

Figure S1. Crystal structure of $(Et_4N)[Fe^{III}(PyPS)]$ (1) showing the mononuclearity of the complex.

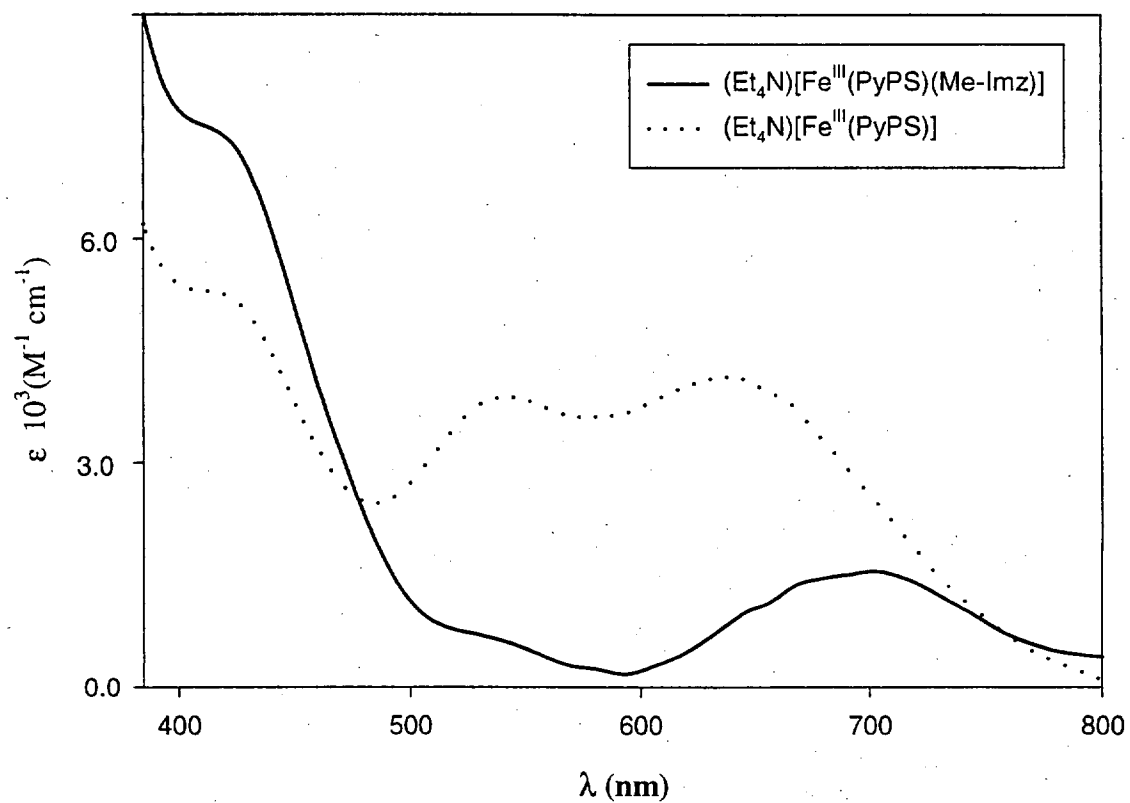


Figure S2. Electronic absorption spectra of $(\text{Et}_4\text{N})[\text{Fe}^{\text{III}}(\text{PyPS})]$ (1) in DMF at 22 °C and $(\text{Et}_4\text{N})[\text{Fe}^{\text{III}}(\text{PyPS})(\text{N-MeIm})]$ in acetone at -70 °C.

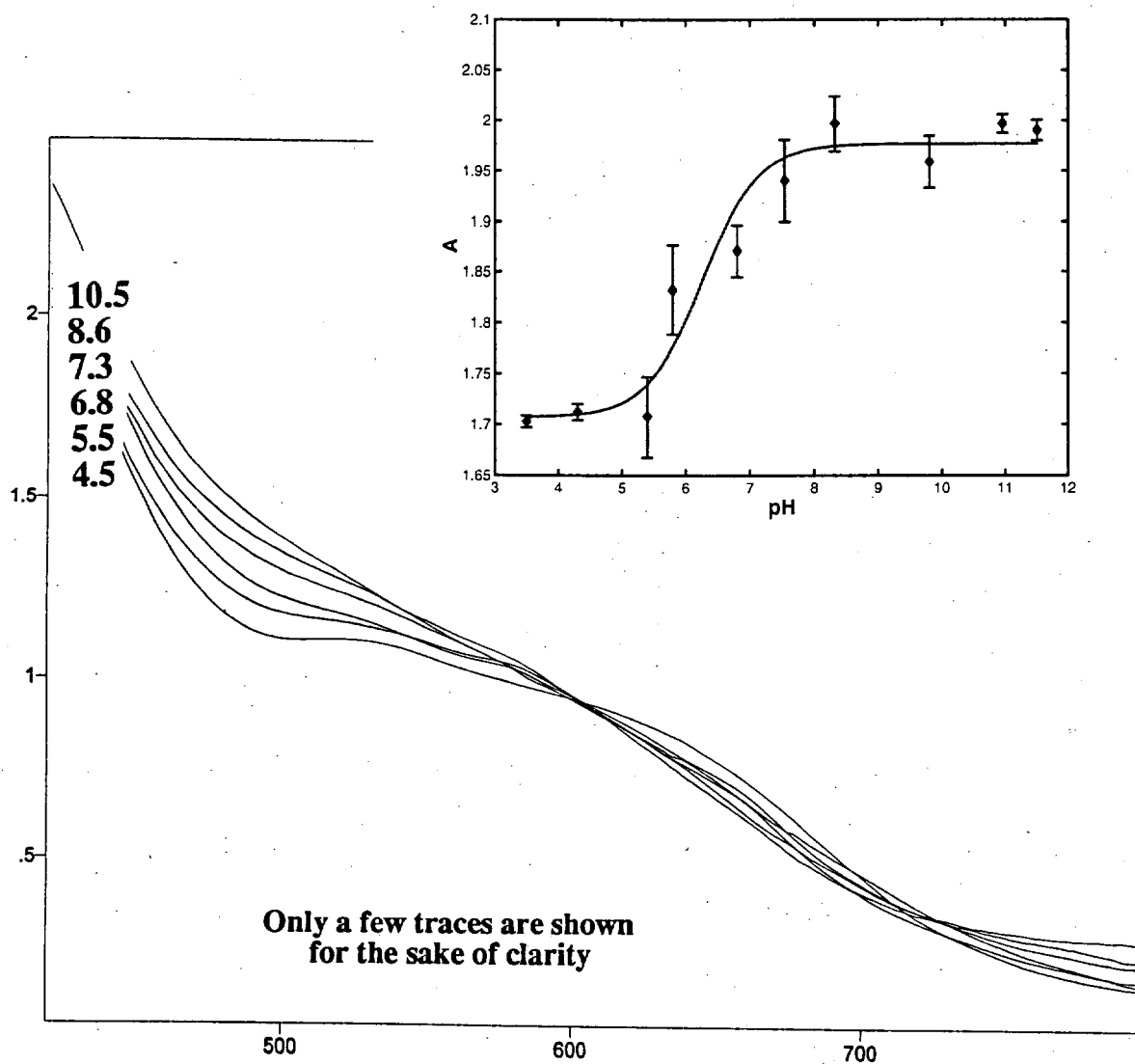


Figure S3. Changes in the electronic absorption spectrum of [Fe(PyPS)] in 70:30 water:acetone mixture with pH (at -30 °C). Inset: Plot of A_{420} vs. the apparent pH; the pK_a of the bound water in [Fe(PyPS)(H₂O)] is 6.3 ± 0.4 .

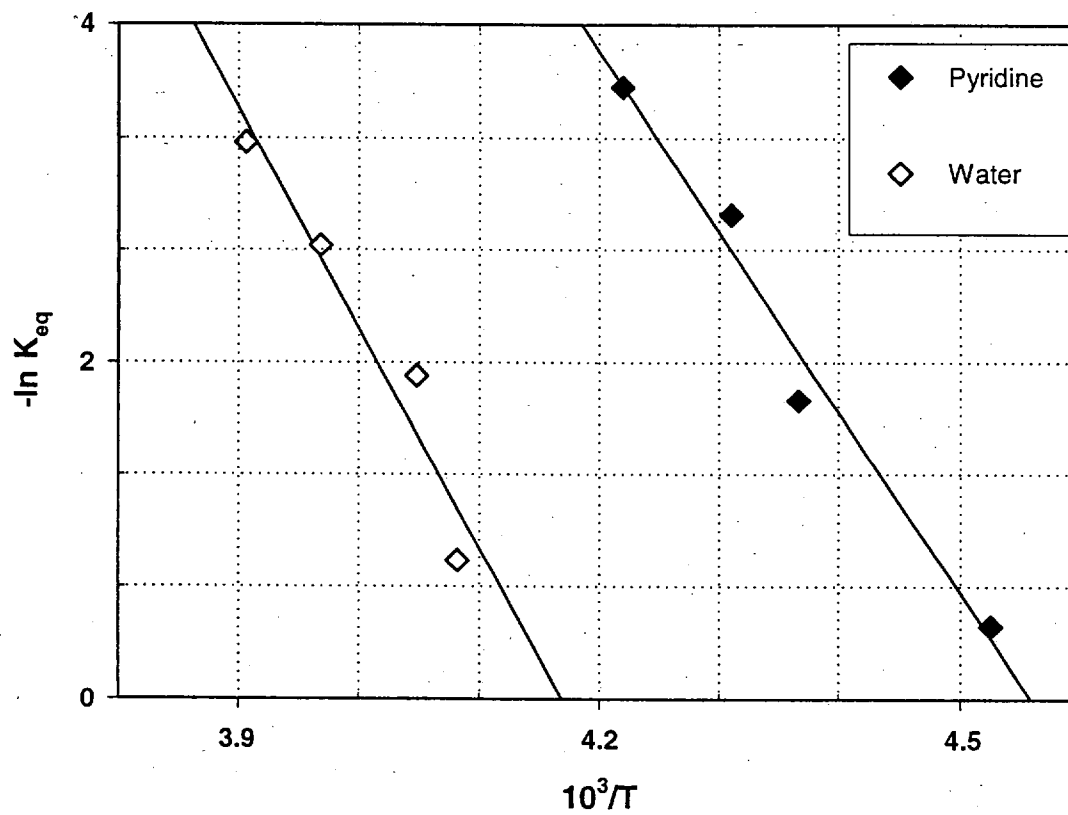


Figure S4. The van't Hoff plots for binding of water and pyridine to the iron(III) center in $[\text{Fe}^{\text{III}}(\text{PyPS})]^+$. See experimental section for details.

