Structural, Spectroscopic, and Computational Characterization of the Azide Adduct of Fe^{III}(2,6-diacetylpyridinebis(semioxamazide)), a Functional Analogue of Iron Superoxide Dismutase

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Supporting Information.

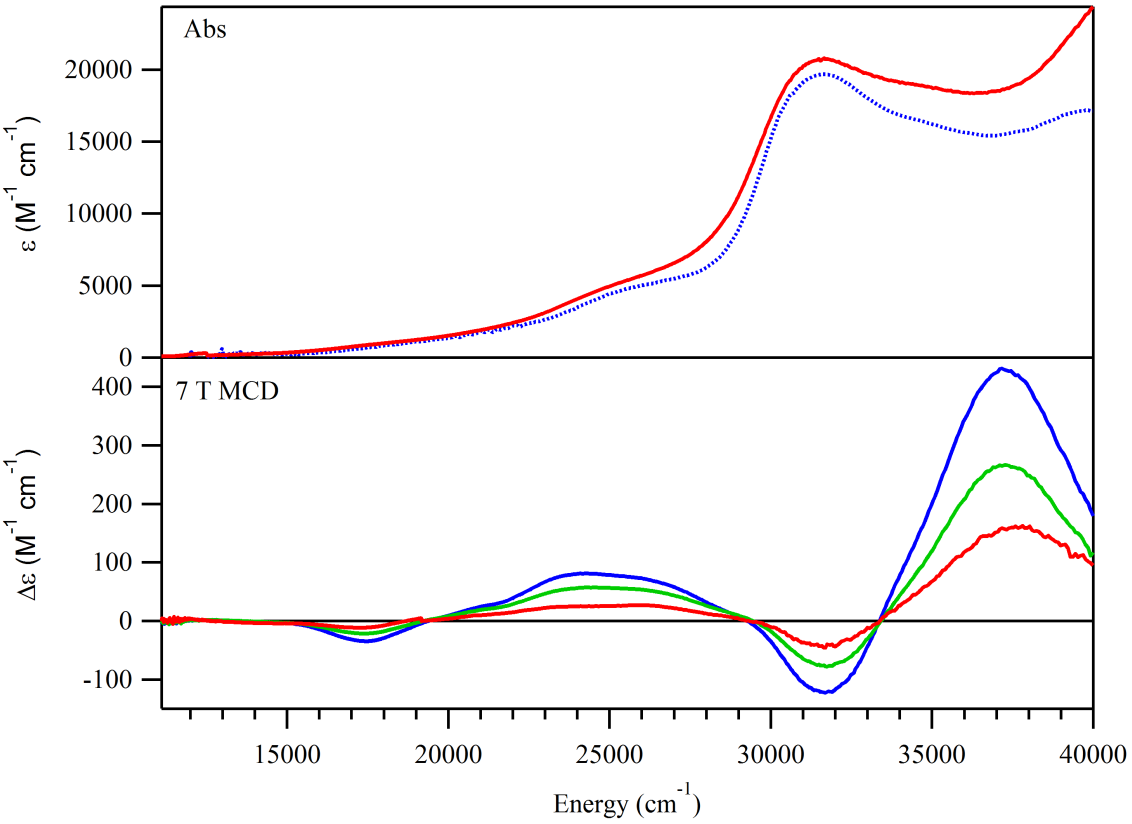

Figure S1: RT (red) and 4.5 K (blue, dotted) Abs (top) and variable temperature (4.5 [blue], 15 [green], and 25 K [red]) MCD (bottom) spectra of frozen solution $Na[Fe^{III}(dapsox)(N_3)_2]$. All MCD features decrease with increasing temperature, consistent with their expected C-term behavior.

