

Supplementary Information

Spectroscopic Investigation of Iron(III) Cysteamine Dioxygenase in the Presence of Substrate (Analogues): Implications for the Nature of Substrate-Bound Reaction Intermediates

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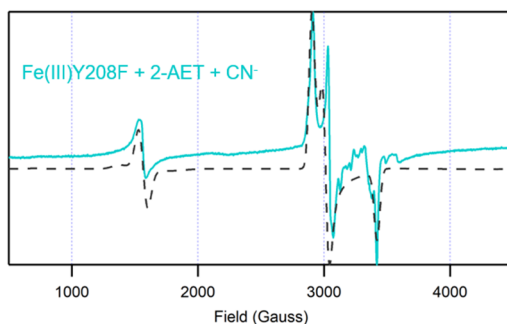


Figure S1. X-band EPR spectra at 20 K of Y208F Fe(III)ADO incubated with a 10-fold excess of cyanide in the presence of a 15-fold excess of 2-AET. An EPR spectral simulation (dashed line) is overlaid on the experimental spectrum (solid line) for comparison. Fit parameters are provided in Table S1.

Table S1. Parameters used to fit experimental EPR spectra via EasySpin (Version 5.2.25)¹

Samples	Species	Percent	g_1	g_2	g_3	E/D	D (cm ⁻¹)
<i>Fe^{III} ADO</i>	Major high-spin	85	2	1.99	1.99	0.28	4.19
	Minor high-spin	15	1.99			0.33	1.44
<i>Fe^{III} ADO with azide</i>	Major high-spin	85	2	1.99	1.99	0.28	4.19
	Minor high-spin	15	1.99			0.33	1.44
<i>2-AET-bound Fe^{III} ADO</i>	Major high-spin	92	2.1	2.00	1.99	0.25	4.24
	Minor high-spin	8	2.00			0.33	1.52
<i>2-AET-bound Fe^{III} ADO with azide</i>	Major high-spin	84	2.01	2.00	1.99	0.28	4.34
	Minor high-spin	6	2.01			0.33	1.63
	Minor low-spin	10	2.38	2.28	1.92		
<i>3-MPA-bound Fe^{III} ADO with azide</i>	Major high-spin	85	2.01	1.99	1.99	0.28	4.19
	Minor high-spin	15	1.99			0.33	1.44
<i>Cys-bound Fe^{III} ADO with azide</i>	Major high-spin	88	2.001	2.00	1.99	0.28	4.19
	Minor high-spin	9	2.01			0.33	1.63
	Minor low-spin	3	2.38	2.28	1.92		
<i>Fe^{III} ADO with cyanide</i>	Major high-spin	75	1.99	1.99	2.00	0.26	1.47
	Minor high-spin	25	1.99			0.33	1.44
<i>2-AET-bound Fe^{III} ADO with cyanide</i>	Minor high-spin	12	2.10	2.00	2.00	0.24	4.29
	Minor high-spin	8	2.00			0.33	1.52
	Major low-spin	80	2.31	2.19	1.96		
<i>Cys-bound Fe^{III} ADO with cyanide</i>	Minor high-spin	14	2.10	2.00	2.00	0.26	3.37
	Minor high-spin	6	2.00			0.32	1.63
	Major low-spin	80	2.31	2.19	1.96		
<i>3-MPA-bound Fe^{III} ADO with cyanide</i>	Major high-spin	64	2.10	2.03	1.99	0.25	4.25
	Minor high-spin	8	2.00			0.33	1.52
	Minor low-spin	28	2.33	2.22	1.93		
<i>2-AET-bound Fe^{III} Y208F with cyanide</i>	Minor high-spin	12	2.1	2.01	2.01	0.24	4.29
	Minor high-spin	8	2			0.33	1.52
	Major low-spin	80	2.31	2.19	1.96		

References

(1) Stoll, S., and Schweiger, A. (2006) EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. *J. Magn. Reson.* 178, 42–55.