Supporting Information

VTVH-MCD and DFT Studies of Thiolate Bonding to $\{FeNO\}^7/\{FeO_2\}^8$ Complexes of Isopenicillin *N* synthase: Substrate Determination of Oxidase versus Oxygenase Activity in Non-Heme Fe Enzymes

Christina D. Brown[1], Michael L. Neidig[1], Matthew B. Neibergall[2], John D. Lipscomb[2], Edward I. Solomon[1]**

[1] Department of Chemistry, Stanford University, Stanford, CA 94305-5080, USA;
[2] Department of Biochemistry, Molecular Biology and Biophysics and the Center for Metals in Biocatalysis, University of Minnesota, Minneapolis, MN 55455

Supporting Information Table 1:

Coordinates [Å] of optimized Fe-IPNS-ACV-NO Complex

Atom	X	Y	Z
C	-2.324936	-1.174203	-2.584401
N	-2.171501	-1.154039	-1.267761
C	-2.809322	-2.282266	-0.782526
C	-3.358287	-3.001852	-1.821474
N	-3.037747	-2.270425	-2.960698
Fe	-0.882464	0.156085	-0.063283
N	0.163266	0.443787	-1.425109
O	0.825161	0.045881	-2.324347
C	-4.122883	-4.286907	-1.869282
N	-2.295432	1.819558	-0.498278
C	-1.982137	3.136359	-0.774631
C	-3.130056	3.892859	-0.871542
N	-4.159846	2.985614	-0.648403
C	-3.613715	1.758289	-0.423765
C	-3.365082	5.347113	-1.130708
O	-0.102699	1.626769	1.268923
O	-2.283767	-0.335973	1.472525
C	-2.484294	0.229661	2.609232
C	-3.557429	-0.368113	3.537765
C	-4.255087	-1.625674	3.023923
S	0.412684	-1.600201	0.805536
C	1.479238	-2.396606	-0.462789
C	2.853234	-2.829786	0.078728
N	2.698617	-3.895455	1.068822
O	-1.881244	1.250827	3.041945
C	3.725548	-1.656125	0.599000
O	4.344306	-1.741563	1.662559
N	3.821618	-0.555679	-0.215133
C	4.704753	0.563509	0.110652
C	5.512954	0.946461	-1.142390
O	5.421781	0.412423	-2.243774
C	4.007554	1.803684	0.818710
C	3.341388	1.349932	2.121319
C	3.025751	2.518006	-0.117183
O	6.391868	1.973541	-0.846404
H	6.879028	2.144706	-1.681223
H	5.426845	0.159698	0.842817
H	4.831678	2.495898	1.059997
H	2.845456	2.201928	2.614754
H	2.593618	0.563543	1.923706
H	4.068516	0.916851	2.823702
H	2.565354	3.380188	0.390357
H	3.527797	2.891055	-1.025049
H	2.207604	1.849259	-0.426177
H	3.407092	-0.570195	-1.142994
H	3.559782	-3.902395	1.628408
H	1.972481	-3.586603	1.727829
H	0.963159	-3.306742	-0.804826
H	1.597089	-1.744083	-1.342500
H	-4.249323	-4.676786	-0.850330
H	-5.127610	-4.158375	-2.306099

H	-3.596073	-5.057544	-2.456468
H	-3.270753	-2.526068	-3.914903
H	-1.934831	-0.440988	-3.283282
H	-2.811777	-2.486056	0.282849
H	-5.015737	-1.974732	3.740739
H	-4.752634	-1.440436	2.059570
H	-3.531313	-2.440051	2.870384
H	-3.061357	-0.559676	4.503585
H	-4.285073	0.436627	3.740685
H	0.722334	1.278375	1.658140
H	-0.804655	1.589042	2.041588
H	-2.402083	5.856453	-1.271715
H	-3.968371	5.516520	-2.038621
H	-3.879989	5.838424	-0.288163
H	-5.149773	3.207754	-0.622366
H	-4.186397	0.866806	-0.190684
H	-0.948564	3.456606	-0.858633
H	3.410384	-3.248821	-0.785601

Supporting Information Table 2: Key Computational Results for Fe-IPNS-ACV-NO

Bond length	(Å)	Bond Angle	(Degrees)	Total Atomic Charge (Mulliken)	
Fe-S	2.35	S-Fe-N_{eq}	169	S	-0.47
Fe-N_{NO}	1.74	S-Fe-N_{ax}	95	Fe	1.35
N-O	1.19	S-Fe-NO	95	NO	-0.37
Fe-O_{OH2}	2.13	S- Fe-O_{Asp}	86	Total Spin Density	
Fe-O_{Asp}	2.14	S- Fe-O_{OH}	95	S	0.13
Fe-N_{eq}	2.23	Fe-N-O	151	Fe	3.44
Fe-N_{ax}	2.20			NO	-0.79