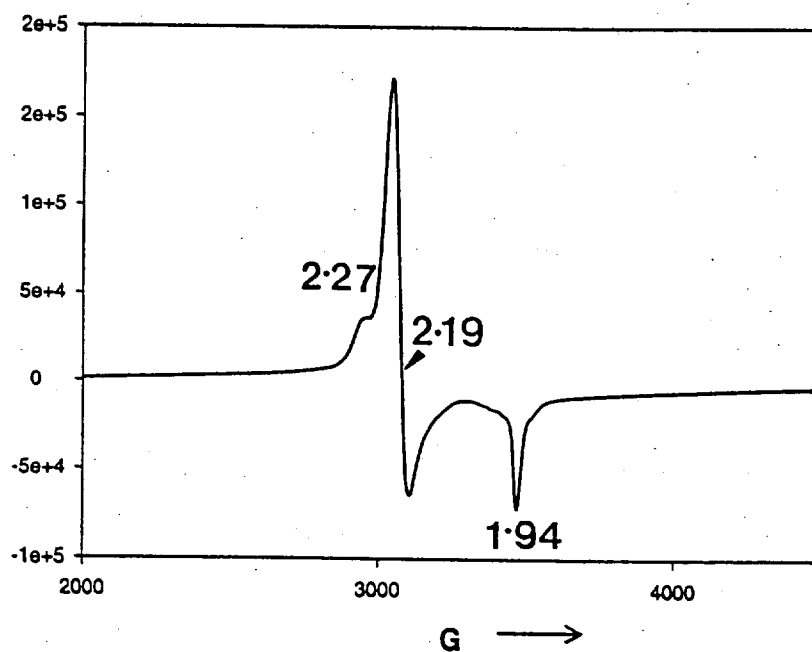


Figure S5. EPR spectrum of $\text{Na}_2[\text{Fe}^{\text{III}}(\text{PyP}\{\text{SO}_2\}_2)(\text{CN})]$ (4) in DMF glass (80 K). For details, see experimental section.

Table S1. Crystal data for (Et₄N)[Fe^{III}(PyPS)] (1)

Identification code	mn840
Empirical formula	C ₂₇ H ₃₁ FeN ₄ O ₂ S ₂
Formula weight	563.53
Crystal size	0.56 x 0.40 x 0.28 mm
Crystal habit	block
Crystal color	dark green
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 14.910(5) Å α = 90° b = 18.369(4) Å β = 91.12(2)° c = 19.222(4) Å γ = 90°
Volume	5264(2) Å ³
Z	8
Density (calculated)	1.422 Mg•m ⁻³
Absorption coefficient	0.764 mm ⁻¹
F(000)	2360
Absorption correction ¹	XABS2
Max. and min. transmission	0.840 and 0.733

- 1) XABS2: an empirical absorption correction program. Parkin, S.; Moezzi, B.; Hope, H. J. *Appl. Cryst.* 1995, 28, 53-56.

Table S2. Data collection for $(\text{Et}_4\text{N})[\text{Fe}^{\text{III}}(\text{PyPS})]$ (1)

Diffractometer	Siemens R3m/V
Temperature	140(2) K
Radiation source	normal-focus sealed tube
Wavelength	0.71073 Å (MoK α)
Monochromator	graphite
θ range for data collection	1.37 to 25.01 $^\circ$
Scan type	ω
Index ranges	$-17 \leq h \leq 17, 0 \leq k \leq 21, 0 \leq l \leq 22$
Reflections collected	9969
Independent reflections	9274 ($R_{\text{int}} = 0.0395$)
Standard reflections	2
Percent decay of standards	1.5

Table S3. Solution and refinement of (Et₄N)[Fe^{III}(PyPS)] (1)

System for solution	SHELXS-97 (Sheldrick, 1990)
Structure solution	direct
System for refinement	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full-matrix least-squares on F ²
Hydrogen atoms	mixed
Data / restraints / parameters	9274 / 0 / 657
Goodness-of-fit on F ²	1.009
Weighting scheme	$w^{-1} = \sigma^2(\text{Fo}^2) + (0.0336\text{P})^2 + 7.9225\text{P}$, where $\text{P} = (\text{Fo}^2 + 2\text{Fc}^2)/3$
R indices (all data)	R1 = 0.0983, wR2 = 0.1153
R indices calcd from obsd data	R1 = 0.0527, wR2 = 0.0983
Observed data (>2sigma(I))	6159
Largest diff. peak and hole	0.412 and -0.449 eÅ ⁻³

$$1) \quad R1 = \frac{\sum ||\text{Fo}-\text{Fc}||}{\sum |\text{Fo}|}$$

$$wR2 = \left[\frac{\sum [w(\text{Fo}^2 - \text{Fc}^2)^2]}{\sum [w(\text{Fo}^2)^2]} \right]^{1/2}$$

$$2) \quad \text{Goodness-of-Fit} = \left[\frac{\sum [w(\text{Fo}^2 - \text{Fc}^2)^2]}{(M-N)} \right]^{1/2}$$

where M is the number of reflections

and N is the number of parameters refined.

- 3) Refinement is based on F² for ALL reflections except for those with very negative F² or flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses of fit S are based on F², conventional R-factors R are based on F, with F set to zero for negative F². The observed criterion of F² > 2σ(F²) is used only for calculating R indices for observed data and is not relevant to the choice of reflections for refinement. R-factors based on F² are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{Et}_4\text{N})[\text{Fe}^{\text{III}}(\text{PyPS})]$ (1)U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Fe (1)	11161 (1)	3329 (1)	6235 (1)	21 (1)
S (1)	11490 (1)	2173 (1)	5832 (1)	25 (1)
S (2)	10357 (1)	3241 (1)	7246 (1)	28 (1)
O (1)	10112 (2)	4045 (2)	4321 (2)	46 (1)
O (2)	13081 (2)	4733 (2)	7123 (2)	39 (1)
N (1)	10390 (2)	3398 (2)	5352 (2)	27 (1)
N (2)	11574 (2)	4295 (2)	5754 (2)	26 (1)
N (3)	12144 (2)	3738 (2)	6877 (2)	23 (1)
C (1)	10491 (3)	2100 (2)	5323 (2)	21 (1)
C (2)	10174 (3)	1418 (2)	5101 (2)	27 (1)
C (3)	9402 (3)	1363 (3)	4699 (2)	33 (1)
C (4)	8921 (3)	1987 (3)	4518 (2)	40 (1)
C (5)	9220 (3)	2663 (3)	4733 (2)	36 (1)
C (6)	10007 (3)	2727 (2)	5127 (2)	25 (1)
C (7)	10475 (3)	3958 (2)	4899 (2)	32 (1)
C (8)	11168 (3)	4500 (2)	5167 (2)	31 (1)
C (9)	11432 (4)	5135 (3)	4832 (2)	40 (1)
C (10)	12117 (4)	5537 (3)	5132 (3)	41 (1)
C (11)	12526 (3)	5318 (2)	5749 (2)	34 (1)
C (12)	12235 (3)	4682 (2)	6057 (2)	27 (1)
C (13)	12558 (3)	4378 (2)	6743 (2)	27 (1)
C (14)	12157 (3)	3424 (2)	7546 (2)	24 (1)
C (15)	12929 (3)	3367 (2)	7970 (2)	31 (1)
C (16)	12884 (4)	2997 (3)	8600 (2)	39 (1)
C (17)	12082 (4)	2713 (3)	8821 (2)	41 (1)
C (18)	11311 (3)	2775 (3)	8414 (2)	32 (1)
C (19)	11342 (3)	3131 (2)	7768 (2)	25 (1)
Fe (2)	13829 (1)	8372 (1)	6055 (1)	20 (1)
S (3)	13481 (1)	7203 (1)	5675 (1)	25 (1)
S (4)	14588 (1)	8300 (1)	7111 (1)	23 (1)
O (3)	15028 (2)	8976 (2)	4194 (2)	42 (1)
O (4)	11858 (2)	9833 (2)	6706 (2)	36 (1)
N (4)	14655 (2)	8381 (2)	5223 (2)	24 (1)
N (5)	13486 (2)	9322 (2)	5512 (2)	23 (1)
N (6)	12842 (2)	8846 (2)	6625 (2)	21 (1)
C (20)	14520 (3)	7088 (2)	5250 (2)	24 (1)
C (21)	14834 (3)	6389 (2)	5102 (2)	27 (1)
C (22)	15654 (3)	6307 (3)	4774 (2)	34 (1)
C (23)	16159 (3)	6901 (3)	4597 (2)	40 (1)
C (24)	15850 (3)	7596 (3)	4732 (2)	34 (1)
C (25)	15025 (3)	7698 (2)	5059 (2)	24 (1)