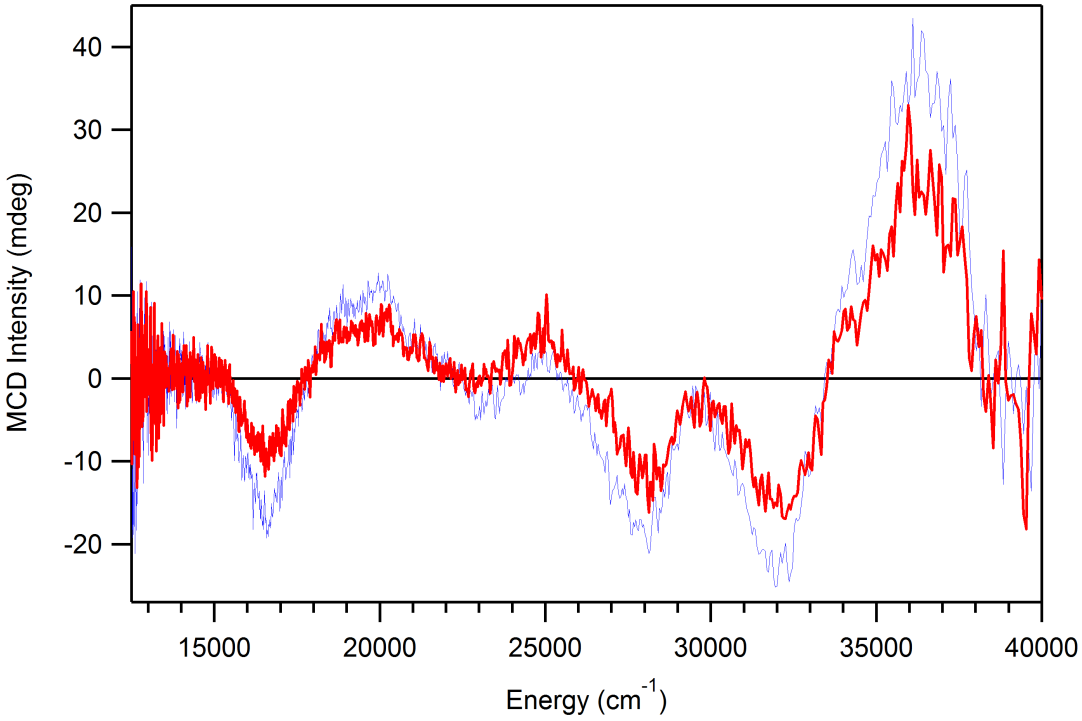

Figure S2: 4.5 (blue, dotted) and 15 K (red) 7 T MCD spectra of a solid state mull of $(Na[Fe^{III}(dapsox)(N_3)_2] \cdot DMF)_2$ in polydimethylsiloxane.

