Supporting Information
for

S K-edge XAS and DFT Studies of High and Low Spin $\{FeNO\}^7$ Thiolate Complexes: Exchange Stabilization of Electron Delocalization in $\{FeNO\}^7$ and $\{FeO_2\}^8$

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Estimation of oxidation state using pre-edge transition energy:

The pre-edge energy of the d orbital can be expressed as the energy difference between Fe d orbital and S 1s orbital:

$$E_{pre\text{-}edge}=E_d-E_{1s} \quad (1)$$

Following Zener[1], the energy of the d orbital can be expressed as a function of Z_{eff}:

$$E_d=-cZ_{eff}^2 \quad (2)$$

where c is a constant.

Using Slater's screening constants[2], for Fe d electrons, Z_{eff} can be expressed as function of the oxidation state n:

$$Z_{eff}=5.55+0.35n \quad (3)$$

Combine equations 1-3,

$$E_{pre\text{-}edge}= -c(5.55+0.35n)^2-E_{1s}. \quad (4)$$

The d-hole weighted pre-edge energy ($E_{pre\text{-}edge}$) of Fe^{III}-SOR is 2469.8 eV (3 transitions to t_2 hole at 2469.4 eV, 2 transitions to e hole at 2470.5 eV), and the oxidation state n of Fe^{III}-SOR is defined as 3.0. The d-hole weighted pre-edge energy of Fe^{II}-SOR is 2472.5, (2 transitions to t_2 hole at 2472.1 eV , 2 transitions to e hole are calculated by DFT to be higher than t_2 hole by 0.9eV), and the oxidation state is defined as 2.0. Using the value of $E_{pre\text{-}edge}$ and n of the reference complexes, we can obtain the value of the constants c and $E_{1s,}$ and then the oxidation state of complex I and II can be obtained using the corresponding value of $E_{pre\text{-}edge}$. The oxidation state of complex I is calculated to be 2.75 from equation 4, using the weighted pre-edge energy of 2470.5 eV (3 transitions to t_2 at 2470.1 eV and 2 transitions to e at 2471.0 eV). Similarly, the oxidation state of complex II is calculated to be 2.67 using 2470.7 eV as the weighted pre-edge energy (4 transitions at 2470.5 eV and 1 transition at 2471.6 eV).

The MO compositions of Complex II (unoccupied) using different basis sets：

Table S1. CP(PPP) for Fe and TZVP for the remaining atoms as in the literature[3-5]:

MO	Energy (ev)	Fe d (%)	NO 2p (%)
85α	-2.062	42.5	7.7
86α	-0.987	6.2	79.8
87α	-0.797	8.5	79
84β	-1.195	63.8	25.8
85β	-0.988	62.2	26.1
86β	-0.765	62.5	6.6
87β	-0.162	68.9	0

Table S2. 6-311+G(3df) for Fe, S, N, O and 6-311+G* for C, H (this study)

MO	Energy (eV)	Fe d (%)	NO 2p (%)
85α	-1.952	42.8	7.1
86α	-1.029	5.9	70.4
87α	-0.828	8.8	74.4
84β	-1.222	61.5	23.9
85β	-1.024	60.4	25.4
86β	-0.871	58.2	10.6
87β	-0.106	66.4	0

The MO compositions of model A and model C:

Table S3. The MO compositions of model A (thiolates replaces by ammines in complex II)

MO	Energy (eV)	Fe d (%)	NO 2p (%)
77α	-9.806	61.5	1.52
78α	-9.396	8.61	83.71
79α	-9.342	7.62	85.11
76β	-9.609	51.23	42.99
77β	-9.571	58.3	34.5
78β	-9.056	67.4	9.91
79β	-8.273	73.75	0

Table S4. The MO compositions of model C (thiolates replaces by ammines in complex II + axial ligand)

MO	Energy (eV)	Fe d (%)	NO 2p (%)
84α	-6.248	21.27	72.99
85α	-4.609	71.2	0.12
86α	-4.229	57.41	15.52
83β	-5.89	16.49	77.05
84β	-5.841	30.66	56.81
85β	-4.446	71.88	0.02
86β	-3.881	50.7	23.78

Occupied orbitals of complex I, complex II and complex II + axial L:

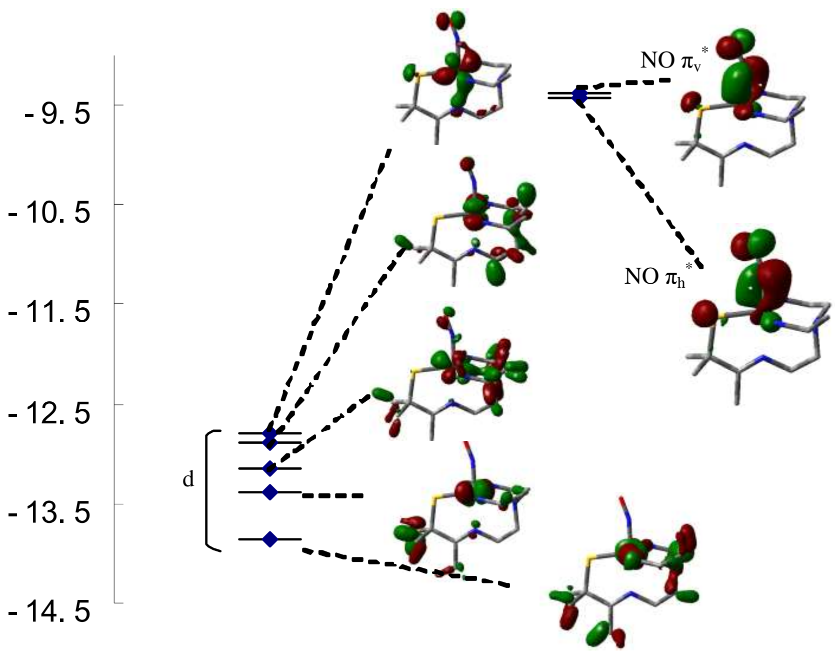


Figure S1. Occupied Fe d and NO π* orbitals of complex I.

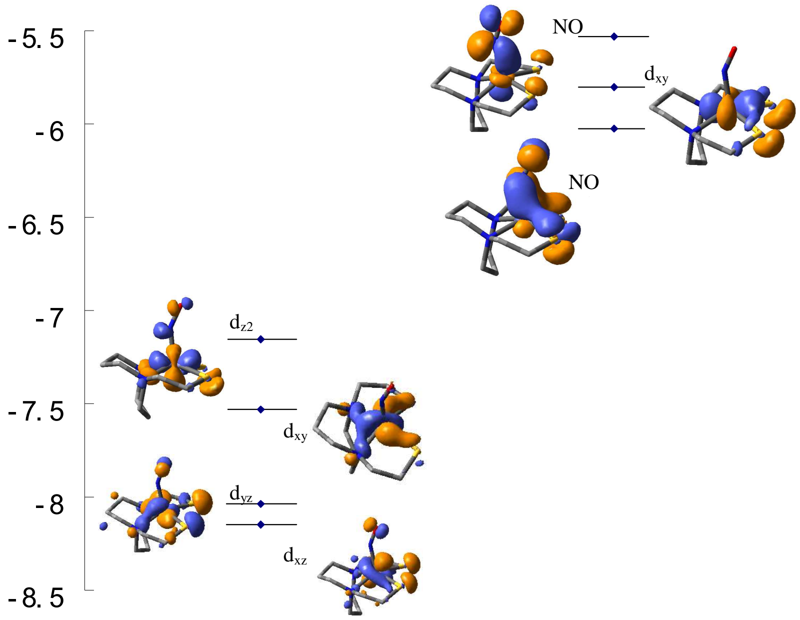


Figure S2. Occupied Fe d and NO π* orbitals of complex II.