Supporting Information Table 3:

Coordinates [Å] of optimized Fe-IPNS-ACV-O_2 Complex

Atom	X	Y	Z
C	-2.722403	-2.238448	-1.117472
N	-1.806583	-1.221610	-1.328178
C	-1.358688	-1.365601	-2.570553
N	-1.957898	-2.434419	-3.158297
C	-2.836424	-3.014901	-2.248929
Fe	-1.030086	0.155353	0.140016
O	-2.636728	-0.359749	1.274780
C	-2.953772	0.015444	2.469881
C	-4.144969	-0.683855	3.129197
C	-4.732595	-1.873270	2.370343
C	-3.653741	-4.227789	-2.562751
N	-2.348003	1.803745	-0.548718
C	-3.662438	1.734020	-0.695654
N	-4.176458	2.968156	-0.946347
C	-3.135177	3.890453	-0.953689
C	-2.008795	3.134770	-0.707631
C	-3.351103	5.357651	-1.162093
S	0.332637	-1.376559	1.236329
C	1.270400	-2.275238	-0.050437
C	2.667782	-2.718445	0.403998
N	2.561871	-3.700900	1.487817
O	0.245946	0.757797	-1.079907
O	1.140706	0.164334	-1.824283
O	-0.489725	1.638804	1.572696
C	3.682759	-1.582404	0.727297
O	4.510511	-1.752285	1.630080
N	3.702146	-0.477096	-0.082565
C	4.713348	0.550464	0.103147
C	5.463704	0.825885	-1.205222
O	5.319076	0.216173	-2.253987
C	4.182799	1.852334	0.776592
C	3.535013	1.524333	2.128283
C	3.223662	2.639723	-0.127495
O	-2.377723	0.914623	3.132016
O	6.366822	1.864457	-1.022655
H	6.822695	1.957281	-1.886830
H	5.445114	0.100247	0.797425
H	5.073750	2.476207	0.959044
H	3.215904	2.449503	2.635263
H	2.652005	0.878362	1.989127
H	4.226858	0.984166	2.792043
H	2.899261	3.563796	0.377928
H	3.704849	2.932086	-1.074840
H	2.321269	2.056892	-0.367991
H	2.968384	-0.323048	-0.778926
H	3.491928	-3.742644	1.922611
H	1.959331	-3.288163	2.211087
H	0.698199	-3.180546	-0.304507
H	1.332759	-1.645476	-0.957271
H	-4.260694	-4.499760	-1.688674
H	-4.340793	-4.058753	-3.408928

H	-3.021537	-5.096426	-2.811299
H	-1.769320	-2.769123	-4.097927
H	-0.579651	-0.762061	-3.029094
H	-3.218798	-2.336015	-0.157951
H	-5.577686	-2.310522	2.925236
H	-5.098065	-1.572346	1.376534
H	-3.976727	-2.660061	2.226750
H	-3.809786	-0.985327	4.134898
H	-4.912078	0.091425	3.301510
H	0.363278	1.383011	1.974155
H	-1.210489	1.466465	2.296697
H	-2.385715	5.880456	-1.127314
H	-3.813377	5.575523	-2.139472
H	-3.994004	5.793505	-0.379251
H	-5.158713	3.183202	-1.083877
H	-4.257856	0.831834	-0.604859
H	-0.978405	3.460100	-0.610593
H	3.115373	-3.237138	-0.469160

Supporting Information Table 3: Key Computational Results for Fe-IPNS-ACV-O_2

Bond length	(Å)	Bond Angle	(Degrees)	Total Atomic Charge (Mulliken)	
Fe-S	2.33	S-Fe-N_{eq}	170	S	-0.45
Fe-O_{O2}	1.87	S-Fe-N_{ax}	96	Fe	1.46
O-O	1.31	S-Fe-O2	97	O2	-0.56
Fe-O_{OH2}	2.13	S- Fe-O_{Asp}	92	Total Spin Density	
Fe-O_{Asp}	2.03	S- Fe-O_{OH2}	90	S	0.16
Fe-N_{eq}	2.22	Fe-O-O	134	Fe	3.79
Fe-N_{ax}	2.16			O2	-0.22

Supporting Information Table 5:

Coordinates [Å] of optimized Fe-IPNS-ACV Complex

Atom	X	Y	Z
C	-3.483321	1.805638	-0.217130
N	-2.209484	1.882310	-0.578327
C	-2.004321	3.198136	-0.961284
C	-3.165601	3.932083	-0.829536
N	-4.095269	3.012667	-0.358593
Fe	-0.906297	0.088404	-0.236734
S	0.446841	-1.706334	0.609224
C	1.552171	-2.430520	-0.706262
C	2.958447	-2.839491	-0.204087
C	3.816570	-1.656588	0.325248
N	3.796809	-0.480260	-0.396591
C	4.662465	0.626528	-0.019134
C	3.972111	1.797639	0.730574
C	2.983090	2.539914	-0.179273
C	-3.507318	5.370434	-1.079049
N	-2.125952	-1.164694	-1.446761
C	-2.821494	-0.973920	-2.560848
N	-3.623844	-2.045280	-2.805368
C	-3.433620	-2.977358	-1.789713
C	-2.497439	-2.406852	-0.961524
C	-4.158083	-4.278905	-1.712180
O	0.107596	1.522632	0.867897
O	-2.254798	-0.339842	1.323185
C	-2.230659	0.213666	2.477655
O	-1.539415	1.227004	2.792993
C	-3.114483	-0.389566	3.576976
C	-3.970246	-1.590377	3.164256
N	2.835295	-3.912203	0.793166
O	4.502789	-1.774713	1.342706
C	5.435411	1.081203	-1.260282
O	6.301796	2.141141	-0.965729
O	5.345162	0.608060	-2.402849
C	3.331822	1.285667	2.026833
H	6.745235	2.334556	-1.819480
H	5.404653	0.190197	0.675151
H	4.782251	2.497725	0.996514
H	2.792313	2.097479	2.539578
H	2.630200	0.458092	1.829435
H	4.090724	0.884486	2.715232
H	2.453826	3.329393	0.374691
H	3.503553	3.010351	-1.029936
H	2.214293	1.859486	-0.577136
H	3.409637	-0.474719	-1.335426
H	3.696516	-3.889131	1.352165
H	2.097509	-3.610992	1.444397
H	1.073392	-3.343512	-1.091903
H	1.648109	-1.734508	-1.555949
H	-3.821985	-4.829108	-0.823183
H	-5.249699	-4.143821	-1.628222
H	-3.965597	-4.917270	-2.590946
H	-4.239857	-2.154540	-3.604819

H	-2.782673	-0.093408	-3.194585
H	-2.050653	-2.788797	-0.048637
H	-4.552377	-1.967285	4.020411
H	-4.674916	-1.323520	2.361436
H	-3.338526	-2.406895	2.786346
H	-2.436940	-0.663789	4.403361
H	-3.738852	0.427576	3.978221
H	0.885729	1.048332	1.226423
H	-0.564682	1.536906	1.682045
H	-2.619919	5.904501	-1.445341
H	-4.301380	5.482301	-1.836350
H	-3.843898	5.877958	-0.159678
H	-5.055069	3.220767	-0.102609
H	-3.959737	0.916574	0.182669
H	-1.025839	3.543481	-1.281399
H	3.507983	-3.242044	-1.080745

Supporting Information Table 6:

Coordinates [Å] of optimized Fe-PAH Complex

Atom	X	Y	Z
Fe	0.618639	-0.350455	0.738725
O	1.681544	-1.390310	-0.722066
C	2.938064	-1.526918	-0.818136
O	3.779572	-1.018533	0.019813
C	3.541067	-2.333530	-1.942193
N	0.228444	1.591478	0.083203
C	1.129482	2.571356	0.068348
N	0.587188	3.696942	-0.465730
C	-0.729941	3.439635	-0.818363
C	-0.927907	2.123310	-0.465401
C	-1.635149	4.455662	-1.433490
N	-1.125604	-1.322449	0.192918
C	-1.236936	-2.182423	-0.818182
N	-2.541577	-2.484260	-1.027588
C	-3.323755	-1.787004	-0.114566
C	-2.418162	-1.072863	0.636672
C	-4.815014	-1.873278	-0.070243
H	3.899223	-3.295679	-1.543003
H	4.414084	-1.808795	-2.353489
H	2.802433	-2.523404	-2.729723
H	2.149066	2.489228	0.432154
H	1.073269	4.579739	-0.596505
H	-1.828633	1.526851	-0.574603
H	-1.781059	5.328338	-0.776359
H	-1.246360	4.821873	-2.397473
H	-2.621199	4.010024	-1.620316
H	-0.406286	-2.569884	-1.399196
H	-2.889394	-3.122195	-1.738307
H	-2.601878	-0.401242	1.468750
H	-5.160890	-2.901392	0.123917
H	-5.272947	-1.536669	-1.014425
H	-5.200463	-1.234639	0.735480
O	2.298590	0.006000	1.643552
H	3.187736	-0.504691	0.848632
H	2.511703	-0.184134	2.572154
O	-0.458990	0.387659	2.597599
H	-0.444828	-0.023727	3.481340
H	-0.243581	1.328050	2.736644