C(26)	14628 (3)	8923 (2)	4746 (2)	29 (1)
C(27)	13943 (3)	9496 (2)	4945 (2)	29 (1)
C(28)	13735 (4)	10119 (3)	4571 (2)	39 (1)
C(29)	13043 (4)	10552 (3)	4803 (3)	44 (1)
C(30)	12583 (3)	10368 (2)	5397 (2)	36 (1)
C(31)	12816 (3)	9735 (2)	5740 (2)	27 (1)
C(32)	12432 (3)	9467 (2)	6410 (2)	25 (1)
C(33)	12790 (3)	8601 (2)	7321 (2)	21 (1)
C(34)	12025 (3)	8632 (2)	7724 (2)	29 (1)
C(35)	12051 (3)	8377 (3)	8400 (2)	34 (1)
C(36)	12835 (3)	8097 (2)	8688 (2)	35 (1)
C(37)	13605 (3)	8060 (2)	8295 (2)	30 (1)
C(38)	13597 (3)	8311 (2)	7605 (2)	22 (1)
N(7)	14107 (2)	4135 (2)	2835 (2)	22 (1)
C(39)	13692 (3)	3982 (2)	2120 (2)	27 (1)
C(40)	13402 (3)	3203 (3)	1999 (2)	38 (1)
C(41)	14887 (3)	3628 (2)	2994 (2)	25 (1)
C(42)	15670 (3)	3689 (3)	2496 (2)	33 (1)
C(43)	14412 (3)	4919 (2)	2822 (2)	29 (1)
C(44)	14829 (3)	5193 (3)	3496 (2)	38 (1)
C(45)	13433 (3)	4003 (3)	3400 (2)	33 (1)
C(46)	12655 (3)	4538 (3)	3409 (3)	51 (2)
N(8)	10992 (2)	5935 (2)	7908 (2)	28 (1)
C(47)	11471 (3)	6081 (2)	7229 (2)	35 (1)
C(48)	11588 (3)	6870 (3)	7041 (2)	40 (1)
C(49)	10054 (3)	6233 (3)	7895 (3)	43 (1)
C(50)	9427 (4)	5928 (4)	7355 (3)	71 (2)
C(51)	11024 (4)	5121 (2)	8014 (3)	49 (2)
C(52)	10563 (4)	4843 (3)	8662 (3)	55 (2)
C(53)	11461 (3)	6334 (3)	8506 (2)	39 (1)
C(54)	12427 (4)	6137 (4)	8636 (3)	73 (2)

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Table S5. Bond lengths (Å) for (Et₄N)[Fe^{III}(PyPS)] (1)

Fe(1)-N(1)	2.035(3)	Fe(1)-N(3)	2.041(3)
Fe(1)-N(2)	2.099(3)	Fe(1)-S(2)	2.3104(13)
Fe(1)-S(1)	2.3147(13)	S(1)-C(1)	1.770(4)
S(2)-C(19)	1.773(4)	O(1)-C(7)	1.237(5)
O(2)-C(13)	1.242(5)	N(1)-C(7)	1.355(5)
N(1)-C(6)	1.423(5)	N(2)-C(8)	1.324(5)
N(2)-C(12)	1.339(5)	N(3)-C(13)	1.354(5)
N(3)-C(14)	1.408(5)	C(1)-C(2)	1.403(6)
C(1)-C(6)	1.407(6)	C(2)-C(3)	1.378(6)
C(3)-C(4)	1.392(7)	C(4)-C(5)	1.380(7)
C(5)-C(6)	1.389(6)	C(7)-C(8)	1.518(6)
C(8)-C(9)	1.394(6)	C(9)-C(10)	1.378(7)
C(10)-C(11)	1.383(7)	C(11)-C(12)	1.383(6)
C(12)-C(13)	1.504(6)	C(14)-C(15)	1.401(6)
C(14)-C(19)	1.404(6)	C(15)-C(16)	1.392(6)
C(16)-C(17)	1.379(7)	C(17)-C(18)	1.383(7)
C(18)-C(19)	1.405(6)	Fe(2)-N(4)	2.037(3)
Fe(2)-N(6)	2.047(3)	Fe(2)-N(5)	2.093(3)
Fe(2)-S(4)	2.3093(13)	Fe(2)-S(3)	2.3226(13)
S(3)-C(20)	1.778(4)	S(4)-C(38)	1.772(4)
O(3)-C(26)	1.230(5)	O(4)-C(32)	1.235(5)
N(4)-C(26)	1.355(5)	N(4)-C(25)	1.408(5)
N(5)-C(31)	1.335(5)	N(5)-C(27)	1.335(5)
N(6)-C(32)	1.356(5)	N(6)-C(33)	1.415(5)
C(20)-C(21)	1.398(6)	C(20)-C(25)	1.403(6)
C(21)-C(22)	1.395(6)	C(22)-C(23)	1.373(7)
C(23)-C(24)	1.383(7)	C(24)-C(25)	1.405(6)
C(26)-C(27)	1.521(6)	C(27)-C(28)	1.384(6)
C(28)-C(29)	1.383(7)	C(29)-C(30)	1.387(7)
C(30)-C(31)	1.377(6)	C(31)-C(32)	1.502(6)
C(33)-C(34)	1.392(6)	C(33)-C(38)	1.416(6)
C(34)-C(35)	1.382(6)	C(35)-C(36)	1.382(7)
C(36)-C(37)	1.389(6)	C(37)-C(38)	1.403(6)
N(7)-C(45)	1.512(5)	N(7)-C(43)	1.512(5)
N(7)-C(41)	1.516(5)	N(7)-C(39)	1.524(5)
C(39)-C(40)	1.511(6)	C(41)-C(42)	1.527(6)
C(43)-C(44)	1.513(6)	C(45)-C(46)	1.520(6)
N(8)-C(49)	1.503(6)	N(8)-C(51)	1.509(6)
N(8)-C(53)	1.523(6)	N(8)-C(47)	1.523(5)
C(47)-C(48)	1.504(6)	C(49)-C(50)	1.492(7)
C(51)-C(52)	1.521(6)	C(53)-C(54)	1.501(7)

Table S6. Bond angles (°) for (Et₄N)[Fe^{III}(PyPS)] (1)

N(1) -Fe(1) -N(3)	150.28(14)	N(1) -Fe(1) -N(2)	75.28(14)
N(3) -Fe(1) -N(2)	75.01(14)	N(1) -Fe(1) -S(2)	114.33(11)
N(3) -Fe(1) -S(2)	83.95(10)	N(2) -Fe(1) -S(2)	126.21(10)
N(1) -Fe(1) -S(1)	84.17(10)	N(3) -Fe(1) -S(1)	112.74(10)
N(2) -Fe(1) -S(1)	124.25(10)	S(2) -Fe(1) -S(1)	109.53(5)
C(1) -S(1) -Fe(1)	94.19(14)	C(19) -S(2) -Fe(1)	92.65(15)
C(7) -N(1) -C(6)	120.3(4)	C(7) -N(1) -Fe(1)	121.7(3)
C(6) -N(1) -Fe(1)	114.6(3)	C(8) -N(2) -C(12)	122.7(4)
C(8) -N(2) -Fe(1)	118.8(3)	C(12) -N(2) -Fe(1)	118.5(3)
C(13) -N(3) -C(14)	122.0(4)	C(13) -N(3) -Fe(1)	122.0(3)
C(14) -N(3) -Fe(1)	113.5(3)	C(2) -C(1) -C(6)	118.7(4)
C(2) -C(1) -S(1)	120.7(3)	C(6) -C(1) -S(1)	120.6(3)
C(3) -C(2) -C(1)	120.6(4)	C(2) -C(3) -C(4)	120.0(4)
C(5) -C(4) -C(3)	120.3(4)	C(4) -C(5) -C(6)	120.2(4)
C(5) -C(6) -C(1)	120.1(4)	C(5) -C(6) -N(1)	124.7(4)
C(1) -C(6) -N(1)	115.2(4)	O(1) -C(7) -N(1)	129.1(5)
O(1) -C(7) -C(8)	120.2(4)	N(1) -C(7) -C(8)	110.6(4)
N(2) -C(8) -C(9)	120.2(5)	N(2) -C(8) -C(7)	113.6(4)
C(9) -C(8) -C(7)	126.1(4)	C(10) -C(9) -C(8)	118.0(5)
C(9) -C(10) -C(11)	120.9(5)	C(10) -C(11) -C(12)	118.5(5)
N(2) -C(12) -C(11)	119.7(4)	N(2) -C(12) -C(13)	113.9(4)
C(11) -C(12) -C(13)	126.3(4)	O(2) -C(13) -N(3)	128.9(4)
O(2) -C(13) -C(12)	120.4(4)	N(3) -C(13) -C(12)	110.5(4)
C(15) -C(14) -C(19)	120.0(4)	C(15) -C(14) -N(3)	124.0(4)
C(19) -C(14) -N(3)	116.0(4)	C(16) -C(15) -C(14)	119.4(4)
C(17) -C(16) -C(15)	120.6(5)	C(16) -C(17) -C(18)	120.7(4)
C(17) -C(18) -C(19)	119.8(5)	C(18) -C(19) -C(14)	119.4(4)
C(18) -C(19) -S(2)	120.8(4)	C(14) -C(19) -S(2)	119.8(3)
N(4) -Fe(2) -N(6)	150.32(14)	N(4) -Fe(2) -N(5)	75.38(14)
N(6) -Fe(2) -N(5)	74.95(13)	N(4) -Fe(2) -S(4)	113.40(11)
N(6) -Fe(2) -S(4)	84.18(10)	N(5) -Fe(2) -S(4)	126.63(10)
N(4) -Fe(2) -S(3)	84.04(10)	N(6) -Fe(2) -S(3)	113.74(10)
N(5) -Fe(2) -S(3)	124.31(10)	S(4) -Fe(2) -S(3)	109.06(5)
C(20) -S(3) -Fe(2)	93.57(15)	C(38) -S(4) -Fe(2)	94.06(14)
C(26) -N(4) -C(25)	120.6(3)	C(26) -N(4) -Fe(2)	121.8(3)
C(25) -N(4) -Fe(2)	114.5(3)	C(31) -N(5) -C(27)	122.0(4)
C(31) -N(5) -Fe(2)	119.2(3)	C(27) -N(5) -Fe(2)	118.8(3)
C(32) -N(6) -C(33)	121.6(3)	C(32) -N(6) -Fe(2)	121.3(3)
C(33) -N(6) -Fe(2)	115.1(3)	C(21) -C(20) -C(25)	119.8(4)
C(21) -C(20) -S(3)	120.1(3)	C(25) -C(20) -S(3)	120.2(3)
C(22) -C(21) -C(20)	119.5(4)	C(23) -C(22) -C(21)	121.0(4)
C(22) -C(23) -C(24)	120.1(4)	C(23) -C(24) -C(25)	120.3(4)
C(20) -C(25) -C(24)	119.3(4)	C(20) -C(25) -N(4)	115.9(4)
C(24) -C(25) -N(4)	124.8(4)	O(3) -C(26) -N(4)	129.3(4)
O(3) -C(26) -C(27)	120.1(4)	N(4) -C(26) -C(27)	110.4(4)
N(5) -C(27) -C(28)	120.6(4)	N(5) -C(27) -C(26)	113.4(4)
C(28) -C(27) -C(26)	125.8(4)	C(29) -C(28) -C(27)	117.9(5)
C(28) -C(29) -C(30)	120.7(4)	C(31) -C(30) -C(29)	118.4(5)
N(5) -C(31) -C(30)	120.4(4)	N(5) -C(31) -C(32)	113.3(4)

