Functionalized Pyridine in Pyclen-based Iron(III) Complexes: Evaluation of Fundamental Properties

Magy A. Mekhail, Kristof Pota, Timothy M. Schwartz, Kayla N. Green

[a] Department of Chemistry and Biochemistry, Texas Christian University, 2950 W. Bowie, Fort Worth, TX 76129, United States

Table of Contents

Table S1. Binding stability constant (log β) for ligands **L1**, **L2**, **L3**, and **L5** with Fe(II)

		L1 OH	**L2** H	**L3** CL	**L4** CF_3	**L5** CN
Fe(II)	[ML]/([M][L])	14.18(5)	14.46(7)	12.41(2)	14.12(4)	12.30(2)
	[MHL]/([ML][H])	6.18(3)	4.62(7)	3.82(5)	4.25 (6)	3.94(6)
	$[MH_2L]$/([MHL][H])	3.83(11)	-	-	-	-
	[ML]/([MLOH][H])	8.91(7)	9.28(11)	9.31(3)	9.12(8)	9.27(4)
	$[ML(OH)]$/($[ML(OH)_2]$[H])	11.49(7)	13.1(4)	12.92(8)	12.15(9)	12.33(6)

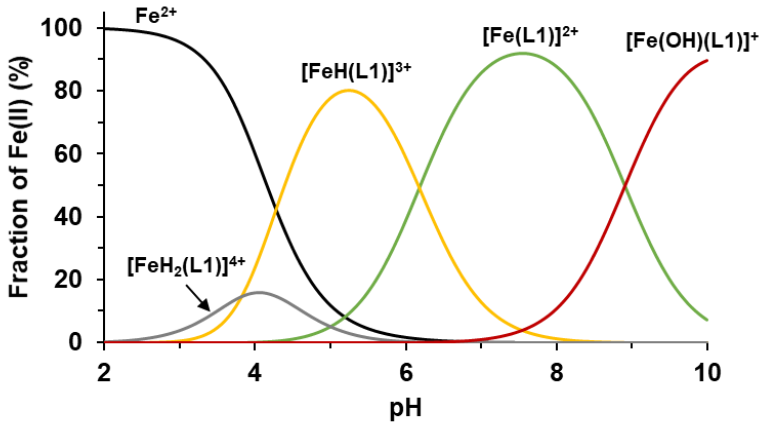

Figure S1. Species distribution curves for [**FeL1**] (I = 0.15 M NaCl, T = 25 °C, $[\mathbf{L1}]_{tot}$ = $[\mathbf{Fe}]_{tot}$ = 2 mM).

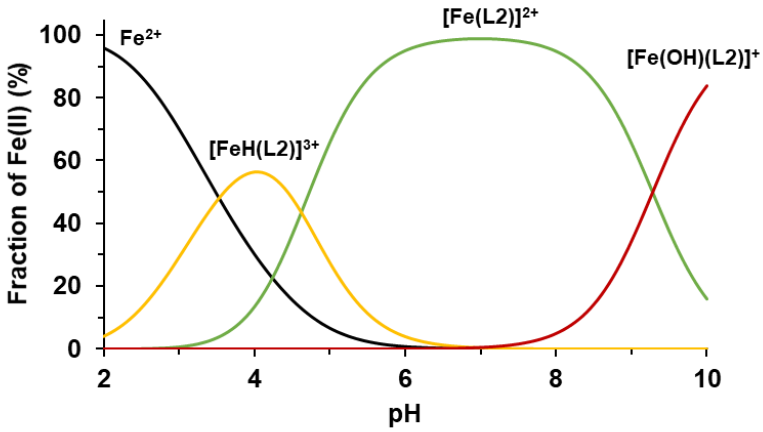

Figure S2. Species distribution curves for [**FeL2**] (I = 0.15 M NaCl, T = 25 °C, $[\mathbf{L2}]_{tot}$ = $[\mathbf{Fe}]_{tot}$ = 2 mM).

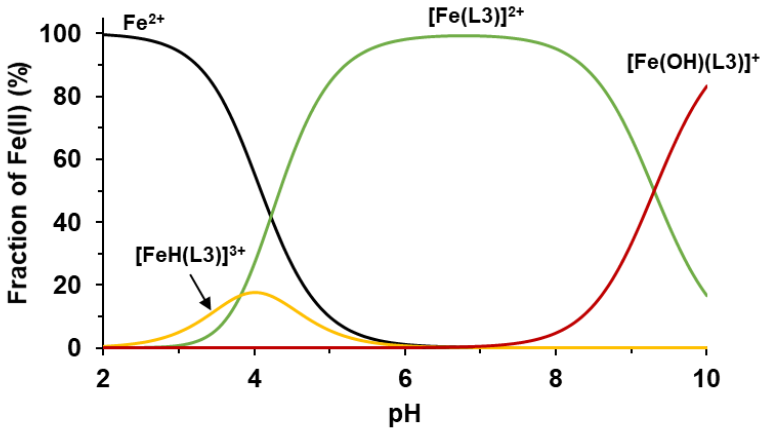

Figure S3. Species distribution curves for [**FeL3**] (I = 0.15 M NaCl, T = 25 °C, [**L3**]$_{tot}$ = [**Fe**]$_{tot}$ = 2 mM).