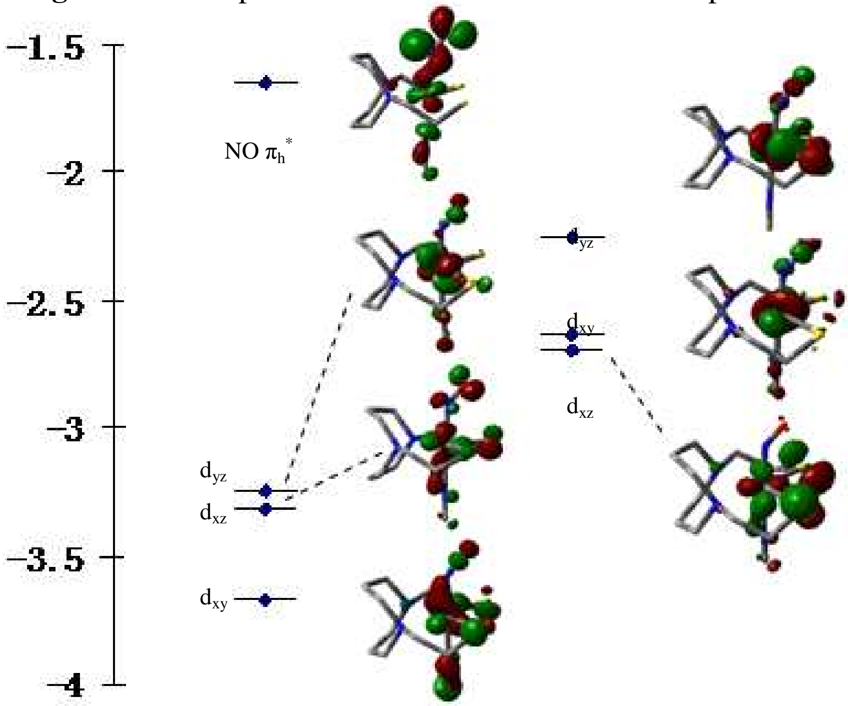
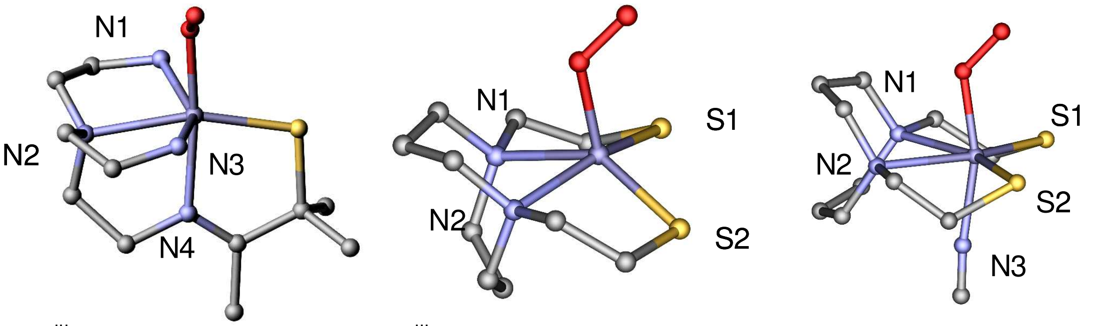


Figure S3. Occupied Fe d and NO π* orbitals of complex II + axial L.

$\{FeO_2\}^8$ Calculations



$Fe^{III}(S=5/2)-O_2(S=1/2)$ S=2

Fe-S	2.26 Å
Fe-O	1.97 Å
Fe-N1	2.23 Å
Fe-N2	2.32 Å
Fe-N3	2.21 Å
Fe-N4	2.18 Å
Fe-O-O	125.9°

Complex I

$Fe^{III}(S=3/2)-O_2(S=1/2)$ S=1

Fe-S1	2.24 Å
Fe-S2	2.25 Å
Fe-O	1.97 Å
Fe-N1	2.14 Å
Fe-N2	2.16 Å
Fe-O-O	121.3 °

Complex II

S=0

	$Fe^{III}(S=1/2)$ $O_2(S=-1/2)$	$Fe^{II}(S=0)$ $O_2(S=0)$
Fe-S1	2.29 Å	2.28 Å
Fe-S2	2.29 Å	2.28 Å
Fe-O	1.89 Å	1.76 Å
Fe-N1	2.20 Å	2.19 Å
Fe-N2	2.20 Å	2.19 Å
Fe-N3	2.00 Å	2.01 Å
Fe-O-O	123.3 °	123.7 °

Complex II + axial L

Figure S4. Geometric parameters of the DFT calculated $\{FeO_2\}^8$ system of complex I, complex II, and complex II + axial L.

Complete references for Gaussian 03 and 09:

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Optimized geometries:

Complex I

C	-3.76482	0.29278	-1.13859
H	-3.24119	0.18065	-2.09055
H	-4.25053	1.26942	-1.14499
H	-4.54968	-0.46582	-1.08179
C	-2.78864	0.21765	0.05993
C	-2.04723	-1.11364	0.03144
C	-2.87305	-2.37975	0.02357
H	-2.60666	-3.02546	0.86548
H	-2.69272	-2.95578	-0.88935
C	-0.02711	-2.38426	-0.13228
H	-0.50969	-3.21617	0.38918
C	1.40161	-2.25658	0.42176
H	1.35351	-2.41236	1.49815
H	2.01923	-3.07268	0.02650
C	1.99970	-0.18230	2.55784
H	1.55621	-1.07809	2.99408
H	2.63270	0.25239	3.33638
C	2.87101	-0.52999	1.34855
H	3.44084	0.35311	1.05067
H	3.60034	-1.30281	1.62809
N	-0.76564	-1.12985	-0.00121
N	0.90402	0.73294	2.16259
H	0.06029	0.54909	2.69475
N	2.05785	-0.94602	0.17972
N	1.30669	2.27771	-0.31997
O	1.51341	3.39728	-0.56263
S	-1.64094	1.66426	-0.07661
Fe	0.43622	0.72377	-0.08132
C	-3.57903	0.34074	1.38263
H	-2.91755	0.29752	2.25071
H	-4.09699	1.30042	1.40881
H	-4.33273	-0.44569	1.48402
H	-3.93939	-2.18326	0.08539
H	-0.01515	-2.66419	-1.19053
C	1.99815	-0.95345	-2.32022
H	1.50636	-1.91978	-2.43114
H	2.64312	-0.83662	-3.19601
C	2.86318	-0.92345	-1.06090
H	3.44767	-0.00015	-1.05411
H	3.57923	-1.75667	-1.08555
N	0.95889	0.10227	-2.25559
H	0.12693	-0.17000	-2.76908
H	1.28892	0.95402	-2.69942
H	1.14746	1.69848	2.36022

Complex II

Fe	0.00024	-0.59444	0.20377
S	-1.56014	-1.99883	-0.63424
S	1.56205	-1.99838	-0.63255
N	-1.45716	0.97163	-0.00759

N	1.45618	0.97298	-0.00827
N	0.00075	-0.85890	1.96852
O	0.00183	-1.59894	2.89308
C	-3.02242	-0.87892	-0.68005
H	-3.23901	-0.60249	-1.71873
H	-3.90137	-1.41436	-0.30424
C	-2.80550	0.34907	0.18826
H	-3.58438	1.11010	0.00844
H	-2.85481	0.05681	1.24075
C	-1.29324	2.00195	1.05760
H	-2.14588	2.69849	1.00606
H	-1.34729	1.47735	2.01548
C	-0.00106	2.81259	0.98555
H	-0.00122	3.49711	1.84288
H	-0.00161	3.45740	0.09989
C	1.29193	2.00318	1.05700
H	2.14391	2.70047	1.00500
H	1.34692	1.47866	2.01487
C	-1.32385	1.58761	-1.37174
H	-1.48630	2.67085	-1.29561
H	-2.12867	1.19681	-1.99821
C	-0.00110	1.26559	-2.08651
H	-0.00064	0.19830	-2.33692
H	-0.00161	1.80935	-3.04128
C	1.32163	1.58900	-1.37235
H	2.12665	1.19922	-1.99920
H	1.48290	2.67240	-1.29616
C	2.80524	0.35162	0.18673
H	3.58330	1.11331	0.00620
H	2.85556	0.05952	1.23922
C	3.02242	-0.87623	-0.68163
H	3.90295	-1.41020	-0.30741
H	3.23662	-0.59969	-1.72078
Complex II + axial L (model B)			
Fe	0.02886	-0.63404	-0.08565
S	1.85542	-2.07437	0.05488
S	-1.68855	-2.21403	0.04482
N	1.41597	1.07643	-0.11347
N	-1.50641	0.97379	-0.12574
N	0.02151	-0.81416	-1.80325
O	0.11014	-1.57068	-2.70898
C	2.95211	-0.75879	0.70498
H	2.73702	-0.57538	1.76117
H	3.99366	-1.09243	0.63217
C	2.80582	0.51007	-0.12429
H	3.50832	1.29721	0.20183
H	3.04597	0.26129	-1.15962
C	1.24713	1.86863	-1.35804
H	2.04215	2.63264	-1.40449
H	1.41564	1.17956	-2.18449

C	-0.09706	2.58079	-1.57014
H	-0.10398	2.90404	-2.61886
H	-0.13069	3.50594	-0.99598
C	-1.39016	1.77662	-1.36734
H	-2.23714	2.48248	-1.41874
H	-1.50052	1.07679	-2.19465
C	1.26206	1.91563	1.10610
C	-0.10967	2.56908	1.38061
C	-1.42585	1.81439	1.09751
C	-2.84137	0.29186	-0.14619
H	-3.61172	1.01614	0.17337
H	-3.05114	0.02154	-1.18268
C	-2.88547	-0.98310	0.68612
H	-3.89711	-1.39906	0.61535
H	-2.68479	-0.77953	1.74109
H	-0.12033	2.77510	2.45667
H	-0.14504	3.55169	0.90650
H	-2.23373	2.56533	1.05575
H	-1.63179	1.15326	1.93230
H	1.51458	1.27722	1.94540
H	2.00973	2.72599	1.06329
N	0.01460	-0.54942	1.98386
C	0.00909	-0.53875	3.15542