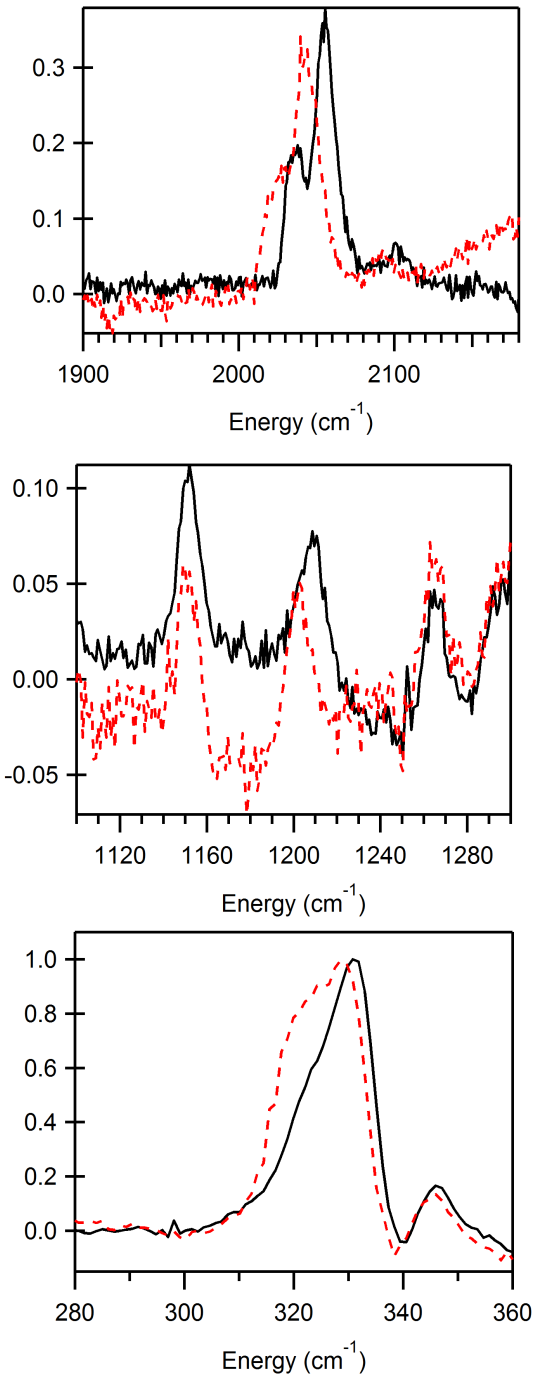

Figure S3: Frozen-solution rR spectra of **1** at 77 K obtained with 19 460 cm^{-1} (514 nm) laser excitation. Spectra of **1** synthesized with natural abundance azide are shown in black while spectra of **1** prepared with ^{15}N terminally labeled azide are shown as dashed, red lines. Selected regions are shown to highlight the four isotopically sensitive features arising from the $\nu_{as}(N_3^-)$ stretches (top), the $\nu_s(N_3^-)$ stretch (middle), and the $\nu(Fe-N_3)$ stretch (bottom). For ease of comparison the spectra have been normalized using the $\nu(Fe-N_3)$ peak.

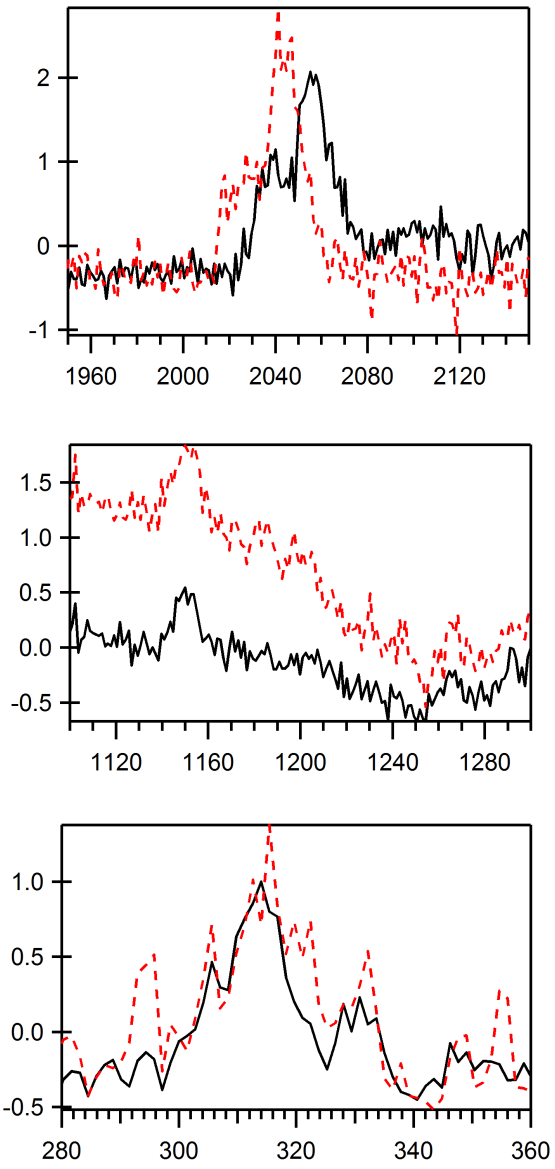

Figure S4: Frozen-solution rR spectra of 1 at 77 K obtained with 21 830 cm^{-1} (458 nm) laser excitation. Spectra of **1** synthesized with natural abundance azide are shown in black while spectra of **1** prepared with ^{15}N terminally labeled azide are shown as dashed, red lines. Selected regions are shown to highlight the four isotopically sensitive features arising from the $\nu_{as}(N_3^-)$ stretches (top), the $\nu_s(N_3^-)$ stretch (middle), and the $\nu(Fe-N_3)$ stretch (bottom). For ease of comparison the spectra have been normalized using the $\nu(Fe-N_3)$ peak.

