Supporting Information for

Mössbauer Spectroscopy and Theoretical Studies of iron nitrosyl and bi-metallic complexes

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Table SI-1. Comparisons of the experimental and calculated metric parameters.

Parameter	**1-A$^+$**		**2-A$^+$**		**3-A$^+$**	
(Å or °)	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
M-N(N_2S_2)	2.023	2.075	1.998	2.027	1.924	1.971
	2.013	2.075	1.975	2.027	1.922	1.971
M-S	2.237	2.279	2.197	2.235	2.158	2.189
	2.232	2.279	2.201	2.235	2.147	2.189
M-N(NO)	1.685	1.742	1.765	1.779	-	-
N-O	1.150	1.165	1.108	1.161	-	-
Fe'-S	2.283	2.357	2.284	2.358	2.286	2.365
	2.286	2.357	2.287	2.358	2.305	2.365
Fe'-C(CO)	1.752	1.764	1.752	1.763	1.743	1.768
C-O	1.152	1.152	1.148	1.153	1.152	1.151
Fe'-C(Cp), average	2.095	2.140	2.093	2.138	2.084	2.136
M-Fe'	3.203	3.317	3.153	3.215	3.016	3.154
N-M-N	79.7	78.7	81.7	80.8	83.7	83.1
S-M-S	85.2	85.5	85.8	87.4	88.3	88.8
M-N-O	163.8	157.6	131.4	124.4	-	-
S-Fe'-S	82.9	81.9	81.9	81.8	81.5	80.7
Fe'-C-O	174.5	177.9	175.1	178.4	176.8	178.9
M-S-S-Fe'	145.1	147.5	141.7	142.1	133.3	139.0

Table SI-2. Experimental and computed zero-field Mössbauer parameters.

Species	**^{57}Fe center**	**ρ - 11616 (au^{-3})[a]**	**δ (mm·s^{-1})[b]**	**ΔE_Q (mm·s^{-1})**	**δ exp (mm·s^{-1})**	**ΔE_Q exp (mm·s^{-1})**
1	Fe(N_2S_2)	0.438	0	0.962	0.23(2)	1.37
1-A$^+$	Fe(N_2S_2)	0.381	0.021	0.729	0.23(2)	1.15
	Fe(CO)Cp	0.201	0.087	2.212	0.34(2)	1.79
2-A$^+$	Fe(CO)Cp	0.214	0.083	2.220	0.33	1.78
3-A$^+$	Fe(CO)Cp	0.167	0.100	2.225	0.33	1.75

a. The electron densities at nuclei were scaled by subtracting 11616 au^{-3}.

b. The isomer shifts calculated with α = - 0.367 mm·s^{-1}·au^3 are relative numbers scaled to Fe(NO)(N_2S_2)in the metalloligand **1**.

Table SI-3. Computed magnetic hyperfine parameters.

Species	**g_{iso}/g_{xyz}**		**A_{iso} (MHz)**	**A_{xyz} (MHz)**	**$A^{Fe}_{x,y,z}/g_n\beta_n$ (T)** **$A^{Fe}_{iso}/g_n\beta_n$ (T)**
1	2.067	($Fe(N_2S_2)$) (MHz)	-32.8	(23.5, -56.8, -65.0)	(17, -41.5, -47.5) -24
(Doublet)	(2.031,				
	2.083,	^{14}N (NO)	31.7	(6.2, 21.4, 67.4)	
	2.088**)**	^{14}N (N_2S_2)	-0.1	(-0.8, -0.9, 1.3)	
1-A^+	2.047	^{57}Fe ($Fe(N_2S_2)$)	-26.7	(32.7, -53.3, -59.3)	(24, -39, -43) -19.5
(Doublet)	(2.017,				
	2.056,	^{57}Fe (Fe'(CO)Cp)	3.6	(2.6, 2.9, 5.3)	(2, 2, 4) 2.6
	2.068)				
		^{14}N (NO)	35.1	(20.9, 21.3, 63.2)	
		^{14}N (N_2S_2)	-0.5	(0.5, -0.8, -1.1)	

For ^{57}Fe, the A-values given in MHz can be converted to hyperfine fields (in kiloGauss) at the ^{57}Fe nucleus by multiplying with 7.31; 1 T = 10 kiloGauss.