C(30)-C(31)-C(32)	126.1(4)	O(4)-C(32)-N(6)	129.0(4)
O(4)-C(32)-C(31)	119.7(4)	N(6)-C(32)-C(31)	111.1(4)
C(34)-C(33)-N(6)	125.0(4)	C(34)-C(33)-C(38)	120.0(4)
N(6)-C(33)-C(38)	115.0(4)	C(35)-C(34)-C(33)	120.1(4)
C(36)-C(35)-C(34)	120.6(4)	C(35)-C(36)-C(37)	120.2(4)
C(36)-C(37)-C(38)	120.4(4)	C(37)-C(38)-C(33)	118.6(4)
C(37)-C(38)-S(4)	120.7(3)	C(33)-C(38)-S(4)	120.6(3)
C(45)-N(7)-C(43)	111.6(3)	C(45)-N(7)-C(41)	106.0(3)
C(43)-N(7)-C(41)	111.0(3)	C(45)-N(7)-C(39)	110.8(3)
C(43)-N(7)-C(39)	106.1(3)	C(41)-N(7)-C(39)	111.4(3)
C(40)-C(39)-N(7)	115.0(3)	N(7)-C(41)-C(42)	115.0(3)
C(44)-C(43)-N(7)	114.9(3)	N(7)-C(45)-C(46)	115.0(4)
C(49)-N(8)-C(51)	112.9(4)	C(49)-N(8)-C(53)	104.5(3)
C(51)-N(8)-C(53)	111.2(4)	C(49)-N(8)-C(47)	112.0(4)
C(51)-N(8)-C(47)	106.1(3)	C(53)-N(8)-C(47)	110.2(4)
C(48)-C(47)-N(8)	115.7(4)	C(50)-C(49)-N(8)	116.4(5)
N(8)-C(51)-C(52)	115.5(4)	C(54)-C(53)-N(8)	115.8(4)

Table S7. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for**(Et₄N)[Fe^{III}(PyPS)] (1)**

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [(ha^*)^2 U_{11} + \dots + 2hka^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
Fe(1)	21(1)	20(1)	21(1)	0(1)	-1(1)	-1(1)
S(1)	21(1)	24(1)	29(1)	-4(1)	-4(1)	2(1)
S(2)	21(1)	36(1)	28(1)	-1(1)	3(1)	-2(1)
O(1)	61(3)	50(2)	27(2)	8(2)	-12(2)	4(2)
O(2)	31(2)	36(2)	51(2)	-9(2)	-2(2)	-13(2)
N(1)	31(2)	24(2)	26(2)	-1(2)	-5(2)	1(2)
N(2)	31(2)	22(2)	26(2)	0(2)	5(2)	2(2)
N(3)	24(2)	21(2)	24(2)	-5(2)	3(2)	-2(2)
C(1)	16(2)	24(2)	23(2)	-4(2)	2(2)	0(2)
C(2)	25(3)	28(2)	27(2)	-6(2)	2(2)	0(2)
C(3)	32(3)	35(3)	32(3)	-8(2)	-2(2)	-7(2)
C(4)	29(3)	53(3)	38(3)	-11(2)	-14(2)	4(3)
C(5)	31(3)	39(3)	38(3)	-7(2)	-10(2)	7(2)
C(6)	26(3)	26(2)	23(2)	-4(2)	2(2)	0(2)
C(7)	40(3)	31(3)	25(2)	3(2)	3(2)	9(2)
C(8)	39(3)	25(2)	28(2)	-1(2)	8(2)	6(2)
C(9)	55(4)	37(3)	30(3)	4(2)	14(2)	11(3)
C(10)	55(4)	27(3)	42(3)	3(2)	26(3)	-2(3)
C(11)	38(3)	22(2)	42(3)	-2(2)	16(2)	-2(2)
C(12)	24(3)	22(2)	34(2)	-6(2)	11(2)	-1(2)
C(13)	20(3)	25(2)	36(3)	-5(2)	6(2)	3(2)
C(14)	24(3)	21(2)	27(2)	-8(2)	-3(2)	0(2)
C(15)	27(3)	30(2)	36(3)	-13(2)	0(2)	3(2)
C(16)	49(4)	40(3)	28(3)	-14(2)	-16(2)	19(3)
C(17)	62(4)	38(3)	21(2)	-2(2)	-4(2)	9(3)
C(18)	38(3)	35(3)	24(2)	-4(2)	2(2)	3(2)
C(19)	27(3)	23(2)	25(2)	-4(2)	-1(2)	6(2)
Fe(2)	22(1)	19(1)	19(1)	-1(1)	2(1)	1(1)
S(3)	24(1)	23(1)	26(1)	-5(1)	4(1)	-4(1)
S(4)	21(1)	24(1)	24(1)	-3(1)	-2(1)	2(1)
O(3)	52(2)	52(2)	22(2)	3(2)	11(2)	-9(2)
O(4)	28(2)	31(2)	48(2)	-6(2)	1(2)	12(2)
N(4)	24(2)	24(2)	24(2)	0(2)	3(2)	-3(2)
N(5)	28(2)	20(2)	21(2)	2(2)	-4(2)	-2(2)
N(6)	19(2)	21(2)	23(2)	-1(2)	0(2)	1(2)
C(20)	21(3)	31(2)	18(2)	-4(2)	-2(2)	3(2)
C(21)	28(3)	29(2)	25(2)	-4(2)	0(2)	0(2)
C(22)	29(3)	43(3)	30(2)	-16(2)	-1(2)	8(2)
C(23)	28(3)	60(4)	31(3)	-20(2)	7(2)	3(3)
C(24)	27(3)	43(3)	32(3)	-9(2)	9(2)	-8(2)
C(25)	20(3)	31(2)	20(2)	-4(2)	0(2)	-2(2)
C(26)	35(3)	28(2)	24(2)	-1(2)	-1(2)	-11(2)

C(27)	35(3)	27(2)	23(2)	1(2)	-8(2)	-11(2)
C(28)	56(4)	33(3)	27(3)	-7(2)	-10(2)	-12(3)
C(29)	64(4)	25(3)	40(3)	13(2)	-22(3)	-3(3)
C(30)	40(3)	23(2)	45(3)	-1(2)	-12(2)	3(2)
C(31)	29(3)	19(2)	31(2)	-1(2)	-11(2)	-1(2)
C(32)	18(3)	23(2)	34(2)	-3(2)	-6(2)	1(2)
C(33)	20(3)	20(2)	23(2)	-6(2)	-3(2)	-4(2)
C(34)	20(3)	30(2)	36(3)	-12(2)	1(2)	-4(2)
C(35)	37(3)	38(3)	29(2)	-11(2)	15(2)	-10(2)
C(36)	55(4)	33(3)	18(2)	-5(2)	7(2)	-5(2)
C(37)	38(3)	30(3)	22(2)	-2(2)	-3(2)	-2(2)
C(38)	21(2)	22(2)	23(2)	-6(2)	1(2)	-2(2)
N(7)	26(2)	22(2)	17(2)	1(1)	0(2)	3(2)
C(39)	29(3)	35(3)	18(2)	0(2)	-3(2)	6(2)
C(40)	46(3)	37(3)	32(3)	-4(2)	-4(2)	-10(2)
C(41)	29(3)	22(2)	25(2)	2(2)	-3(2)	8(2)
C(42)	27(3)	35(3)	37(3)	-3(2)	1(2)	2(2)
C(43)	41(3)	18(2)	29(2)	2(2)	-1(2)	5(2)
C(44)	47(3)	28(3)	38(3)	-6(2)	-7(2)	1(2)
C(45)	34(3)	44(3)	20(2)	3(2)	4(2)	1(2)
C(46)	39(4)	77(4)	38(3)	0(3)	7(2)	15(3)
N(8)	29(2)	25(2)	31(2)	4(2)	7(2)	5(2)
C(47)	41(3)	34(3)	31(3)	-1(2)	20(2)	-1(2)
C(48)	48(3)	39(3)	33(3)	9(2)	10(2)	2(2)
C(49)	27(3)	56(3)	45(3)	6(3)	5(2)	3(3)
C(50)	51(4)	113(6)	49(4)	10(4)	-3(3)	-29(4)
C(51)	76(4)	22(3)	51(3)	4(2)	30(3)	-3(3)
C(52)	81(5)	33(3)	51(3)	7(3)	34(3)	-3(3)
C(53)	50(4)	37(3)	30(3)	1(2)	-1(2)	-3(2)
C(54)	45(4)	94(5)	80(5)	28(4)	-19(3)	-4(4)

Table S8. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{Et}_4\text{N})[\text{Fe}^{\text{III}}(\text{PyPS})]$ (**1**)

	x	y	z	U(eq)
H(2)	10494	990	5230	32
H(3)	9199	900	4544	40
H(4)	8385	1947	4246	48
H(5)	8886	3087	4612	43
H(9)	11149	5286	4409	48
H(10)	12311	5971	4911	50
H(11)	12996	5598	5956	40
H(15)	13477	3578	7828	37
H(16)	13411	2940	8881	47
H(17)	12059	2473	9258	49
H(18)	10762	2577	8571	39
H(21)	14492	5974	5224	33
H(22)	15867	5832	4672	41
H(23)	16721	6835	4381	47
H(24)	16198	8006	4603	40
H(28)	14058	10246	4167	47
H(29)	12881	10979	4552	52
H(30)	12118	10671	5564	44
H(34)	11485	8829	7534	35
H(35)	11525	8395	8671	41
H(36)	12846	7929	9155	42
H(37)	14141	7863	8494	36
H(39A)	13163	4302	2052	33
H(39B)	14133	4114	1762	33
H(40A)	13140	3156	1529	57
H(40B)	12954	3067	2342	57
H(40C)	13924	2881	2046	57
H(41A)	14664	3121	2984	31
H(41B)	15113	3728	3472	31
H(42A)	16115	3312	2609	49
H(42B)	15947	4170	2545	49
H(42C)	15450	3623	2017	49
H(43A)	14855	4976	2448	35
H(43B)	13890	5230	2701	35
H(44A)	15001	5705	3443	56
H(44B)	15363	4903	3613	56
H(44C)	14394	5149	3870	56
H(45A)	13751	4024	3856	39
H(45B)	13188	3506	3343	39
H(46A)	12190	4354	3717	76
H(46B)	12404	4593	2937	76
H(46C)	12869	5011	3579	76
H(47A)	12072	5852	7259	42