Supporting Information Table 7:

Coordinates [Å] of optimized Fe-PAH-NO Complex

Atom	X	Y	Z
Fe	0.499160	-0.633197	0.615451
N	0.444718	1.451185	-0.014752
C	1.439205	2.109375	-0.604489
N	1.095635	3.409679	-0.785353
C	-0.186168	3.617467	-0.289052
C	-0.569005	2.380101	0.181377
C	-0.877539	4.940017	-0.331827
N	-1.412085	-0.863143	-0.228834
C	-1.612852	-1.272820	-1.477522
N	-2.943008	-1.320676	-1.737070
C	-3.643246	-0.924050	-0.605939
C	-2.664554	-0.644990	0.322520
C	-5.133897	-0.868236	-0.543341
O	1.469541	-1.322176	-0.966046
C	2.738885	-1.302165	-1.245138
O	3.568301	-0.560628	-0.653962
C	3.222665	-2.264122	-2.314798
O	2.344564	-0.049963	1.506753
O	-0.353924	0.351722	2.427936
H	2.395950	1.682509	-0.894247
H	1.685368	4.116645	-1.216183
H	-1.512543	2.098260	0.637099
H	-1.008321	5.300371	-1.365048
H	-1.874741	4.854826	0.120066
H	-0.322322	5.711499	0.225906
H	-0.831884	-1.540391	-2.181751
H	-3.358978	-1.610869	-2.617778
H	-2.781433	-0.303645	1.346025
H	-5.586777	-1.856515	-0.723523
H	-5.549775	-0.166051	-1.283875
H	-5.453731	-0.532789	0.452082
H	2.532796	-2.278552	-3.169960
H	3.241987	-3.280783	-1.890648
H	4.234269	-1.995440	-2.640015
H	2.957149	-0.131874	0.663107
H	2.739110	-0.672163	2.147254
H	-0.388302	-0.187045	3.244213
H	0.232865	1.108659	2.621885
N	0.384522	-2.124191	1.619789
O	0.021732	-2.462326	2.684876

Supporting Information Table 8:

Coordinates [Å] of optimized Fe-PAH-O_2 Complex

Atom	X	Y	Z
Fe	0.409908	-0.653255	0.416641
N	0.541410	1.412519	0.002028
C	1.490079	1.995012	-0.730998
N	1.357435	3.341348	-0.669563
C	0.275662	3.661342	0.142352
C	-0.216242	2.441124	0.550469
C	-0.148515	5.064107	0.426387
N	-1.590700	-0.792993	-0.160774
C	-2.379023	-1.842952	0.083105
N	-3.627517	-1.595708	-0.371939
C	-3.667318	-0.331614	-0.947010
C	-2.383972	0.147036	-0.806334
C	-4.897149	0.250892	-1.560157
O	1.399416	-1.295299	-1.088802
C	2.680195	-1.339317	-1.378458
O	3.533719	-0.641328	-0.786862
C	3.088809	-2.302204	-2.472834
O	2.293555	-0.374331	1.452125
O	-0.224056	0.038122	2.434017
H	2.283491	1.481549	-1.265929
H	1.963292	4.009606	-1.138753
H	-1.050838	2.233512	1.212020
H	-0.436044	5.599025	-0.493130
H	-1.016690	5.062817	1.098558
H	0.652766	5.640854	0.915706
H	-2.088363	-2.754549	0.594922
H	-4.409586	-2.242440	-0.309468
H	-1.982203	1.101488	-1.128527
H	-5.715878	0.340957	-0.828160
H	-5.261883	-0.360389	-2.401253
H	-4.681360	1.255411	-1.947314
H	2.449729	-2.173316	-3.358110
H	2.940410	-3.333205	-2.114678
H	4.142941	-2.153538	-2.732129
H	2.923808	-0.301662	0.646816
H	2.578605	-1.198326	1.893757
H	-0.806737	0.802293	2.289592
H	0.599759	0.392708	2.827158
O	0.329129	-2.389070	1.221012
O	-0.277059	-2.767453	2.264617

Complete Reference 31

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