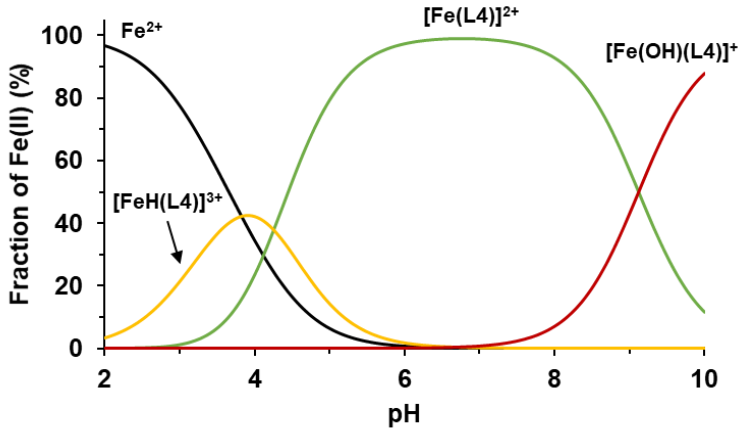

Figure S4. Species distribution curves for [**FeL4**] (I = 0.15 M NaCl, T = 25 °C, [**L4**]$_{tot}$ = [**Fe**]$_{tot}$ = 2 mM).

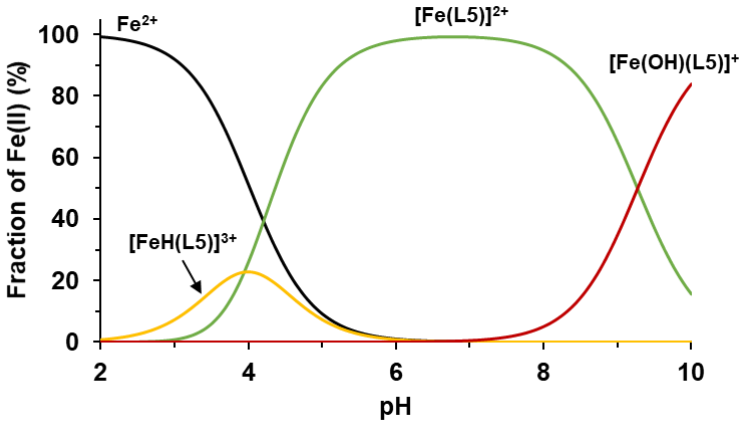

Figure S5. Species distribution curves for [**FeL5**] (I = 0.15 M NaCl, T = 25 °C, [**L5**]$_{tot}$ = [**Fe**]$_{tot}$ = 2 mM).

Table S2. Crystal data, intensity collections, and structure refinement parameters for **FeL1**-**FeL6**.

Complex	**FeL1**	**Fe L2**	**FeL3**	**FeL4**	**Fe L5**	**FeL6**
Formula	$C_{11}H_{18}N_4OCl_3Fe$	$C_{12}H_{18}Cl_2F_3FeN_4O_3S$	$C_{12}H_{17}Cl_3F_3FeN_4O_3S$	$C_{13}H_{17}Cl_2F_6FeN_4O_3S$	$C_{14}H_{21}Cl_2F_3FeN_5O_4S$	$C_{12}H_{17}Cl_2F_3FeN_5O_5S$
M.W.	498.11	482.113	516.558	550.112	539.166	527.11
Unit cell	triclinic	Monoclinic	Monoclinic	monoclinic	monoclinic	orthorhombic
Space group	P-1	$P2_1/c$	$P2_1/m$	$P2_1/m$	$P2_1/m$	Pnma
a (Å)	6.8687(2)	10.5619(5)	6.9779(4)	6.9632(3)	10.1639(3)	27.5290(9)
b (Å)	8.6082(2)	7.1060(3)	10.3829(6)	10.2625(5)	8.8011(3)	10.3020(3)
c (Å)	13.7369(4)	25.1299(12)	13.9933(8)	14.6539(7)	12.5028(4)	7.0168(2)
α	80.288(2)	90	90	90	90	90
β	81.571(2)	101.3380(1)	97.673(2)	97.751(2)	109.928(2)	90
γ	88.256(2)	90	90	90	90	90
Volume ($Å^3$)	791.92(4)	1849.26(15)	1004.75(10)	1037.60(8)	1051.45(6)	1989.99(10)
Z	2	4	2	2	2	4
$D_{calc.}$(g/cm^3)	2.089	1.732	1.707	1.761	1.703	1.759
Reflections Collected	56363	102235	83932	84300	37464	87940
Independent Reflections	4462	5398	2977	3075	2152	1733
R_{int}	0.0889	0.0230	0.0621	0.0524	0.0990	0.0260
Completeness to θ	0.0173	0.0134	0.0136	0.0147	0.0309	0.0135
GooF	1.083	1.069	1.050	1.054	0.995	1.213
R_1,wR_2 [I>2sigma(I)]	0.0438, 0.0902	0.0215, 0.0555	0.0261, 0.0608	0.0300, 0.0761	0.0499, 0.1025	0.0379, 0.0937
R_1, wR_2	0.0638, 0.0970	0.0221, 0.0558	0.0267, 0.0613	0.0337, 0.0786	0.0624, 0.1086	0.0381, 0.0938