H(47B)	11132	5838	6847	42
H(48A)	11910	6906	6603	60
H(48B)	11932	7117	7411	60
H(48C)	10998	7100	6988	60
H(49A)	9791	6148	8357	51
H(49B)	10088	6767	7826	51
H(50A)	9584	6119	6897	106
H(50B)	8811	6069	7461	106
H(50C)	9475	5396	7353	106
H(51A)	11660	4968	8037	59
H(51B)	10742	4884	7602	59
H(52A)	10624	4312	8688	82
H(52B)	9926	4974	8639	82
H(52C)	10844	5064	9076	82
H(53A)	11426	6864	8413	47
H(53B)	11127	6239	8937	47
H(54A)	12643	6369	9067	110
H(54B)	12786	6306	8246	110
H(54C)	12483	5607	8680	110

Table S9. Crystal data for $(\text{Et}_4\text{N})[\text{Fe}^{\text{III}}(\text{PyP}\{\text{SO}_2\}_2)]$ (2)

Identification code	mn940
Empirical formula	$\text{C}_{27}\text{H}_{31}\text{FeN}_4\text{O}_6\text{S}_2$
Formula weight	627.53
Crystal size	0.20 x 0.18 x 0.09 mm
Crystal habit	needle
Crystal color	red
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 7.7471(4) \text{ \AA}$ $\alpha = 90^\circ$ $b = 21.4308(12) \text{ \AA}$ $\beta = 92.9000(10)^\circ$ $c = 17.0590(9) \text{ \AA}$ $\gamma = 90^\circ$
Volume	$2828.6(3) \text{ \AA}^3$
Z	4
Density (calculated)	$1.474 \text{ Mg}\cdot\text{m}^{-3}$
Absorption coefficient	0.729 mm^{-1}
F(000)	1308
Absorption correction ¹	Empirical
Max. and min. transmission	0.9373 and 0.8679

1) SADABS

Blessing, R. H., Acta Cryst. (1995). A51, 33-38.

Table S10. Data collection for $(\text{Et}_4\text{N})[\text{Fe}^{\text{III}}(\text{PyP}\{\text{SQ}_2\}_2)]$ (2)

Diffractometer	Bruker SMART
Temperature	90(2) K
Radiation source	normal-focus sealed tube
Wavelength	0.71073 Å (MoK α)
Monochromator	graphite
θ range for data collection	1.53 to 31.54 $^\circ$
Scan type	ω
Index ranges	$-11 \leq h \leq 11, 0 \leq k \leq 31, 0 \leq l \leq 24$
Reflections collected	28791
Independent reflections	9083 ($R_{\text{int}} = 0.0619$)
Standard reflections	50 frames remeasured at end
Percent decay of standards	<0.1

Table S11. Solution and refinement of $(Et_4N)[Fe^{III}(PyP\{SO_2\}_2)]$ (2)

System for solution	SHELXS-97 (Sheldrick, 1990)
Structure solution	direct
System for refinement	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full-matrix least-squares on F^2
Hydrogen atoms	constr
Data / restraints / parameters	9083 / 0 / 372
Goodness-of-fit on F^2	0.872
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (0.0546P)^2$ where $P = (F_o^2 + 2F_c^2)/3$

R indices (all data) R1 = 0.0834, wR2 = 0.1038

R indices calcd from obsd data R1 = 0.0415, wR2 = 0.0910

Observed data (>2sigma(I)) 5729

Largest diff. peak and hole 0.505 and -0.412 eÅ⁻³

$$1) R1 = \sum ||F_o - F_c|| / \sum |F_o|$$

$$wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$

$$2) \text{ Goodness-of-Fit} = [\sum [w(F_o^2 - F_c^2)^2] / (M - N)]^{1/2}$$

where M is the number of reflections

and N is the number of parameters refined.

- 3) Refinement is based on F^2 for ALL reflections except for those with very negative F^2 or flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The observed criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating R indices for observed data and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

There is disorder in the position of one of the oxygen atoms bonded to sulfur. The set of disordered atoms is O(5A) and O(5B); they were refined to relative occupancies of 0.769(4)/0.231(4).

Table S12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{Et}_4\text{N})[\text{Fe}^{\text{III}}(\text{PyP}\{\text{SO}_2\}_2)]$ (2)

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U (eq)
Fe	7806 (1)	721 (1)	6518 (1)	17 (1)
S (1)	9795 (1)	1980 (1)	6596 (1)	20 (1)
S (2)	6155 (1)	29 (1)	7880 (1)	23 (1)
O (1)	9588 (2)	1288 (1)	6865 (1)	24 (1)
O (2)	10395 (2)	1985 (1)	5787 (1)	24 (1)
O (3)	5147 (2)	1466 (1)	4560 (1)	22 (1)
O (4)	9899 (2)	-1041 (1)	6190 (1)	27 (1)
O (5A)	5472 (3)	207 (1)	8611 (1)	30 (1)
O (5B)	5473 (8)	-502 (3)	7547 (4)	25 (2)
O (6)	6310 (2)	637 (1)	7370 (1)	24 (1)
N (1)	6584 (2)	1338 (1)	5787 (1)	17 (1)
N (2)	7553 (2)	251 (1)	5457 (1)	17 (1)
N (3)	8941 (2)	-114 (1)	6732 (1)	18 (1)
C (1)	7601 (2)	2255 (1)	6501 (1)	18 (1)
C (2)	7323 (3)	2836 (1)	6826 (1)	22 (1)
C (3)	5721 (3)	3125 (1)	6729 (1)	26 (1)
C (4)	4406 (3)	2822 (1)	6305 (1)	26 (1)
C (5)	4656 (3)	2237 (1)	5979 (1)	22 (1)
C (6)	6262 (2)	1942 (1)	6069 (1)	18 (1)
C (7)	6026 (2)	1165 (1)	5047 (1)	18 (1)
C (8)	6662 (2)	524 (1)	4858 (1)	18 (1)
C (9)	6415 (3)	215 (1)	4145 (1)	20 (1)
C (10)	7138 (3)	-376 (1)	4076 (1)	23 (1)
C (11)	8069 (3)	-651 (1)	4704 (1)	21 (1)
C (12)	8236 (2)	-319 (1)	5398 (1)	18 (1)
C (13)	9148 (2)	-539 (1)	6153 (1)	18 (1)
C (14)	9554 (2)	-239 (1)	7515 (1)	18 (1)
C (15)	11253 (3)	-412 (1)	7717 (1)	24 (1)
C (16)	11780 (3)	-496 (1)	8499 (1)	26 (1)
C (17)	10618 (3)	-420 (1)	9088 (1)	28 (1)
C (18)	8925 (3)	-247 (1)	8892 (1)	25 (1)
C (19)	8406 (3)	-151 (1)	8109 (1)	19 (1)
N (4)	8729 (2)	3038 (1)	3994 (1)	23 (1)
C (20)	8980 (3)	3244 (1)	4843 (1)	33 (1)
C (21)	9858 (4)	3866 (1)	4979 (2)	54 (1)
C (22)	7654 (3)	3511 (1)	3516 (1)	31 (1)
C (23)	5894 (3)	3652 (1)	3819 (2)	41 (1)
C (24)	10439 (3)	2986 (1)	3601 (2)	33 (1)
C (25)	11723 (3)	2534 (1)	3991 (2)	36 (1)
C (26)	7829 (3)	2407 (1)	4022 (1)	23 (1)
C (27)	7422 (3)	2102 (1)	3235 (1)	27 (1)

Table S13. Bond lengths (Å) for (Et₄N)[Fe^{III}(PyP{SO₂})₂] (2)

Fe-O(1)	1.9112 (14)	Fe-O(6)	1.9127 (15)
Fe-N(3)	2.0175 (17)	Fe-N(1)	2.0201 (17)
Fe-N(2)	2.0708 (17)	S(1)-O(2)	1.4788 (16)
S(1)-O(1)	1.5633 (16)	S(1)-C(1)	1.798 (2)
S(2)-O(5B)	1.366 (7)	S(2)-O(5A)	1.431 (2)
S(2)-O(6)	1.5742 (16)	S(2)-C(19)	1.809 (2)
O(3)-C(7)	1.229 (2)	O(4)-C(13)	1.223 (3)
N(1)-C(7)	1.364 (2)	N(1)-C(6)	1.409 (3)
N(2)-C(12)	1.336 (3)	N(2)-C(8)	1.339 (2)
N(3)-C(13)	1.360 (3)	N(3)-C(14)	1.420 (2)
C(1)-C(2)	1.384 (3)	C(1)-C(6)	1.411 (3)
C(2)-C(3)	1.389 (3)	C(3)-C(4)	1.381 (3)
C(4)-C(5)	1.388 (3)	C(5)-C(6)	1.397 (3)
C(7)-C(8)	1.500 (3)	C(8)-C(9)	1.391 (3)
C(9)-C(10)	1.391 (3)	C(10)-C(11)	1.392 (3)
C(11)-C(12)	1.381 (3)	C(12)-C(13)	1.514 (3)
C(14)-C(15)	1.394 (3)	C(14)-C(19)	1.395 (3)
C(15)-C(16)	1.387 (3)	C(16)-C(17)	1.392 (3)
C(17)-C(18)	1.387 (3)	C(18)-C(19)	1.391 (3)
N(4)-C(20)	1.516 (3)	N(4)-C(24)	1.520 (3)
N(4)-C(22)	1.522 (3)	N(4)-C(26)	1.523 (3)
C(20)-C(21)	1.510 (4)	C(22)-C(23)	1.513 (4)
C(24)-C(25)	1.518 (3)	C(26)-C(27)	1.511 (3)

