Supplementary Materials: pH Dependent Reversible Formation of a Binuclear Ni_2 Metal-Center Within a Peptide Scaffold

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Table S1. Cartesian coordinates for diprotonated mononuclear computational model.

Ni	−2.985135	−0.031619	−0.178560
S	−1.743194	−1.825451	−0.429911
N	−3.964080	1.600612	0.102848
S	−4.817341	−1.129247	0.170119
C	−5.190115	1.433327	0.893085
C	−5.999930	0.285683	0.314604
H	−6.374382	0.518530	−0.687922
H	−6.824953	−0.027229	0.965429
C	−1.320174	−1.887424	−2.226242
H	−2.255814	−1.925073	−2.796327
C	−0.394208	−3.055879	−2.530821
H	−0.845038	−0.912057	−2.390968
H	−4.922151	1.218433	1.940665
H	−5.804520	2.343287	0.898201
H	−0.119310	−3.020468	−3.594487
H	−0.876729	−4.024608	−2.342371
H	0.528279	−3.003284	−1.939663
C	−3.607632	2.797631	−0.337038
C	−4.452905	4.031275	−0.176841
O	−2.478352	2.982798	−0.946625
H	−5.476535	3.882721	−0.545724
H	−3.983760	4.842709	−0.741389
H	−4.509892	4.328984	0.880340
O	−1.360277	0.838382	−0.591012
H	−0.801696	0.887859	0.207924
H	−1.880857	2.073105	−0.856301
H	−5.145513	−1.523389	−1.090133
H	−2.542567	−2.927757	−0.402168

Table S2. Cartesian coordinates for monoprotonated mononuclear computational model 1.

Ni	−2.762083	0.095212	−0.091059
S	−1.502386	−1.652619	−0.326083
N	−3.895584	1.629494	0.089158
S	−4.457719	−1.187008	0.183132
C	−5.210483	1.359322	0.693197
C	−5.769217	0.086897	0.090943
H	−6.059257	0.248483	−0.957489
H	−6.645049	−0.271147	0.650939
C	−1.469965	−1.879362	−2.154619
H	−2.514057	−1.870058	−2.490878
C	−0.721738	−3.137750	−2.570713
H	−0.982321	−0.963241	−2.512750
H	−5.083619	1.219427	1.780602

H	−5.905409	2.197520	0.535493
H	−0.685637	−3.202184	−3.668358
H	−1.221517	−4.043316	−2.198689
H	0.309745	−3.135021	−2.194201
C	−3.559665	2.866016	−0.250412
C	−4.515401	4.033835	−0.098868
O	−2.401791	3.163920	−0.730727
H	−5.425780	3.893057	−0.697942
H	−4.001024	4.936894	−0.442169
H	−4.820790	4.171303	0.947949
O	−1.137771	1.121474	−0.506115
H	−0.596651	1.185982	0.301023
H	−1.664423	2.150421	−0.656203
H	−2.303650	−2.722333	−0.066321

Table S3. Cartesian coordinates for monoprotonated mononuclear computational model 2.

Ni	−2.576261	0.109883	−0.264504
S	−1.110795	−1.535403	−0.185145
N	−3.916314	1.513468	−0.082218
S	−3.932188	−1.298937	0.509338
C	−5.160267	1.103673	0.579411
C	−5.488633	−0.333434	0.209166
H	−5.735932	−0.416555	−0.855620
H	−6.302288	−0.746429	0.819746
C	−0.814051	−1.850625	−1.969926
H	−0.484089	−0.913377	−2.438164
C	−2.020430	−2.424347	−2.706980
H	0.030491	−2.556949	−1.997577
H	−5.060743	1.182995	1.678959
H	−6.011795	1.738523	0.287583
H	−1.767970	−2.660228	−3.752678
H	−2.844952	−1.695645	−2.715294
H	−2.374445	−3.346189	−2.223028
C	−3.694029	2.814376	−0.284766
C	−4.741067	3.854570	0.070420
O	−2.605694	3.257002	−0.784434
H	−5.653700	3.723457	−0.529274
H	−4.323411	4.844603	−0.136951
H	−5.028818	3.797162	1.130033
O	−1.295344	1.238859	−1.132775
H	−0.458454	1.136707	−0.644219
H	−1.762071	2.228692	−0.983709
H	−4.073319	−2.178250	−0.516574

Table S4. Cartesian coordinates for unprotonated mononuclear computational model.