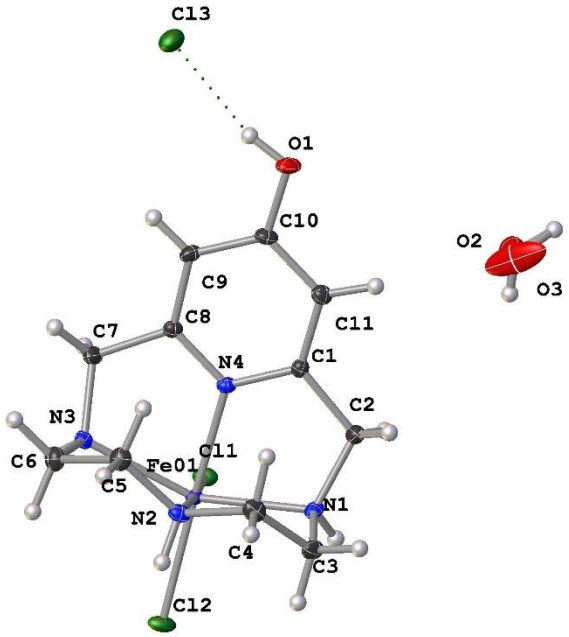

Figure S6. Solid state structure of **FeL1** showing atom labeling.

Table S3. Bond Lengths for **FeL1.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe01	Cl1	2.3151(7)	N3	C7	1.483(3)
Fe01	Cl2	2.2856(6)	N2	C4	1.474(3)
Fe01	N4	2.0650(19)	N2	C5	1.474(3)
Fe01	N1	2.175(2)	C3	C4	1.511(4)
Fe01	N3	2.178(2)	C9	C8	1.376(3)
Fe01	N2	2.157(2)	C9	C10	1.398(3)
O1	C10	1.336(3)	C6	C5	1.511(4)
N4	C8	1.346(3)	C11	C1	1.377(3)
N4	C1	1.348(3)	C11	C10	1.395(3)
N1	C3	1.490(3)	C8	C7	1.509(3)
N1	C2	1.488(3)	C1	C2	1.502(3)
N3	C6	1.488(3)			

Table S4 Bond Angles for **FeL1.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	Fe01	Cl1	92.06(2)	C7	N3	Fe01	109.70(15)
N4	Fe01	Cl1	92.13(6)	C7	N3	C6	113.4(2)
N4	Fe01	Cl2	175.42(6)	C4	N2	Fe01	110.31(15)
N1	Fe01	Cl1	102.13(6)	C5	N2	Fe01	109.92(15)
N1	Fe01	Cl2	100.00(6)	C5	N2	C4	115.36(19)
N1	Fe01	N4	77.28(8)	C4	C3	N1	108.9(2)
N3	Fe01	Cl1	97.36(6)	C10	C9	C8	118.2(2)
N3	Fe01	Cl2	103.90(6)	C5	C6	N3	110.0(2)
N3	Fe01	N4	77.39(8)	C10	C11	C1	118.4(2)
N3	Fe01	N1	148.41(8)	C3	C4	N2	107.7(2)
N2	Fe01	Cl1	177.28(6)	C9	C8	N4	122.0(2)
N2	Fe01	Cl2	88.69(6)	C7	C8	N4	114.6(2)
N2	Fe01	N4	87.21(8)	C7	C8	C9	123.4(2)
N2	Fe01	N1	80.30(8)	C11	C1	N4	121.7(2)
N2	Fe01	N3	79.92(8)	C2	C1	N4	114.6(2)
C8	N4	Fe01	119.42(15)	C2	C1	C11	123.6(2)
C1	N4	Fe01	120.71(15)	C6	C5	N2	107.2(2)
C1	N4	C8	119.80(19)	C1	C2	N1	111.6(2)
C3	N1	Fe01	106.03(15)	C9	C10	O1	122.6(2)
C2	N1	Fe01	111.99(14)	C11	C10	O1	117.6(2)
C2	N1	C3	113.25(19)	C11	C10	C9	119.8(2)
C6	N3	Fe01	108.24(15)	C8	C7	N3	110.9(2)

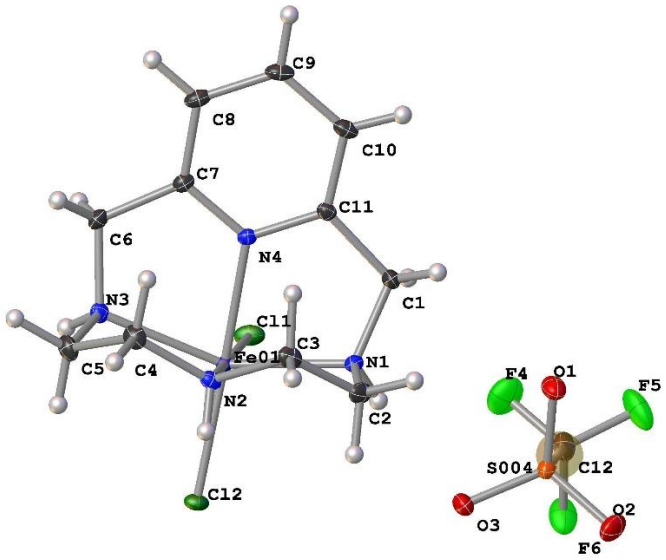

Figure S7. Solid state structure of **FeL2** showing atom labeling.