Table S14. Bond angles (°) for (Et₄N)[Fe^{III}(PyP{SO₂})₂] (2)

O(1)-Fe-O(6)	106.24 (7)	O(1)-Fe-N(3)	101.89 (6)
O(6)-Fe-N(3)	93.13 (7)	O(1)-Fe-N(1)	94.81 (6)
O(6)-Fe-N(1)	104.33 (7)	N(3)-Fe-N(1)	151.43 (7)
O(1)-Fe-N(2)	127.96 (7)	O(6)-Fe-N(2)	125.75 (7)
N(3)-Fe-N(2)	75.42 (7)	N(1)-Fe-N(2)	76.02 (7)
O(2)-S(1)-O(1)	108.85 (9)	O(2)-S(1)-C(1)	104.73 (9)
O(1)-S(1)-C(1)	103.12 (9)	O(5B)-S(2)-O(5A)	115.6 (3)
O(5B)-S(2)-O(6)	119.8 (3)	O(5A)-S(2)-O(6)	107.68 (11)
O(5B)-S(2)-C(19)	105.1 (3)	O(5A)-S(2)-C(19)	105.26 (11)
O(6)-S(2)-C(19)	101.35 (9)	S(1)-O(1)-Fe	126.53 (8)
S(2)-O(6)-Fe	124.31 (9)	C(7)-N(1)-C(6)	120.83 (17)
C(7)-N(1)-Fe	120.70 (14)	C(6)-N(1)-Fe	118.43 (12)
C(12)-N(2)-C(8)	122.17 (17)	C(12)-N(2)-Fe	119.37 (13)
C(8)-N(2)-Fe	118.43 (14)	C(13)-N(3)-C(14)	120.61 (17)
C(13)-N(3)-Fe	121.96 (13)	C(14)-N(3)-Fe	117.41 (13)
C(2)-C(1)-C(6)	120.74 (18)	C(2)-C(1)-S(1)	115.11 (15)
C(6)-C(1)-S(1)	123.90 (16)	C(1)-C(2)-C(3)	120.6 (2)
C(4)-C(3)-C(2)	119.0 (2)	C(3)-C(4)-C(5)	121.2 (2)
C(4)-C(5)-C(6)	120.44 (19)	C(5)-C(6)-N(1)	123.43 (18)
C(5)-C(6)-C(1)	117.99 (19)	N(1)-C(6)-C(1)	118.50 (17)
O(3)-C(7)-N(1)	128.4 (2)	O(3)-C(7)-C(8)	120.81 (18)
N(1)-C(7)-C(8)	110.76 (17)	N(2)-C(8)-C(9)	120.1 (2)
N(2)-C(8)-C(7)	113.55 (17)	C(9)-C(8)-C(7)	126.34 (18)
C(10)-C(9)-C(8)	118.05 (19)	C(9)-C(10)-C(11)	120.97 (19)
C(12)-C(11)-C(10)	117.6 (2)	N(2)-C(12)-C(11)	121.05 (18)
N(2)-C(12)-C(13)	112.94 (17)	C(11)-C(12)-C(13)	126.01 (19)
O(4)-C(13)-N(3)	128.70 (19)	O(4)-C(13)-C(12)	121.30 (19)
N(3)-C(13)-C(12)	109.98 (17)	C(15)-C(14)-C(19)	118.99 (19)
C(15)-C(14)-N(3)	123.37 (19)	C(19)-C(14)-N(3)	117.54 (17)
C(16)-C(15)-C(14)	120.1 (2)	C(15)-C(16)-C(17)	120.6 (2)
C(18)-C(17)-C(16)	119.8 (2)	C(17)-C(18)-C(19)	119.6 (2)
C(18)-C(19)-C(14)	120.93 (19)	C(18)-C(19)-S(2)	117.91 (17)
C(14)-C(19)-S(2)	120.98 (15)	C(20)-N(4)-C(24)	111.76 (18)
C(20)-N(4)-C(22)	111.06 (18)	C(24)-N(4)-C(22)	106.09 (17)
C(20)-N(4)-C(26)	105.42 (17)	C(24)-N(4)-C(26)	111.02 (18)
C(22)-N(4)-C(26)	111.60 (16)	C(21)-C(20)-N(4)	116.0 (2)
C(23)-C(22)-N(4)	115.3 (2)	N(4)-C(24)-C(25)	114.8 (2)
C(27)-C(26)-N(4)	115.60 (18)		

Table S15. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [(h a^*)^2 U_{11} + \dots + 2hka^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
Fe	17(1)	16(1)	18(1)	0(1)	-3(1)	2(1)
S(1)	17(1)	18(1)	23(1)	-2(1)	-6(1)	0(1)
S(2)	17(1)	24(1)	29(1)	1(1)	2(1)	0(1)
O(1)	24(1)	19(1)	28(1)	3(1)	-11(1)	-1(1)
O(2)	19(1)	25(1)	28(1)	1(1)	4(1)	2(1)
O(3)	20(1)	23(1)	21(1)	5(1)	-4(1)	1(1)
O(4)	26(1)	20(1)	35(1)	-3(1)	-5(1)	7(1)
O(5A)	30(1)	39(1)	22(1)	4(1)	8(1)	8(1)
O(5B)	15(3)	33(4)	27(4)	5(3)	1(2)	-3(3)
O(6)	24(1)	24(1)	25(1)	2(1)	4(1)	7(1)
N(1)	16(1)	14(1)	20(1)	-2(1)	-3(1)	0(1)
N(2)	14(1)	18(1)	18(1)	0(1)	0(1)	-2(1)
N(3)	17(1)	17(1)	20(1)	3(1)	1(1)	2(1)
C(1)	18(1)	19(1)	16(1)	2(1)	0(1)	0(1)
C(2)	25(1)	21(1)	21(1)	-1(1)	1(1)	-2(1)
C(3)	31(1)	18(1)	30(1)	-3(1)	7(1)	5(1)
C(4)	23(1)	24(1)	32(1)	4(1)	4(1)	7(1)
C(5)	18(1)	21(1)	26(1)	3(1)	-1(1)	0(1)
C(6)	19(1)	16(1)	19(1)	3(1)	-1(1)	0(1)
C(7)	13(1)	20(1)	19(1)	2(1)	2(1)	-4(1)
C(8)	14(1)	20(1)	19(1)	3(1)	1(1)	-3(1)
C(9)	18(1)	24(1)	18(1)	0(1)	1(1)	-6(1)
C(10)	23(1)	26(1)	19(1)	-5(1)	5(1)	-9(1)
C(11)	18(1)	19(1)	26(1)	-4(1)	5(1)	-3(1)
C(12)	14(1)	16(1)	23(1)	1(1)	3(1)	-2(1)
C(13)	14(1)	18(1)	23(1)	2(1)	0(1)	-1(1)
C(14)	18(1)	14(1)	22(1)	4(1)	-2(1)	-1(1)
C(15)	20(1)	23(1)	29(1)	9(1)	0(1)	0(1)
C(16)	20(1)	25(1)	33(1)	8(1)	-6(1)	-3(1)
C(17)	32(1)	27(1)	24(1)	2(1)	-9(1)	-3(1)
C(18)	29(1)	24(1)	21(1)	-1(1)	0(1)	-1(1)
C(19)	19(1)	15(1)	22(1)	0(1)	-2(1)	-2(1)
N(4)	27(1)	20(1)	22(1)	4(1)	-5(1)	-6(1)
C(20)	43(1)	30(1)	25(1)	-3(1)	-12(1)	-2(1)
C(21)	67(2)	39(2)	53(2)	-13(1)	-24(2)	-14(2)
C(22)	41(1)	21(1)	30(1)	7(1)	-13(1)	-3(1)
C(23)	43(2)	33(2)	44(2)	1(1)	-11(1)	12(1)
C(24)	27(1)	36(2)	34(1)	9(1)	-2(1)	-9(1)
C(25)	25(1)	41(2)	42(2)	1(1)	-2(1)	-3(1)
C(26)	26(1)	20(1)	23(1)	4(1)	-4(1)	-2(1)
C(27)	33(1)	22(1)	24(1)	2(1)	-5(1)	-3(1)

Table S16. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{Et}_4\text{N})[\text{Fe}^{\text{III}}(\text{PyP}\{\text{SO}_2\}_2)]$ (2)

	x	y	z	U(eq)
H(2B)	8236	3039	7118	27
H(3A)	5533	3524	6950	31
H(4A)	3308	3018	6235	32
H(5A)	3730	2037	5694	26
H(9A)	5771	401	3718	24
H(10A)	6995	-594	3592	27
H(11A)	8572	-1052	4657	25
H(15A)	12051	-472	7319	29
H(16A)	12945	-606	8634	32
H(17A)	10983	-485	9621	34
H(18A)	8125	-195	9291	30
H(20A)	7832	3260	5072	40
H(20B)	9667	2921	5133	40
H(21A)	9932	3959	5542	81
H(21B)	9188	4193	4701	81
H(21C)	11024	3851	4783	81
H(22A)	8315	3905	3497	37
H(22B)	7494	3353	2971	37
H(23A)	5305	3961	3478	61
H(23B)	6031	3816	4354	61
H(23C)	5206	3268	3820	61
H(24A)	10978	3405	3591	39
H(24B)	10204	2853	3050	39
H(25A)	12784	2529	3702	54
H(25B)	11219	2114	3991	54
H(25C)	11994	2666	4533	54
H(26A)	8569	2120	4345	28
H(26B)	6735	2460	4290	28
H(27A)	6843	1702	3314	40
H(27B)	8497	2031	2970	40
H(27C)	6662	2375	2912	40

Table S17. Crystal data and structure refinement for $(\text{Et}_4\text{N})_2[\text{Fe}^{\text{II}}(\text{PyPS})]$ (3)