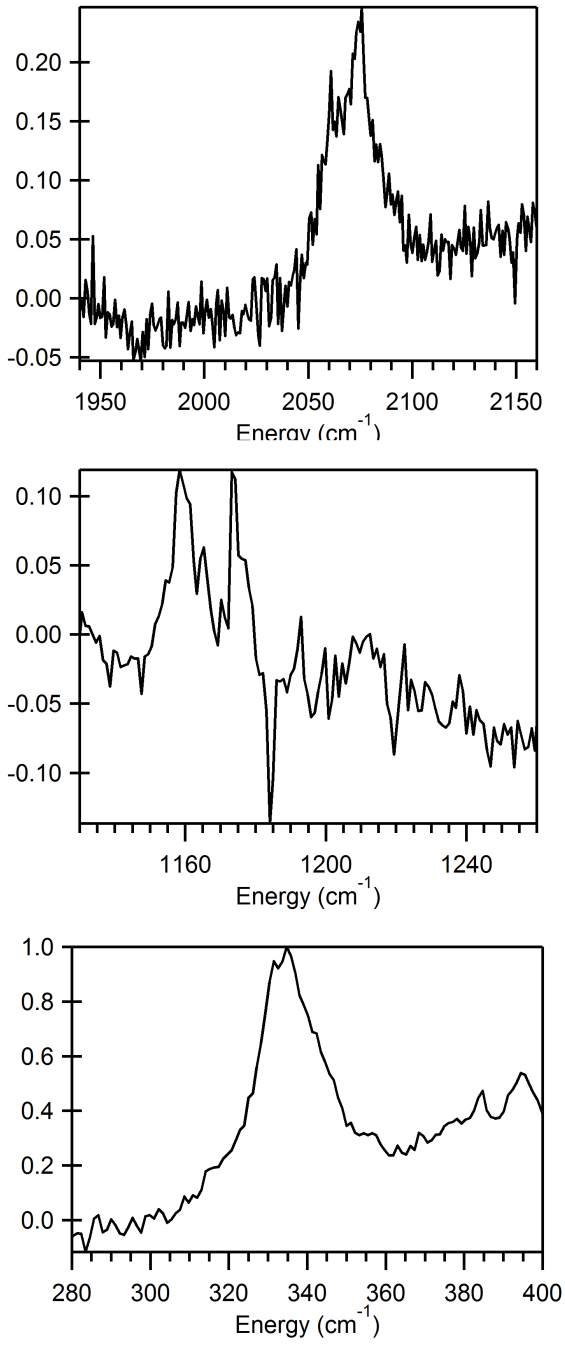

Figure S5: Solid state rR spectra of **2** at 77 K obtained with 20 490 cm^{-1} (488 nm) laser excitation. Selected regions are shown to highlight the four isotopically sensitive features arising from the $\nu_{as}(N_3^-)$ stretches (top), the $\nu_s(N_3^-)$ stretch (middle), and the $\nu(Fe-N_3)$ stretch (bottom).

Table S1: Cartesian coordinates (Å) of $\mathbf{1_{opt}}$

Atom	x	y	z	Atom	x	y	z
C	-1.734	3.933	3.361	C	5.244	1.787	1.369
N	-2.715	4.179	2.444	N	3.043	5.934	0.244
O	0.577	3.252	3.451	C	6.681	1.350	1.321
C	-0.399	3.514	2.712	N	1.842	0.720	2.364
N	-0.411	3.469	1.367	C	4.283	2.201	4.628
O	-1.883	4.030	4.561	N	1.517	0.065	1.416
C	1.002	2.998	-0.366	C	4.819	2.091	6.070
N	0.794	3.095	0.914	N	1.203	-0.584	0.510
O	3.094	2.561	4.455	Fe	2.397	2.683	2.456
C	-0.080	3.299	-1.363	H	2.160	2.555	-2.896
N	3.188	2.366	0.314	H	4.516	1.833	-3.264
O	4.153	2.375	7.044	H	6.015	1.455	-1.292
C	2.365	2.576	-0.726	H	7.077	1.280	2.344
N	4.591	2.025	2.464	H	7.300	2.067	0.749
C	2.823	2.389	-2.046	H	6.785	0.362	0.832
N	5.168	1.893	3.667	H	-3.630	4.462	2.774
C	4.140	1.984	-2.247	H	-2.499	4.074	1.458
N	6.106	1.639	6.129	H	-0.467	4.319	-1.195
C	4.980	1.772	-1.153	H	-0.931	2.609	-1.218
N	2.985	4.622	2.199	H	0.263	3.220	-2.405
C	4.460	1.977	0.138	H	6.550	1.551	7.035
N	3.012	5.282	1.200	H	6.598	1.448	5.262