Table S5. Bond Lengths for **FeL2.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe01	Cl2	2.2600(4)	N3	C5	1.4899(18)
Fe01	Cl1	2.2721(4)	N3	C6	1.4904(17)
Fe01	N4	2.1140(11)	N1	C1	1.4825(17)
Fe01	N3	2.1779(11)	N1	C2	1.4887(18)
Fe01	N1	2.1578(11)	N2	C3	1.4789(17)
Fe01	N2	2.1976(11)	N2	C4	1.4744(18)
S004	O3	1.4507(11)	C11	C1	1.5088(18)
S004	O2	1.4461(11)	C11	C10	1.3855(18)
S004	O1	1.4437(11)	C3	C2	1.516(2)
S004	C12	1.8294(16)	C4	C5	1.5189(19)
F6	C12	1.3300(18)	C7	C8	1.3918(18)
F5	C12	1.3353(17)	C7	C6	1.5025(19)
F4	C12	1.3321(18)	C8	C9	1.385(2)
N4	C11	1.3414(16)	C10	C9	1.393(2)
N4	C7	1.3374(16)			

Table S6. Bond Angles for **FeL2.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Fe01	Cl2	98.370(13)	C1	N1	Fe01	110.23(8)
N4	Fe01	Cl2	172.57(3)	C2	N1	Fe01	109.05(8)
N4	Fe01	Cl1	89.05(3)	C2	N1	C1	113.51(11)
N3	Fe01	Cl2	101.53(3)	C3	N2	Fe01	109.88(8)
N3	Fe01	Cl1	102.51(3)	C4	N2	Fe01	110.32(8)
N3	Fe01	N4	76.36(4)	C4	N2	C3	116.05(11)
N1	Fe01	Cl2	102.70(3)	C1	C11	N4	114.48(11)
N1	Fe01	Cl1	95.66(3)	C10	C11	N4	121.13(12)
N1	Fe01	N4	76.74(4)	C10	C11	C1	124.32(12)
N1	Fe01	N3	147.08(4)	C2	C3	N2	106.76(11)
N2	Fe01	Cl2	87.40(3)	C11	C1	N1	110.88(11)
N2	Fe01	Cl1	173.29(3)	C5	C4	N2	107.18(11)
N2	Fe01	N4	85.21(4)	C3	C2	N1	110.83(11)
N2	Fe01	N3	79.53(4)	C8	C7	N4	120.81(12)
N2	Fe01	N1	79.66(4)	C6	C7	N4	115.20(11)
O2	S004	O3	114.66(7)	C6	C7	C8	123.95(12)
O1	S004	O3	114.70(7)	C9	C8	C7	118.41(12)
O1	S004	O2	115.42(7)	C9	C10	C11	118.10(13)
C12	S004	O3	102.88(7)	C10	C9	C8	120.34(12)
C12	S004	O2	103.73(7)	C4	C5	N3	109.00(11)
C12	S004	O1	103.08(7)	C7	C6	N3	112.04(11)
C11	N4	Fe01	118.36(9)	F6	C12	S004	111.68(11)
C7	N4	Fe01	120.39(9)	F5	C12	S004	111.23(11)
C7	N4	C11	121.21(11)	F5	C12	F6	107.44(13)
C5	N3	Fe01	106.43(8)	F4	C12	S004	110.82(11)
C6	N3	Fe01	112.96(8)	F4	C12	F6	107.71(13)
C6	N3	C5	112.20(11)	F4	C12	F5	107.78(14)

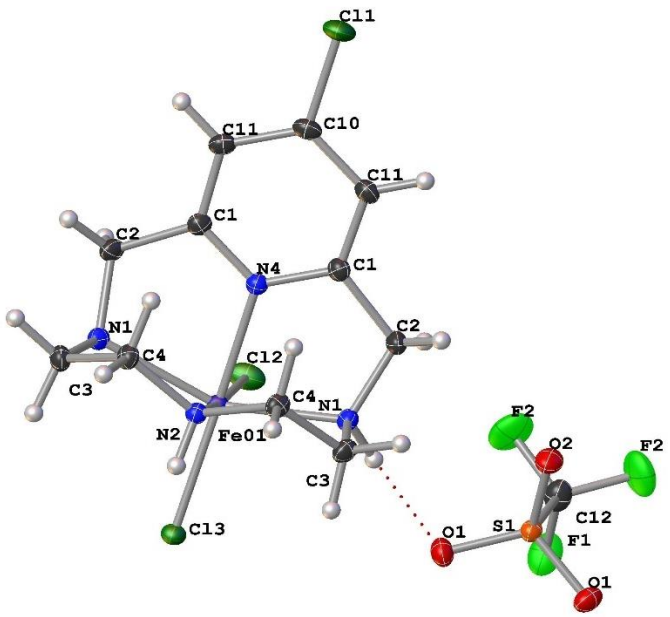

Figure S8. Solid state structure of **FeL3** showing atom labeling.