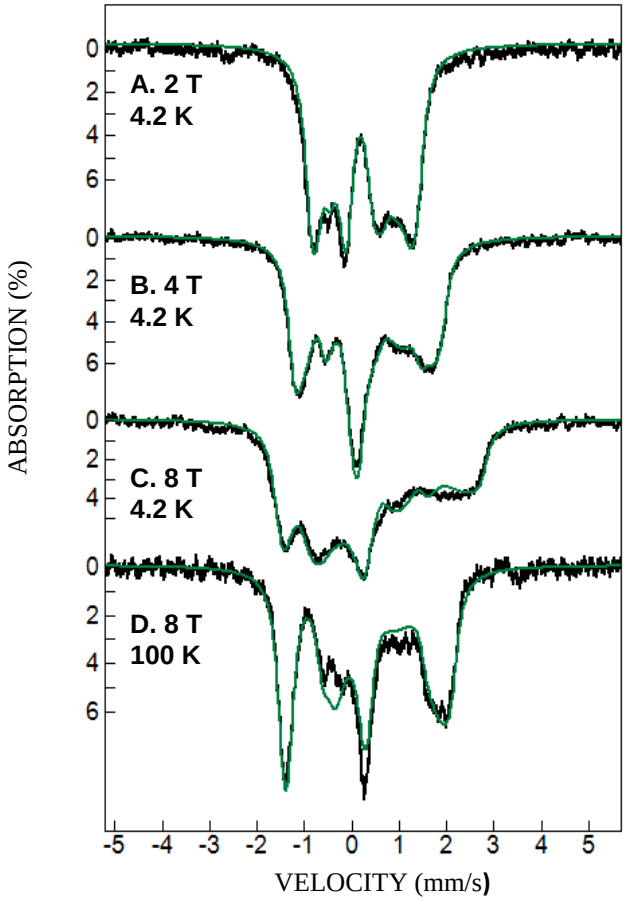

Figure SI-1. Variable-field, variable-temperature Mössbauer spectra (hash marks) of Complex 1, in a polycrystalline powder suspended in mineral oil. The solid lines are spectral fits obtained by group fitting the variable field and temperature data assuming that the Fe-NO system consists of the Fe(III) ion with S = 3/2 electronic ground state spin coupled by strong antiferromagnetic coupling with S = 1 from NO^-, with the parameters listed in Table SI-1.

Table SI-5. Mössbauer parameters of complex 1 in the spectral simulations with $S_{Fe} = 3/2$ coupled by strong antiferromagnetic coupling with $S_{NO} = 1$.

	1 **N_2S_2FeNO**
S_{Fe}	3/2
$J\ (cm^{-1})$	> 50 cm^{-1} (not determinable)[a]
$D\ (cm^{-1})$	> 0 (not determinable) [a]
$\boldsymbol{\delta}$ *(mm/s) (4.2 K)*	0.23(2)
$\boldsymbol{\delta}$ *(mm/s) (100 K)*	0.20
$\boldsymbol{\Delta E_Q}$ *(mm/s) (4.2K)*	1.37(2)
(100 K)	1.3(5)
α, β, γ	(0, 8, 9)
$\boldsymbol{\eta}$	0.2
$\boldsymbol{A}^{Fe}_{x,y,z}/g_n\beta_n$ *(T)*	-21.5, -13, +6
α', β', γ'	(5, 0, 3)
$\boldsymbol{\Gamma}$ *(mm/s)*	0.30

[a] Spectral fittings in high applied magnetic field were insensitive to the value of D and for values above 50 cm^{-1} they were insensitive to the value of J, as long as $D << J$.

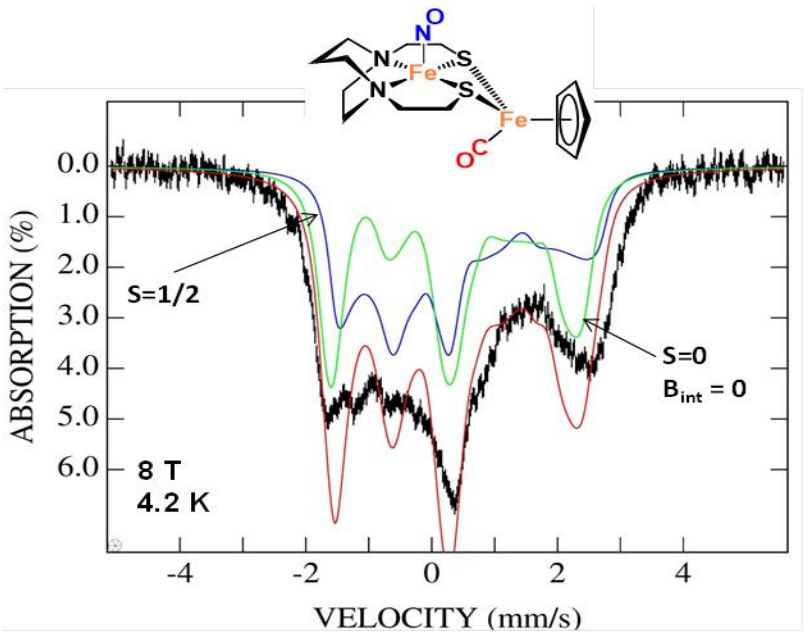

Figure SI-2. 8.0 T Mössbauer spectrum of Complex 1-A (hash marks). In colors are: a least-squares simulation of an S = ½ FeNO (blue) with the parameters of Complex 1, a diamagnetic iron center (green) with the zero-field parameters discussed above for Fe'Cp(CO)$^+$ and the sum of these simulations (red).