, W., Wang, H., Chen, Z., Ye, Q., Tian, Y., Xu, X., Huang, Z., Li, P., and Tan, X. (2014) Probing the metal specificity mechanism of superoxide dismutase from human pathogen *Clostridium difficile*, *Chem Commun* 50, 584-586.