Identification code	mn981	
Empirical formula	C ₃₅ H ₅₁ Fe N ₅ O ₂ S ₂	
Formula weight	693.78	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 9.5604(5) Å	α = 90°
	b = 15.5545(8) Å	β = 90.6610(10)°
	c = 23.6924(13) Å	γ = 90°
Volume	3523.0(3) Å ³	
Z	4	
Density (calculated)	1.308 Mg/m ³	
Absorption coefficient	0.585 mm ⁻¹	
F(000)	1480	
Crystal size	0.30 x 0.12 x 0.12 mm ³	
Crystal color and habit	brown needle	
Diffractometer	Bruker SMART 1000	
Theta range for data collection	1.57 to 31.51°	
Index ranges	-14 ≤ h ≤ 14, -22 ≤ k ≤ 22, -33 ≤ l ≤ 33	
Reflections collected	33451	
Independent reflections	11178 [R(int) = 0.0820]	
Completeness to theta = 31.51°	95.3 %	
Max. and min. transmission	0.9331 and 0.8441	
Solution method	SHELXS-97 (Sheldrick, 1990)	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11178 / 0 / 405	
Goodness-of-fit on F ²	0.885	
Final R indices [I > 2σ(I)]	R1 = 0.0541, wR2 = 0.1177	
R indices (all data)	R1 = 0.1359, wR2 = 0.1435	
Largest diff. peak and hole	0.510 and -0.590 e.Å ⁻³	

Table S18. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{Et}_4\text{N})_2[\text{Fe}^{\text{II}}(\text{PyPS})]$ (3)U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Fe	8269(1)	7797(1)	8734(1)	21(1)
S(1)	6633(1)	8816(1)	8339(1)	31(1)
S(2)	6725(1)	6717(1)	9068(1)	28(1)
O(1)	10877(3)	7723(2)	7274(1)	52(1)
O(2)	10854(3)	7795(2)	10232(1)	58(1)
N(1)	8942(3)	7802(2)	7867(1)	29(1)
N(2)	10496(2)	7803(2)	8751(1)	24(1)
N(3)	8909(2)	7748(2)	9620(1)	24(1)
C(1)	6690(4)	8378(2)	7646(1)	37(1)
C(2)	5556(4)	8491(2)	7272(2)	57(1)
C(3)	5621(7)	8169(3)	6722(2)	80(2)
C(4)	6795(7)	7762(3)	6537(2)	83(2)
C(5)	7941(5)	7642(2)	6897(1)	57(1)
C(6)	7881(4)	7936(2)	7460(1)	36(1)
C(7)	10287(3)	7753(2)	7741(1)	33(1)
C(8)	11197(3)	7765(2)	8269(1)	31(1)
C(9)	12661(3)	7759(2)	8270(2)	51(1)
C(10)	13367(3)	7741(2)	8783(2)	64(1)
C(11)	12633(3)	7747(2)	9268(2)	51(1)
C(12)	11183(3)	7803(2)	9247(1)	30(1)
C(13)	10272(3)	7799(2)	9761(1)	32(1)
C(14)	7907(3)	7504(2)	10008(1)	27(1)
C(15)	7959(4)	7665(2)	10593(1)	42(1)
C(16)	6886(5)	7386(3)	10940(1)	57(1)
C(17)	5759(5)	6961(3)	10720(2)	63(1)
C(18)	5692(4)	6791(3)	10152(2)	53(1)
C(19)	6751(3)	7039(2)	9784(1)	30(1)
N(4)	10311(3)	10450(2)	7556(1)	34(1)
C(20)	11585(4)	11024(2)	7658(2)	48(1)
C(21)	12921(4)	10564(3)	7837(2)	71(1)
C(22)	10591(4)	9784(2)	7103(2)	46(1)

C(23)	10988(5)	10144(3)	6534(2)	69(1)
C(24)	9952(3)	9957(2)	8085(1)	36(1)
C(25)	9630(4)	10497(2)	8592(2)	52(1)
C(26)	9132(3)	11049(2)	7377(1)	33(1)
C(27)	7736(3)	10609(2)	7277(1)	41(1)
N(5)	5000	10000	10000	60(2)
C(29A)	4552(7)	9030(4)	10305(3)	35(1)
C(30A)	4149(9)	9034(6)	10896(3)	49(2)
C(31A)	5912(7)	10403(4)	10368(3)	37(2)
C(32A)	7336(9)	9987(6)	10359(4)	53(2)
C(29B)	4841(7)	10215(4)	10558(3)	39(2)
C(30B)	4551(10)	9393(6)	10898(4)	57(2)
C(31B)	6548(7)	9541(4)	9893(3)	33(1)
C(32B)	7864(8)	9935(5)	10144(3)	37(2)
N(6)	0	5000	10000	48(1)
C(33A)	1652(6)	4694(4)	9953(2)	27(1)
C(34A)	2732(8)	5358(5)	10063(3)	48(2)
C(35A)	6(6)	5700(4)	9471(2)	27(1)
C(36A)	261(10)	5406(6)	8885(4)	47(2)
C(33B)	728(6)	5771(4)	10219(2)	28(1)
C(34B)	2285(7)	5604(5)	10280(3)	37(2)
C(35B)	271(7)	4592(4)	9532(3)	35(1)
C(36B)	112(10)	5170(7)	9012(4)	52(3)

Two of the NEt_4 cations are disordered with respect to centers of symmetry; the atoms N(5) through C(36B) are all at 0.5 occupancy.

Table S19. Bond lengths (Å) and bond angles (°) for (Et₄N)₂[Fe^{II}(PyPS)] (3)

Fe-N(2)	2.129(2)	N(4)-C(24)	1.512(4)
Fe-N(1)	2.160(2)	N(4)-C(22)	1.517(4)
Fe-N(3)	2.179(2)	N(4)-C(26)	1.518(4)
Fe-S(2)	2.3783(8)	N(4)-C(20)	1.527(4)
Fe-S(1)	2.4094(8)	C(20)-C(21)	1.521(5)
S(1)-C(1)	1.778(3)	C(22)-C(23)	1.513(5)
S(2)-C(19)	1.768(3)	C(24)-C(25)	1.502(5)
O(1)-C(7)	1.249(3)	C(26)-C(27)	1.516(5)
O(2)-C(13)	1.242(3)	N(5)-C(29B)#1	1.374(7)
N(1)-C(7)	1.326(4)	N(5)-C(29B)	1.374(7)
N(1)-C(6)	1.407(4)	N(5)-C(31A)#1	1.377(7)
N(2)-C(8)	1.332(4)	N(5)-C(31A)	1.377(7)
N(2)-C(12)	1.339(4)	N(5)-C(31B)	1.665(6)
N(3)-C(13)	1.344(4)	N(5)-C(31B)#1	1.665(6)
N(3)-C(14)	1.389(4)	N(5)-C(29A)#1	1.730(7)
C(1)-C(2)	1.404(4)	N(5)-C(29A)	1.730(7)
C(1)-C(6)	1.405(5)	C(29A)-C(30A)	1.457(10)
C(2)-C(3)	1.398(7)	C(31A)-C(32A)	1.507(11)
C(3)-C(4)	1.364(8)	C(29B)-C(30B)	1.539(12)
C(4)-C(5)	1.394(7)	C(31B)-C(32B)	1.514(9)
C(5)-C(6)	1.412(4)	N(6)-C(35B)	1.306(7)
C(7)-C(8)	1.515(5)	N(6)-C(35B)#2	1.306(7)
C(8)-C(9)	1.400(4)	N(6)-C(33B)#2	1.477(6)
C(9)-C(10)	1.385(6)	N(6)-C(33B)	1.477(6)
C(10)-C(11)	1.353(6)	N(6)-C(33A)	1.655(6)
C(11)-C(12)	1.389(4)	N(6)-C(33A)#2	1.655(6)
C(12)-C(13)	1.506(5)	N(6)-C(35A)	1.660(6)
C(14)-C(15)	1.409(4)	N(6)-C(35A)#2	1.660(6)
C(14)-C(19)	1.418(4)	C(33A)-C(34A)	1.482(10)
C(15)-C(16)	1.391(6)	C(35A)-C(36A)	1.484(11)
C(16)-C(17)	1.363(6)	C(33B)-C(34B)	1.516(9)
C(17)-C(18)	1.373(5)	C(35B)-C(36B)	1.531(12)
C(18)-C(19)	1.398(4)		