Table S2: Cartesian coordinates (Å) of $\mathbf{1_{xtal}}$

Atom	x	y	z	Atom	x	y	z
C	-1.506	3.632	3.413	C	5.288	1.646	1.259
N	-2.476	4.206	2.715	N	2.991	5.667	0.271
O	0.700	2.731	3.319	C	6.706	1.207	1.200
C	-0.277	3.184	2.632	N	2.007	0.413	2.027
N	-0.312	3.337	1.332	C	4.247	2.052	4.465
O	-1.516	3.476	4.641	N	0.875	0.059	1.824
C	1.112	3.027	-0.441	C	4.596	2.155	5.953
N	0.919	2.950	0.831	N	-0.195	-0.313	1.617
O	3.010	2.253	4.207	Fe	2.477	2.401	2.231
C	0.067	3.484	-1.406	H	2.407	2.830	-2.877
N	3.268	2.309	0.205	H	4.590	2.061	-3.235
O	3.685	2.025	6.771	H	5.938	1.443	-1.408
C	2.475	2.627	-0.835	H	7.018	0.987	2.103
N	4.594	1.880	2.323	H	7.256	1.929	0.832
C	2.954	2.570	-2.146	H	6.779	0.415	0.627
N	5.187	1.802	3.588	H	-3.194	4.508	3.125
C	4.249	2.124	-2.351	H	-2.403	4.284	1.841
N	5.858	2.417	6.264	H	-0.143	4.427	-1.237
C	5.055	1.766	-1.273	H	-0.743	2.944	-1.291
N	2.974	4.440	2.288	H	0.401	3.383	-2.322
C	4.526	1.898	0.009	H	6.093	2.509	7.107
N	2.986	5.069	1.257	H	6.461	2.497	5.628

Table S3: Cartesian coordinates (Å) of $\mathbf{1_{opt} \cdot H_2O}$

Atom	x	y	z	Atom	x	y	z
Fe	-0.255	0.169	0.254	N	1.861	1.194	3.442
C	-2.587	3.897	0.554	C	2.330	-3.655	-0.002
N	-2.077	5.162	0.584	N	-0.276	0.222	-1.776
O	-1.842	1.608	0.427	C	-1.610	-2.389	0.515
C	-1.498	2.813	0.428	N	0.520	0.690	-2.541
N	-0.240	3.277	0.325	C	-2.765	-3.359	0.815
O	-3.771	3.636	0.620	N	1.277	1.135	-3.294
C	1.890	2.479	0.102	H	-2.717	5.944	0.659
N	0.616	2.250	0.220	H	-1.073	5.287	0.511
O	-1.871	-1.159	0.455	H	2.191	4.389	1.029
C	2.439	3.876	0.082	H	1.960	4.455	-0.727
N	2.030	0.108	0.053	H	3.530	3.907	-0.059
O	-3.880	-2.970	1.101	H	4.676	2.190	-0.199
C	2.713	1.264	-0.004	H	5.859	0.003	-0.371
N	0.517	-1.982	0.210	H	-3.071	-5.367	1.044
C	4.114	1.256	-0.155	H	-1.423	-4.892	0.621
N	-0.403	-2.946	0.360	H	4.542	-2.125	-0.266
C	4.771	0.032	-0.251	H	1.508	-4.380	0.084
N	-2.409	-4.672	0.718	H	3.049	-3.835	0.819
C	4.043	-1.158	-0.193	H	2.865	-3.834	-0.954
N	0.062	0.183	2.305	O	-2.024	-1.680	3.379
C	2.648	-1.081	-0.035	H	-1.294	-1.082	3.113
N	0.981	0.699	2.881	H	-2.734	-1.462	2.749
C	1.774	-2.261	0.057				