Table S7. Bond Lengths for **FeL3.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe01	Cl3	2.2407(5)	N4	C1[1]	1.3351(14)
Fe01	Cl2	2.2705(5)	N4	C1	1.3351(14)
Fe01	N4	2.1163(15)	F2	C12[2]	1.3336(16)
Fe01	N2	2.2010(15)	N2	C4[1]	1.4770(14)
Fe01	N1[1]	2.1717(11)	N2	C4	1.4770(14)
Fe01	N1	2.1717(11)	N1	C3	1.4901(16)
S1	O2	1.4383(14)	N1	C2	1.4838(16)
S1	O1[2]	1.4479(10)	C11	C10[1]	1.3871(16)
S1	O1	1.4479(10)	C11	C1	1.3882(17)
S1	C12	1.826(2)	C1	C2	1.5061(18)
Cl1	C10	1.7277(19)	C3	C4	1.5144(18)
F1	C12	1.334(3)			

[1]+X,1/2-Y,+Z; [2]+X,3/2-Y,+Z

Table S8. Bond Angles for **FeL3.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	Fe01	Cl3	100.087(19)	C1	N4	C1[1]	121.67(15)
N4	Fe01	Cl3	173.04(4)	C4	N2	Fe01	110.35(8)
N4	Fe01	Cl2	86.87(4)	C4[1]	N2	Fe01	110.35(8)
N2	Fe01	Cl3	88.61(4)	C4	N2	C4[1]	115.93(14)
N2	Fe01	Cl2	171.30(4)	C3	N1	Fe01[1]	108.23(8)
N2	Fe01	N4	84.43(6)	C2	N1	Fe01[1]	110.83(8)
N1	Fe01	Cl3	102.22(3)	C2	N1	C3	113.44(10)
N1[1]	Fe01	Cl3	102.22(3)	C1	C11	C10[1]	117.50(13)
N1	Fe01	Cl2	98.48(3)	C11	C10	Cl1	119.31(8)
N1[1]	Fe01	Cl2	98.48(3)	C11[1]	C10	Cl1	119.31(8)
N1[1]	Fe01	N4	76.54(3)	C11[1]	C10	C11	121.39(17)
N1	Fe01	N4	76.54(3)	C11	C1	N4[1]	120.96(12)
N1[1]	Fe01	N2	79.50(3)	C2	C1	N4[1]	114.65(11)
N1	Fe01	N2	79.50(3)	C2	C1	C11	124.27(12)
N1	Fe01	N1[1]	147.15(6)	C4	C3	N1	110.33(10)
O1	S1	O2	115.14(5)	C3	C4	N2[1]	107.44(10)
O1[2]	S1	O2	115.14(5)	C1	C2	N1	111.15(10)
O1[2]	S1	O1	114.53(9)	F1	C12	S1	111.24(15)
C12	S1	O2	103.27(10)	F2	C12	S1	111.28(11)
C12	S1	O1[2]	103.18(6)	F2[2]	C12	S1	111.28(11)
C12	S1	O1	103.18(6)	F2[2]	C12	F1	107.46(13)
C1	N4	Fe01	119.16(8)	F2	C12	F1	107.46(13)
C1[1]	N4	Fe01	119.16(8)	F2	C12	F2[2]	107.93(18)

[1]+X,1/2-Y,+Z; [2]+X,3/2-Y,+Z

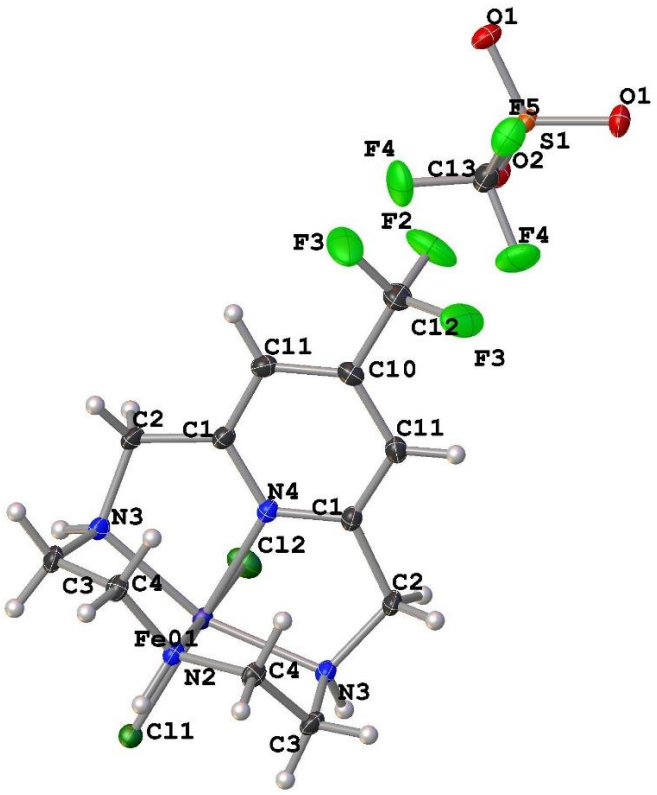

Figure S9. Solid state structure of **FeL4** showing atom labeling.