Ni	−2.621850	0.211296	−0.439613
S	−0.974827	−1.254743	−0.319281
N	−3.945452	1.618635	−0.175455
S	−3.996350	−1.264124	0.281620
C	−5.225326	1.177543	0.400506
C	−5.501469	−0.253219	−0.015595

H	−5.768533	−0.287538	−1.084201
H	−6.342056	−0.670427	0.563637
C	−0.808021	−1.808964	−2.066248
H	−0.803823	−0.920209	−2.714797
C	−1.904974	−2.781142	−2.492036
H	0.185431	−2.283174	−2.147620
H	−5.176040	1.218476	1.506801
H	−6.056649	1.833396	0.078260
H	−1.790985	−3.077404	−3.550788
H	−2.892244	−2.318064	−2.351152
H	−1.884328	−3.686248	−1.868162
C	−3.671345	2.919999	−0.163144
C	−4.692178	3.919297	0.377652
O	−2.569673	3.427953	−0.576873
H	−5.597537	3.948790	−0.247932
H	−4.228945	4.912310	0.380854
H	−5.013313	3.661810	1.398436
O	−1.353100	1.421163	−1.376691
H	−0.547181	1.127692	−0.901680
H	−1.720093	2.348774	−1.020410

Table S5. Cartesian coordinates for dinuclear computational model with disulfide bridge.

Ni	−2.51490301364867	0.64197685369813	−0.17096724008139
Ni	0.74014313849295	0.98469720182281	−0.25947574875621
S	−0.98015818158893	2.30225752472681	−0.39900052038534
S	−0.78388734027928	−0.71981870935281	−0.43109972474445
N	−3.89820352011724	1.81949405065690	0.41418993900667
N	2.20558142116705	0.02681583049738	0.63557993109239
S	−4.14330122753410	−0.71650533789512	−0.83818908936127
S	2.22692530428104	2.45459092517140	−0.97327623272906
C	−5.20830375941819	1.75411807337605	−0.23218757691469
C	−5.16182489046856	0.72439281506730	−1.35627006098373
H	−4.71676265524132	1.16956371690929	−2.26109203348955
H	−6.18064388107189	0.38579521647507	−1.61388440628336
C	3.57563816503567	0.39323461203726	0.24272283541414
C	3.55971134525440	1.18715460743187	−1.05291953587303
H	3.37704205570846	0.52244784789456	−1.91360307958985
H	4.53219291353725	1.68633726119669	−1.20978088316548
C	−3.86325515178102	2.42286682406089	1.61280192114590
C	−2.55952941536209	2.24643745040331	2.41368562965242
C	2.13961128984192	−0.49545890532285	1.87685180144483
C	0.75757611141730	−0.77534205762877	2.47831166955725
C	−1.32022940919935	3.05796849883591	−2.03679315879005
H	−2.26249620258012	3.61290991468094	−1.90194946149018
C	−1.42712281732474	2.06745365940994	−3.18537724159220
H	−0.50731691451799	3.77831849090676	−2.21755363062377
C	−0.46022279602306	−1.25286405245008	−2.16149019636058
H	−0.58365892875014	−0.39054162018782	−2.82649366532772
C	−1.37807030281665	−2.40020494908069	−2.57340484728163
H	0.60106597281388	−1.54580475367127	−2.18552178496583
S	−2.03352780733485	0.49348804505957	2.35590539739753
H	−2.75742111462946	2.55237207998390	3.44716633511636

H	−1.74954960155561	2.85242787886582	1.97951598401016
S	−0.06673637323812	0.70185457513264	3.22483443438733
H	0.89559694366733	−1.50936045028911	3.28200912054422
H	0.07060128961083	−1.17370924886978	1.71955016177179
H	4.03434808320471	0.99661193638393	1.04788658527556
H	4.20284865899031	−0.51523477319337	0.14372455133098
H	−5.96618360675445	1.47501859387065	0.52238244589159
H	−5.50716238839299	2.74760718053940	−0.62293716667775
O	3.14575405743770	−0.78398016527726	2.57962309280428
O	−4.80107896098473	3.08800660308412	2.11823792898870
H	−2.15798061947266	1.28110897007692	−2.93886176952113
H	−0.44989921637217	1.59322818937128	−3.35331965772429
H	−1.73876562368148	2.56844681662362	−4.11977785422421
H	−1.16616579037055	−2.71830674391743	−3.61019372403252
H	−2.43036809087872	−2.08404870954646	−2.50050082080092
H	−1.24069714907167	−3.26766176756834	−1.90981865306189

Table S6. Cartesian coordinates for dinuclear computational model without disulfide bridge.