N(2)-Fe-N(1)	73.07(9)	N(2)-C(8)-C(7)	114.8(2)
N(2)-Fe-N(3)	73.33(9)	C(9)-C(8)-C(7)	124.4(3)
N(1)-Fe-N(3)	146.34(10)	C(10)-C(9)-C(8)	118.6(4)
N(2)-Fe-S(2)	128.44(7)	C(11)-C(10)-C(9)	119.6(3)
N(1)-Fe-S(2)	120.79(7)	C(10)-C(11)-C(12)	119.8(4)
N(3)-Fe-S(2)	79.85(7)	N(2)-C(12)-C(11)	120.7(3)
N(2)-Fe-S(1)	130.44(7)	N(2)-C(12)-C(13)	115.3(2)
N(1)-Fe-S(1)	80.00(8)	C(11)-C(12)-C(13)	123.8(3)
N(3)-Fe-S(1)	124.81(7)	O(2)-C(13)-N(3)	130.3(3)
S(2)-Fe-S(1)	101.05(3)	O(2)-C(13)-C(12)	118.0(3)
C(1)-S(1)-Fe	94.60(12)	N(3)-C(13)-C(12)	111.5(2)
C(19)-S(2)-Fe	96.72(11)	N(3)-C(14)-C(15)	125.9(3)
C(7)-N(1)-C(6)	123.2(3)	N(3)-C(14)-C(19)	115.6(2)
C(7)-N(1)-Fe	121.0(2)	C(15)-C(14)-C(19)	118.5(3)
C(6)-N(1)-Fe	115.63(19)	C(16)-C(15)-C(14)	120.5(4)
C(8)-N(2)-C(12)	120.4(3)	C(17)-C(16)-C(15)	120.7(3)
C(8)-N(2)-Fe	119.8(2)	C(16)-C(17)-C(18)	119.7(4)
C(12)-N(2)-Fe	119.7(2)	C(17)-C(18)-C(19)	122.1(4)
C(13)-N(3)-C(14)	121.7(2)	C(18)-C(19)-C(14)	118.3(3)
C(13)-N(3)-Fe	119.9(2)	C(18)-C(19)-S(2)	121.1(3)
C(14)-N(3)-Fe	117.31(18)	C(14)-C(19)-S(2)	120.4(2)
C(2)-C(1)-C(6)	119.1(3)	C(24)-N(4)-C(22)	106.4(2)
C(2)-C(1)-S(1)	120.2(3)	C(24)-N(4)-C(26)	111.6(2)
C(6)-C(1)-S(1)	120.7(2)	C(22)-N(4)-C(26)	111.0(3)
C(3)-C(2)-C(1)	120.1(5)	C(24)-N(4)-C(20)	110.7(3)
C(4)-C(3)-C(2)	120.7(4)	C(22)-N(4)-C(20)	111.4(3)
C(3)-C(4)-C(5)	120.7(4)	C(26)-N(4)-C(20)	105.9(2)
C(4)-C(5)-C(6)	119.6(5)	C(21)-C(20)-N(4)	115.8(3)
N(1)-C(6)-C(1)	116.0(3)	C(23)-C(22)-N(4)	115.1(3)
N(1)-C(6)-C(5)	124.2(4)	C(25)-C(24)-N(4)	115.5(3)
C(1)-C(6)-C(5)	119.8(3)	N(4)-C(26)-C(27)	114.6(3)
O(1)-C(7)-N(1)	130.6(3)	C(29B)-N(5)-C(31A)#1	130.1(4)
O(1)-C(7)-C(8)	118.1(3)	C(29B)-N(5)-C(31B)	111.0(4)
N(1)-C(7)-C(8)	111.2(2)	C(31A)-N(5)-C(31B)#1	105.5(4)
N(2)-C(8)-C(9)	120.8(3)	C(29B)-N(5)-C(29A)#1	102.8(4)

C(31B)-N(5)-C(29A)#1	94.9(3)	C(35B)-N(6)-C(33A)#2	113.3(3)
C(29B)#1-N(5)-C(29A)	102.8(4)	C(33B)-N(6)-C(33A)#2	100.9(3)
C(31A)-N(5)-C(29A)	106.8(3)	C(35B)#2-N(6)-C(35A)	109.0(4)
C(31B)#1-N(5)-C(29A)	94.9(3)	C(33B)#2-N(6)-C(35A)	105.9(3)
C(30A)-C(29A)-N(5)	117.8(5)	C(33A)-N(6)-C(35A)	97.2(3)
N(5)-C(31A)-C(32A)	111.2(6)	C(35B)-N(6)-C(35A)#2	109.0(4)
N(5)-C(29B)-C(30B)	108.9(6)	C(33B)-N(6)-C(35A)#2	105.8(3)
C(32B)-C(31B)-N(5)	120.2(5)	C(34A)-C(33A)-N(6)	116.8(5)
C(35B)-N(6)-C(33B)	126.5(4)	C(36A)-C(35A)-N(6)	120.4(5)
C(35B)#2-N(6)-C(33A)	113.3(3)	N(6)-C(33B)-C(34B)	110.7(5)
C(33B)#2-N(6)-C(33A)	100.9(3)	N(6)-C(35B)-C(36B)	112.3(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+2 #2 -x,-y+1,-z+2

Table S20. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for
 $(\text{Et}_4\text{N})_2[\text{Fe}^{\text{II}}(\text{PyPS})]$ (3)

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Fe	18(1)	31(1)	15(1)	1(1)	1(1)	0(1)
S(1)	27(1)	39(1)	28(1)	11(1)	-2(1)	1(1)
S(2)	20(1)	41(1)	22(1)	10(1)	-4(1)	-6(1)
O(1)	79(2)	33(1)	43(1)	-2(1)	45(1)	-3(1)
O(2)	70(2)	60(2)	43(2)	3(1)	-40(1)	3(2)
N(1)	34(1)	33(1)	19(1)	-5(1)	7(1)	-13(1)
N(2)	17(1)	16(1)	38(1)	-4(1)	2(1)	-1(1)
N(3)	33(1)	20(1)	19(1)	-4(1)	-8(1)	3(1)
C(1)	47(2)	37(2)	25(2)	17(1)	-13(1)	-23(2)
C(2)	72(3)	47(2)	50(2)	31(2)	-35(2)	-34(2)
C(3)	130(5)	63(3)	45(3)	38(2)	-57(3)	-60(3)
C(4)	165(6)	64(3)	19(2)	13(2)	-27(3)	-66(4)
C(5)	109(3)	48(2)	15(2)	2(1)	3(2)	-44(2)
C(6)	54(2)	38(2)	16(1)	5(1)	3(1)	-25(2)
C(7)	48(2)	17(1)	35(2)	-6(1)	25(1)	-9(1)
C(8)	27(1)	14(1)	51(2)	-5(1)	18(1)	-3(1)
C(9)	27(2)	19(2)	109(3)	-12(2)	37(2)	-3(1)
C(10)	12(1)	31(2)	149(5)	-12(2)	-1(2)	-3(2)
C(11)	23(2)	25(2)	104(3)	-6(2)	-20(2)	-5(1)
C(12)	20(1)	18(1)	53(2)	-2(1)	-14(1)	-2(1)
C(13)	43(2)	17(1)	35(2)	-1(1)	-19(1)	3(1)
C(14)	41(2)	24(2)	16(1)	4(1)	2(1)	14(1)
C(15)	78(3)	31(2)	18(1)	0(1)	-2(2)	21(2)
C(16)	95(3)	57(3)	18(2)	10(2)	16(2)	45(2)
C(17)	59(3)	95(4)	35(2)	30(2)	27(2)	37(2)
C(18)	40(2)	84(3)	36(2)	27(2)	11(2)	15(2)
C(19)	28(2)	43(2)	18(1)	10(1)	7(1)	14(1)
N(4)	35(1)	20(1)	47(2)	4(1)	-1(1)	2(1)
C(20)	41(2)	25(2)	79(3)	15(2)	-5(2)	-9(2)
C(21)	40(2)	53(3)	121(4)	31(3)	-15(2)	-12(2)
C(22)	54(2)	23(2)	60(2)	1(2)	10(2)	12(2)

C(23)	97(4)	43(2)	67(3)	-1(2)	37(3)	22(2)
C(24)	30(2)	28(2)	50(2)	11(1)	-10(1)	-6(1)
C(25)	73(3)	45(2)	36(2)	6(2)	-23(2)	-6(2)
C(26)	40(2)	25(2)	32(2)	2(1)	1(1)	11(1)
C(27)	40(2)	47(2)	34(2)	5(2)	-4(2)	6(2)
N(5)	102(4)	35(2)	42(3)	-19(2)	-34(3)	41(3)
N(6)	48(2)	18(2)	76(3)	-6(2)	-40(2)	4(2)

Table S21. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{Et}_4\text{N})_2[\text{Fe}^{\text{II}}(\text{PyPS})]$ (**3**)

	x	y	z	U(eq)
H(2)	4743	8787	7392	68
H(3)	4840	8234	6474	96
H(4)	6831	7559	6159	99
H(5)	8759	7363	6765	69
H(9)	13161	7766	7925	61
H(10)	14360	7725	8795	77
H(11)	13107	7714	9622	61
H(15)	8733	7967	10752	51
H(16)	6940	7493	11334	68
H(17)	5022	6782	10959	75
H(18)	4899	6495	10004	64
H(20A)	11771	11347	7306	58
H(20B)	11349	11449	7953	58
H(21A)	12770	10266	8196	107
H(21B)	13677	10985	7884	107
H(21C)	13178	10145	7547	107
H(22A)	11355	9403	7238	55
H(22B)	9743	9425	7054	55
H(23A)	10198	10469	6375	103
H(23B)	11225	9671	6279	103
H(23C)	11797	10525	6579	103
H(24A)	9132	9587	8001	43
H(24B)	10746	9574	8181	43
H(25A)	10446	10850	8690	77
H(25B)	9404	10123	8911	77
H(25C)	8830	10871	8507	77
H(26A)	9405	11345	7025	39
H(26B)	9017	11493	7671	39
H(27A)	7821	10192	6970	61
H(27B)	7029	11040	7176	61

H(27C)	7454	10312	7622	61
H(29A)	5352	8657	10266	42
H(29D)	3812	8791	10080	42
H(30A)	3921	8469	11014	74
H(30B)	4889	9266	11126	74
H(30C)	3327	9402	10937	74
H(31A)	5568	10380	10764	44
H(31B)	6009	11018	10292	44
H(32A)	8016	10262	10623	80
H(32B)	7300	9388	10462	80
H(32C)	7744	10030	9987	80
H(29B)	4087	10625	10605	46
H(29C)	5689	10502	10702	46
H(30D)	4452	9524	11305	85
H(30E)	3717	9115	10774	85
H(30F)	5329	8992	10872	85
H(31C)	6667	9504	9487	40
H(31D)	6489	8957	10025	40
H(32D)	8664	9595	10037	56
H(32E)	7979	10509	9997	56
H(32F)	7798	9953	10543	56
H(33A)	1799	4464	9573	32
H(33B)	1821	4222	10207	32
H(34A)	3655	5141	10020	71
H(34B)	2603	5837	9794	71
H(34C)	2625	5593	10436	71
H(35A)	687	6126	9573	32
H(35D)	-894	5976	9478	32
H(36A)	239	5882	8640	70
H(36B)	1184	5138	8877	70
H(36C)	-422	4985	8781	70
H(33C)	341	5923	10588	34
H(33D)	563	6254	9976	34
H(34D)	2769	6104	10433	55
H(34E)	2460	5128	10541	55
H(34F)	2684	5462	9924	55

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H(35B)	-355	4097	9494	42
H(35C)	1209	4359	9545	42
H(36D)	303	4846	8660	78
H(36E)	-843	5382	8972	78
H(36F)	736	5647	9024	78