Table S9. Bond Lengths for **FeL4.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe01	Cl1	2.2347(6)	N4	C1[1]	1.3359(19)
Fe01	Cl2	2.2765(7)	N4	C1	1.3359(19)
Fe01	N4	2.128(2)	F3	C12[1]	1.325(2)
Fe01	N2	2.199(2)	N2	C4[1]	1.4768(19)
Fe01	N3[1]	2.1628(14)	N2	C4	1.4768(19)
Fe01	N3	2.1628(14)	N3	C3	1.490(2)
S1	O2	1.4396(19)	N3	C2	1.486(2)
S1	O1[1]	1.4480(13)	C1	C11	1.391(2)
S1	O1	1.4480(13)	C1	C2	1.501(2)
S1	C13	1.826(3)	C4	C3	1.514(2)
F5	C13	1.332(3)	C11	C10[1]	1.389(2)
F4	C13	1.336(2)	C10	C12	1.514(4)
F2	C12	1.322(3)			

[1]+X,1/2-Y,+Z

Table S10. Bond Angles for **FeL4.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	Fe01	Cl1	100.34(3)	C4	N2	C4[1]	116.10(18)
N4	Fe01	Cl1	173.51(6)	C3	N3	Fe01[1]	108.28(10)
N4	Fe01	Cl2	86.15(6)	C2	N3	Fe01[1]	111.19(10)
N2	Fe01	Cl1	89.01(6)	C2	N3	C3	113.56(14)
N2	Fe01	Cl2	170.65(6)	C11	C1	N4[1]	120.38(16)
N2	Fe01	N4	84.50(8)	C2	C1	N4[1]	114.83(15)
N3	Fe01	Cl1	102.40(4)	C2	C1	C11	124.69(15)
N3[1]	Fe01	Cl1	102.40(4)	C3	C4	N2[1]	107.23(13)
N3	Fe01	Cl2	98.25(4)	C10[1]	C11	C1	117.84(17)
N3[1]	Fe01	Cl2	98.25(4)	C4	C3	N3	110.27(13)
N3	Fe01	N4	76.45(4)	C11	C10	C11[1]	121.1(2)
N3[1]	Fe01	N4	76.45(4)	C12	C10	C11[1]	119.42(11)
N3	Fe01	N2	79.55(4)	C12	C10	C11	119.42(11)
N3[1]	Fe01	N2	79.55(4)	C1	C2	N3	111.22(13)
N3	Fe01	N3[1]	147.07(8)	F3[1]	C12	F2	107.00(17)
O1	S1	O2	115.15(7)	F3	C12	F2	107.00(17)
O1[1]	S1	O2	115.15(7)	F3	C12	F3[1]	107.7(3)
O1	S1	O1[1]	114.61(11)	C10	C12	F2	110.6(2)
C13	S1	O2	103.36(13)	C10	C12	F3[1]	112.14(15)
C13	S1	O1[1]	103.07(8)	C10	C12	F3	112.14(15)
C13	S1	O1	103.07(8)	F5	C13	S1	111.08(19)
C1[1]	N4	Fe01	118.78(10)	F4	C13	S1	111.21(14)
C1	N4	Fe01	118.78(10)	F4[1]	C13	S1	111.21(14)
C1	N4	C1[1]	122.4(2)	F4	C13	F5	107.66(16)
C4	N2	Fe01	110.38(10)	F4[1]	C13	F5	107.66(16)
C4[1]	N2	Fe01	110.38(10)	F4[1]	C13	F4	107.9(2)

[1]+X,1/2-Y,+Z

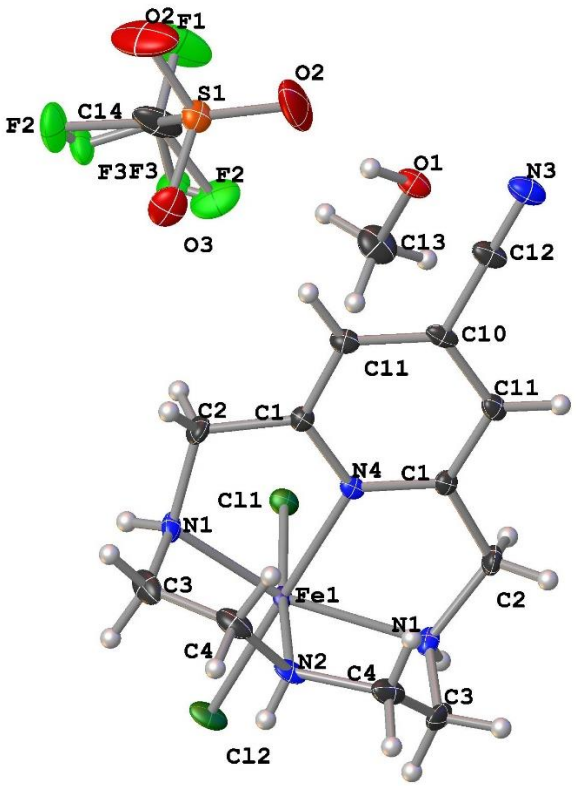

Figure S10. Solid state structure of **FeL5** showing atom labeling.