Complex II, S to N (model A)

Fe	0.00160	-0.72067	-0.03923
N	-1.53510	-1.85733	-0.85013
N	1.53823	-1.84487	-0.86656
N	-1.42568	0.76491	0.07132
N	1.42037	0.77079	0.07047
N	0.00934	-1.43082	1.56609
O	0.01265	-2.12152	2.49105
C	-2.75521	-0.99982	-1.03710
H	-2.70221	-0.56196	-2.03461
H	-3.66652	-1.59947	-0.99507
C	-2.75372	0.06193	0.04662
H	-3.56362	0.78217	-0.10334
H	-2.90569	-0.39612	1.02646
C	-1.30166	1.52589	1.36691
H	-2.15213	2.21215	1.44127
H	-1.40152	0.80088	2.17570
C	-0.00606	2.32077	1.51523
H	-0.00646	2.74478	2.52376
H	-0.00850	3.19017	0.85474
C	1.29325	1.53245	1.36554
H	2.14026	2.22313	1.43811
H	1.39804	0.80865	2.17476
C	-1.30298	1.70830	-1.11257
H	-1.41234	2.73337	-0.75603
H	-2.14378	1.53182	-1.78257
C	-0.00462	1.53766	-1.90102

H	-0.00348	0.56002	-2.40572
H	-0.00630	2.26949	-2.71503
C	1.29440	1.71222	-1.11428
H	2.13451	1.53646	-1.78530
H	1.40213	2.73800	-0.75905
C	2.75112	0.07223	0.04851
H	3.55891	0.79578	-0.09723
H	2.90106	-0.38706	1.02797
C	2.76097	-0.98755	-1.03723
H	3.67057	-1.58906	-0.98674
H	2.72004	-0.54794	-2.03446
H	-1.32739	-2.33817	-1.72413
H	-1.75461	-2.60654	-0.19442
H	1.75501	-2.60969	-0.22830
H	1.32805	-2.30466	-1.75122

Complex II + axial L, S to N (model C)

Fe	0.02674	-0.66990	-0.13036
N	1.64347	-1.92563	-0.01086
N	-1.48541	-2.05657	-0.04932
N	1.37716	0.89401	-0.03407
N	-1.45329	0.77726	-0.08226
N	0.06141	-0.79800	-1.89548
O	0.18968	-1.65339	-2.69208
C	2.77166	-1.10693	0.52608
H	2.63327	-1.03737	1.60300
H	3.73564	-1.58828	0.34104
C	2.73649	0.26128	-0.13650
H	3.49842	0.92048	0.29239
H	2.96814	0.15400	-1.19869
C	1.24433	1.85798	-1.17728
H	2.04869	2.59930	-1.09742
H	1.42669	1.28694	-2.08769
C	-0.09244	2.59438	-1.30500
H	-0.09352	3.05599	-2.29797
H	-0.14320	3.43143	-0.61331
C	-1.36401	1.74421	-1.22612
H	-2.23192	2.41341	-1.18130
H	-1.45964	1.15574	-2.13839
C	1.25291	1.59682	1.28910
C	-0.12074	2.21035	1.63647
C	-1.42897	1.49036	1.24169
C	-2.75197	0.03304	-0.22170
H	-3.57817	0.62750	0.18219
H	-2.94346	-0.09455	-1.28971
C	-2.69301	-1.33060	0.44742
H	-3.60775	-1.89099	0.23656
H	-2.59421	-1.24625	1.52755
H	-0.14313	2.28589	2.72743
H	-0.15521	3.24117	1.28887
H	-2.23716	2.23216	1.23671

H	-1.66898	0.74874	1.99607
H	1.52539	0.87377	2.05036
H	1.99956	2.40029	1.31250
N	0.00765	-0.96122	1.84958
C	0.00075	-1.36529	2.95255
H	-1.68858	-2.52119	-0.93303
H	-1.24765	-2.78562	0.61856
H	1.45118	-2.68122	0.64194
H	1.90607	-2.35942	-0.89498

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