Ni	−1.95724154983937	0.41587677611011	0.77096677378535
Ni	1.41117325675870	0.61228594823025	0.76961751704832
S	−0.34760385247717	1.96014566719011	0.67532962844414
S	−0.19811229781733	−0.93423195505679	0.69849162018455
C	−0.43770721873177	2.45829163066570	−1.10791119537641
C	0.39608721925621	3.70112274411391	−1.39799639431977
H	−1.50490575418095	2.61500183642790	−1.32177839084123
H	−0.09191644066321	1.60583366982723	−1.70824284674929
H	0.02713036187950	4.55997939936934	−0.81654120851186
H	0.34889251343151	3.96191045737697	−2.47087652727604
H	1.44542851787835	3.52446246432583	−1.11379427128554
C	−0.10662218825057	−1.45856081877585	−1.07711128435693
C	−0.95032323641582	−2.69730845328761	−1.35498444513928
H	0.96010109192605	−1.62857761227082	−1.28403854043988
H	−0.44032040152642	−0.61115595438840	−1.69137429611131
H	−0.59124513736368	−3.55205943739428	−0.76135812986570
H	−0.90114905619715	−2.97203416387785	−2.42423211725175
H	−1.99913559924521	−2.50892138833322	−1.07645427854543
N	−3.48190463727620	1.61117659382546	0.75523652693466
C	−3.38172652146058	3.06657772778493	0.77275371410761
H	−2.34977099536056	3.35875235154982	1.00780362439355
H	−4.06593192072265	3.50157504348641	1.52209501452548
H	−3.66686346679785	3.51202070425471	−0.20052521956206
N	2.93601823253994	−0.58256474493317	0.77473274139279
C	2.83792395691288	−2.03735209797209	0.82458929598586
H	1.80375483246188	−2.32578228156498	1.05468869191357
H	3.51377947925314	−2.45400706089037	1.59194604476226
H	3.13549454556174	−2.50442454768404	−0.13463200801790
S	2.80743792594696	2.29410038403829	0.87965019241555
C	4.37657689009744	1.37832137891309	0.68503183317147
C	4.20778899567022	−0.13675894912601	0.69991772953657
H	5.07992748737457	1.64057911055507	1.49176308454332
H	4.86433003525908	1.65023999393693	−0.26563366719926
S	−3.35421548838054	−1.26279991515597	0.91321453065065

C	−4.92408896617903	−0.34989746600857	0.71122514635264
C	−4.75414258740132	1.16497326613674	0.69140122557518
H	−5.62106912595636	−0.59348184412738	1.52936015466862
H	−5.41974300503734	−0.64241389018354	−0.22911159274674
O	5.22972086857331	−0.86976839344558	0.64585953744975
O	−5.77565676350040	1.89731382635771	0.62205178575444

Table S7. Cartesian coordinates for protonated dinuclear computational model with disulfide bridge.

Ni	−2.45974	0.52932	−0.02581
Ni	0.74013	0.98796	−0.14261
S	−0.91908	2.41076	−0.42043
S	−0.65782	−0.72324	−0.31182
N	−3.88712	1.73842	0.42032
N	2.20225	0.05143	0.67054
S	−4.23109	−0.83340	−0.27424
S	2.16302	2.32165	−1.09860
C	−5.10591	1.72223	−0.37494
C	−5.11696	0.46299	−1.24917
H	−4.54437	0.61104	−2.17309
H	−6.13684	0.13188	−1.48971
C	3.56332	0.33659	0.18539
C	3.48430	1.03799	−1.15964
H	3.25006	0.31954	−1.96026
H	4.44065	1.52695	−1.40622
C	−3.92942	2.41520	1.58596
C	−2.68416	2.27200	2.47713
C	2.16048	−0.48813	1.90577
C	0.77649	−0.64596	2.57243
C	−1.27080	3.19162	−2.04330
H	−2.26839	3.64308	−1.93562
C	−1.19308	2.26958	−3.24653
H	−0.53182	4.00324	−2.12567
C	−0.22860	−1.00856	−2.07414
H	0.13139	−0.06300	−2.49662
C	−1.37677	−1.58614	−2.89166
H	0.62732	−1.69986	−2.04402
S	−2.06090	0.54893	2.50774
H	−2.94035	2.60561	3.48791
H	−1.87567	2.89520	2.06300
S	−0.01424	0.97270	2.93543
H	0.91847	−1.19124	3.51154
H	0.10004	−1.19817	1.90651
H	4.08228	0.97844	0.92001
H	4.14929	−0.59774	0.11624
H	−5.97963	1.75011	0.29807
H	−5.18651	2.60925	−1.03083
O	3.16083	−0.88096	2.54667
O	−4.87339	3.13382	1.96701
H	−1.86395	1.40932	−3.10968
H	−0.16629	1.89954	−3.36550
H	−1.48238	2.80010	−4.16919

H	−1.05734	−1.80637	−3.92298
H	−2.20821	−0.86686	−2.94060
H	−1.75405	−2.51689	−2.44206
H	−3.97670	−1.66685	−1.31603

Table S8. Alternative EXAFS models for {Ni(SOD^{mds})} at pH 7.4 [a].