Table S11. Bond Lengths for **FeL5.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	Cl1	2.3122(13)	F1	C14	1.316(6)
Fe1	Cl2	2.2335(13)	N2	C4	1.474(4)
Fe1	N4	2.105(4)	N2	C4[1]	1.474(4)
Fe1	N1	2.170(3)	F2	C14	1.49(2)
Fe1	N1[1]	2.170(3)	F2	F3	0.640(6)
Fe1	N2	2.157(4)	N3	C12	1.139(6)
S1	O3	1.441(4)	C1	C2	1.499(5)
S1	O2[2]	1.427(3)	C1	C11	1.381(4)
S1	O2	1.427(3)	C11	C10[1]	1.390(4)
S1	C14	1.802(6)	C10	C12	1.451(6)
N4	C1[1]	1.341(4)	C3	C4	1.502(5)
N4	C1	1.341(4)	C14	F3	1.165(18)
N1	C2	1.484(4)	C14	F3[2]	1.165(18)
N1	C3	1.484(5)	O1	C13	1.435(8)

[1]+X,3/2-Y,+Z; [2]+X,5/2-Y,+Z

Table S12. Bond Angles for **FeL5.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	Fe1	Cl1	94.84(5)	C4	N2	C4[1]	115.7(4)
N4	Fe1	Cl1	86.71(10)	F3	F2	C14	48.6(11)
N4	Fe1	Cl2	178.45(11)	C2	C1	N4[1]	115.1(3)
N1[1]	Fe1	Cl1	98.36(8)	C11	C1	N4[1]	121.2(3)
N1	Fe1	Cl1	98.36(8)	C11	C1	C2	123.5(3)
N1	Fe1	Cl2	103.16(7)	C1	C2	N1	111.8(3)
N1[1]	Fe1	Cl2	103.16(7)	C10[1]	C11	C1	117.5(3)
N1[1]	Fe1	N4	76.58(7)	C11[1]	C10	C11	121.3(4)
N1	Fe1	N4	76.58(7)	C12	C10	C11	119.3(2)
N1	Fe1	N1[1]	147.33(15)	C12	C10	C11[1]	119.3(2)
N2	Fe1	Cl1	172.67(12)	C4	C3	N1	110.4(3)
N2	Fe1	Cl2	92.49(11)	C3	C4	N2[1]	107.5(3)
N2	Fe1	N4	85.96(15)	C10	C12	N3	179.9(5)
N2	Fe1	N1	79.93(8)	F1	C14	S1	112.3(4)
N2	Fe1	N1[1]	79.93(8)	F2	C14	S1	102.7(9)
O2	S1	O3	114.75(15)	F2[2]	C14	S1	102.7(9)
O2[2]	S1	O3	114.75(15)	F2	C14	F1	107.6(4)
O2[2]	S1	O2	117.3(3)	F2[2]	C14	F1	107.6(4)
C14	S1	O3	101.7(2)	F2[2]	C14	F2	124(2)
C14	S1	O2[2]	102.56(18)	F3[2]	C14	S1	122.4(14)
C14	S1	O2	102.56(18)	F3	C14	S1	122.4(14)
C1	N4	Fe1	119.22(19)	F3	C14	F1	108.0(6)
C1[1]	N4	Fe1	119.22(19)	F3[2]	C14	F1	108.0(6)
C1	N4	C1[1]	121.2(4)	F3	C14	F2[2]	102(2)
C2	N1	Fe1[1]	111.4(2)	F3	C14	F2	24.3(6)
C3	N1	Fe1[1]	107.5(2)	F3[2]	C14	F2[2]	24.3(6)
C3	N1	C2	114.0(3)	F3[2]	C14	F2	102(2)
C4[1]	N2	Fe1	110.9(2)	F3[2]	C14	F3	79(3)
C4	N2	Fe1	110.9(2)	C14	F3	F2	107.1(16)

[1]+X,3/2-Y,+Z; [2]+X,5/2-Y,+Z

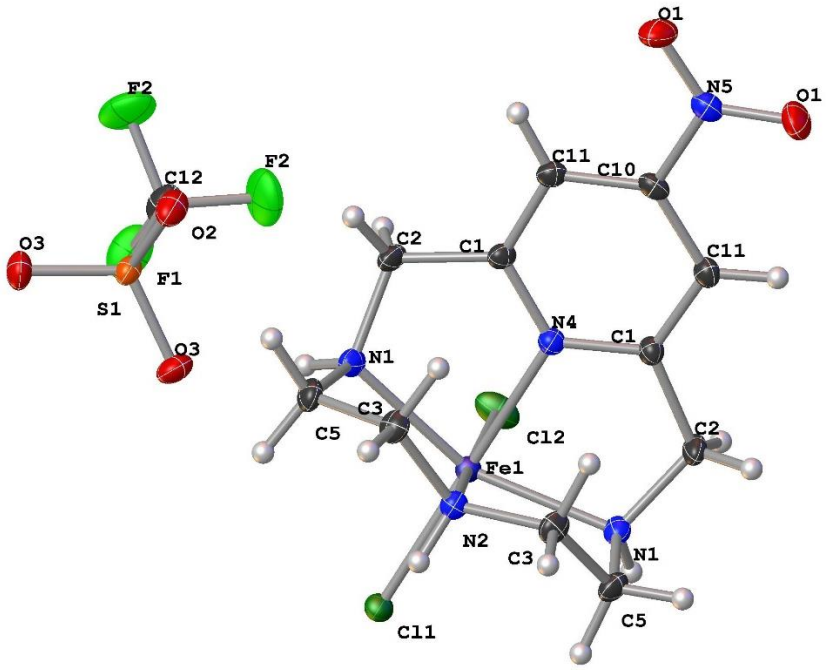

Figure S11. Solid state structure of **FeL6** showing atom labeling.

Table S13. Bond Lengths for **FeL6.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	Cl1	2.2356(7)	N4	C1	1.335(2)
Fe1	Cl2	2.2755(8)	N4	C1[1]	1.335(2)
Fe1	N4	2.131(2)	N2	C3	1.477(2)
Fe1	N2	2.198(2)	N2	C3[1]	1.477(2)
Fe1	N1[1]	2.1687(17)	N1	C2	1.484(3)
Fe1	N1	2.1687(17)	N1	C5	1.489(3)
S1	O3	1.4489(15)	N5	C10	1.485(4)
S1	O3[2]	1.4489(15)	C1	C11	1.392(3)
S1	O2	1.440(2)	C1	C2	1.504(3)
S1	C12	1.824(3)	C10	C11[1]	1.381(2)
F1	C12	1.332(4)	C10	C11	1.381(2)
F2	C12	1.335(3)	C3	C5	1.518(3)
O1	N5[1]	1.225(2)			

[1]+X,3/2-Y,+Z; [2]+X,1/2-Y,+Z

Table S14. Bond Angles for **FeL6.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	Fe1	Cl1	99.84(3)	C3[1]	N2	Fe1	110.53(12)
N4	Fe1	Cl1	173.93(7)	C3	N2	C3[1]	115.8(2)
N4	Fe1	Cl2	86.23(7)	C2	N1	Fe1[1]	110.86(12)
N2	Fe1	Cl1	89.29(7)	C5	N1	Fe1[1]	108.42(12)
N2	Fe1	Cl2	170.87(7)	C5	N1	C2	113.51(16)
N2	Fe1	N4	84.63(9)	O1	N5	O1[1]	124.6(3)
N1[1]	Fe1	Cl1	102.40(5)	C10	N5	O1	117.67(13)
N1	Fe1	Cl1	102.40(5)	C10	N5	O1[1]	117.67(13)
N1[1]	Fe1	Cl2	98.36(5)	C11	C1	N4[1]	120.43(19)
N1	Fe1	Cl2	98.36(5)	C2	C1	N4[1]	114.71(17)
N1	Fe1	N4	76.52(5)	C2	C1	C11	124.86(18)
N1[1]	Fe1	N4	76.52(5)	C11[1]	C10	N5	118.16(13)
N1	Fe1	N2	79.50(5)	C11	C10	N5	118.16(13)
N1[1]	Fe1	N2	79.50(5)	C11	C10	C11[1]	123.5(3)
N1	Fe1	N1[1]	147.08(9)	C10[1]	C11	C1	116.37(19)
O3	S1	O3[2]	114.55(14)	C5	C3	N2[1]	107.38(17)
O2	S1	O3[2]	115.20(8)	C1	C2	N1	111.03(16)
O2	S1	O3	115.20(8)	F1	C12	S1	111.5(3)
C12	S1	O3[2]	103.27(9)	F2[2]	C12	S1	111.11(18)
C12	S1	O3	103.27(9)	F2	C12	S1	111.11(18)
C12	S1	O2	102.91(16)	F2[2]	C12	F1	107.7(2)
C1	N4	Fe1	118.62(12)	F2	C12	F1	107.7(2)
C1[1]	N4	Fe1	118.62(12)	F2[2]	C12	F2	107.5(3)
C1	N4	C1[1]	122.7(2)	C3	C5	N1	110.29(16)
C3	N2	Fe1	110.53(12)				

[1]+X,3/2-Y,+Z; [2]+X,1/2-Y,+Z

Table S15. The Oxidation (E_{Pa}) and reduction (E_{Pc}) potentials (V) for pyridinophanes **L1-L6.**

Ligands	E_{Pa} (V)	E_{Pc} (V)
L1	1.350	-1.854
L2	1.665	-1.672
L3	1.573	-1.633
L4	1.663	-1.761
L5	1.532	-1.451
L6	1.375	-0.783