	Reported	**Best Fit[b]**	**S_3N**	**S_2NO**	**S_2N_2Ni**
Shell #1 Ni–S					
N	2	2.36(13)	3	2	2
R (Å)	2.1804(14)	2.1737(15)	2.180(1)	2.1822(14)	2.174(2)
σ^2 (Å^2)	0.0026(2)	0.0038(3)	0.0050(2)	0.00026(20)	0.0032(14)
Shell #2 Ni–N					
N	2	1.6(7)	1	1	2
R (Å)	1.907(16)	1.893(18)	1.823(11)	1.802(6)	1.912(11)
σ^2 (Å^2)	0.0013(6)	0.0063(7)	0.0082(15)	0.0053(6)	0.006(2)
Shell #3 Ni–O					
N				1	
R (Å)	N/A	N/A	N/A	1.935(6)	N/A
σ^2 (Å^2)				0.0006(6)	
Shell #4 Ni–Ni					
N					1
R (Å)	N/A	N/A	N/A	N/A	2.62(5)
σ^2 (Å^2)					0.017(2)
Eo (eV)	8347.1	8447.3	8446.8	8447.5	8447.2
ε^2	0.69	0.61	0.80	0.67	0.65

All values for the number of shells was restrained to the nearest whole number [b]. The best fit (i.e. lowest ε^2) allowed the number of scatterers in each shell to refine.

Table S9. Alternative EXAFS models for {Ni(SOD^{mds})} at pH 9.6 [a].

	Reported	**Best Fit[b]**	**S3N**	**S2N2**	**S2N2Ni**
Shell #1 Ni–S					
N	3	2.8(4)	2	2	2
R (Å)	2.229(2)	2.202(2)	2.200(2)	2.203(2)	2.204(2)
σ^2 (Å^2)	0.0044(2)	0.0019(5)	0.00012(2)	0.00014(2)	0.00012(2)
Shell#2 Ni–S					
N			1		
R (Å)	N/A	N/A	2.5(2)	N/A	N/A
σ^2 (Å^2)			0.06(7)		
Shell #3 Ni–N					
N	1	1.2(4)	1	2	2
R (Å)	1.889(9)	1.886(11)	1.926(8)	1.935(8)	1.894(8)
σ^2 (Å^2)	0.0013(8)	0.003(2)	0.0009(8)	0.0053(11)	0.0094(11)
Shell #4 Ni–Ni					
N	1	0.7(2)			1
R (Å)	3.25(3)	3.219(10)	N/A	N/A	3.21(3)
σ^2 (Å^2)	0.0061(15)	0.006(2)			0.0075(15)
Eo (eV)	8346.4	8346.2	8346.8	8346.2	8346.5
ε^2	1.47	1.01	1.56	1.81	1.77

All values for the number of shells was restrained to the nearest whole number [b]. The best fit (i.e. lowest ε^2) allowed the number of scatterers in each shell to refine.

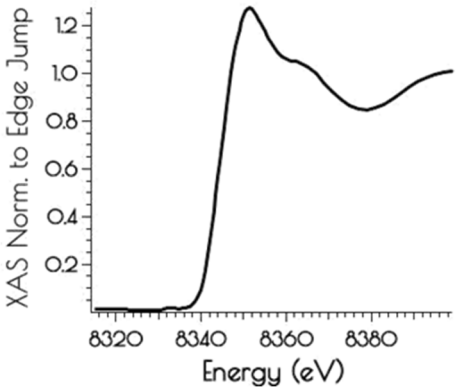

Figure S1. Ni K−edge XANES for the oxidation products of {Ni(SOD^{mds})}at pH 7.4.

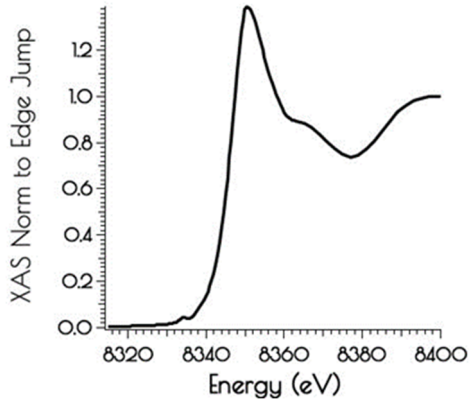

Figure S2. Ni K−edge XANES for the oxidation products of {Ni(SOD^{mds})}at pH 9.6.