Table S1. Crystallographic data.[a]

Compound	$[Fe(1\text{-}Me\text{-}2\text{-}S\text{-}imid)_2 \cdot 0.5\ Cp_2Fe]_x$
Formula	$C_{13}H_{15}Fe_{1.5}N_4S_2$
fw	375.18
Color, habit	golden, needle
Crystal size, mm	0.04 x 0.08 x 0.45
Crystal system	tetragonal
Space group	P4/n (No. 85)
a, Å	13.2862(7)
c, Å	8.7665(4)
V, Å^3	1547.5(1)
Z	4
ρ_{calc}, g/cm^3	1.610
F(000)	768
Radiation	Mo
μ, cm^{-1}	16.88
Transmission factors (relative)	0.56-1.00
$2\theta_{max}$, deg	60
Crystal decay, %	negligible
Total reflections	13597
Unique reflections	2131
R_{merge}	0.061
No. of variables	97
R	0.077
R_w	0.063
gof	1.32
Max Δ/σ (final cycle)	0.002
Residual density, e/Å^3	-1.05, +1.30

[a] Temperature 180 K, Rigaku / ADSC CCD area detector, Mo K_α radiation (λ = 0.71069 Å), graphite monochromator, takeoff angle -10.0°, aperture 94.0 x 94.0 mm at a distance of 39.25(5) mm from the crystal, function minimized $\Sigma w(|F_o^2|-|F_c^2|)^2$ where $w = 1/\sigma^2(F_o^2)$, $R = \Sigma||F_o^2|-|F_c^2||/\Sigma|F_o^2|$, $R_w = (\Sigma w(|F_o^2|-|F_c^2|)^2/\Sigma w F_o^4|)^{1/2}$, and gof = $[\Sigma w(|F_o^2|-|F_c^2|)^2/(m-n)]^{1/2}$ where m = number of observations and n = number of variables.

Table S2. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}	occ
Fe(1)	0.7500	0.2500	0.0000	1.319(10)	1/4
Fe(2)	0.7500	0.2500	0.5000	1.336(10)	1/4
Fe(3)	0.2500	0.2500	0.58166(10)	2.139(12)	1/4
S(1)	0.62187(6)	0.31672(6)	0.15814(9)	1.71(2)	
N(1)	0.6407(2)	0.1738(2)	0.3812(3)	1.42(6)	
N(2)	0.5293(2)	0.1341(2)	0.2031(3)	1.55(6)	
C(1)	0.5963(2)	0.2049(2)	0.2521(4)	1.32(6)	
C(2)	0.6013(2)	0.0795(2)	0.4115(4)	1.96(8)	
C(3)	0.5330(3)	0.0543(3)	0.3028(4)	2.27(8)	
C(4)	0.4625(2)	0.1423(3)	0.0722(4)	2.28(8)	
C(5)	0.3311(4)	0.2759(6)	0.3871(5)	4.28(14)	0.900
C(6)	0.1970(13)	0.1567(11)	0.427(2)	4.1(3)	0.350
C(7)	0.2891(6)	0.1744(5)	0.7735(5)	7.2(2)	0.900
C(8)	0.1999(15)	0.1342(12)	0.736(2)	7.0(4)	0.350
H(1)	0.6200	0.0371	0.4986	2.4	
H(2)	0.4941	-0.0083	0.2967	2.7	
H(3)	0.4174	0.1999	0.0861	2.7	
H(4)	0.5026	0.1519	-0.0205	2.7	
H(5)	0.4226	0.0805	0.0628	2.7	

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

Table S3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Fe(1)	S(1)	2.3677(8)	Fe(2)	N(1)	2.054(2)
S(1)	C(1)	1.732(3)	N(1)	C(1)	1.342(3)
N(1)	C(2)	1.383(4)	N(2)	C(1)	1.364(3)
N(2)	C(3)	1.375(4)	N(2)	C(4)	1.455(4)
C(2)	C(3)	1.358(4)			

Table S4. Bond Angles(°)*

atom	atom	atom	angle	atom	atom	atom	angle
S(1)	Fe(1)	S(1)^a	110.05(2)	S(1)	Fe(1)	S(1)^b	110.05(2)
S(1)	Fe(1)	S(1)^c	108.32(4)	N(1)	Fe(2)	N(1)^d	104.91(6)
N(1)	Fe(2)	N(1)^e	104.91(6)	N(1)	Fe(2)	N(1)^c	119.05(13)
Fe(1)	S(1)	C(1)	95.67(10)	Fe(2)	N(1)	C(1)	125.9(2)
Fe(2)	N(1)	C(2)	128.0(2)	C(1)	N(1)	C(2)	106.0(2)
C(1)	N(2)	C(3)	108.0(3)	C(1)	N(2)	C(4)	126.5(3)
C(3)	N(2)	C(4)	125.5(3)	S(1)	C(1)	N(1)	125.4(2)
S(1)	C(1)	N(2)	124.7(2)	N(1)	C(1)	N(2)	109.9(3)
N(1)	C(2)	C(3)	109.9(3)	N(2)	C(3)	C(2)	106.2(3)

* here and elsewhere superscripts refer to the following symmetry operations:

(a) 1/2+y, 1-x, -z (b) 1-y, -1/2+x, -z (c) 3/2-x, 1/2-y, z (d) 1/2+y, 1-x, 1-z (e) 1-y, -1/2+x, 1-z

Table S5. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	0.0187(3)	0.0187	0.0127(4)	0.0000	0.0000	0.0000
Fe(2)	0.0163(3)	0.0163	0.0182(5)	0.0000	0.0000	0.0000
Fe(3)	0.0331(4)	0.0331	0.0151(5)	0.0000	0.0000	0.0000
S(1)	0.0243(5)	0.0201(5)	0.0205(4)	0.0057(4)	0.0032(4)	0.0025(4)
N(1)	0.0145(15)	0.023(2)	0.0167(13)	-0.0013(12)	0.0001(11)	0.0039(12)
N(2)	0.0146(15)	0.027(2)	0.0174(13)	-0.0045(12)	0.0003(11)	-0.0048(12)
C(1)	0.014(2)	0.021(2)	0.0153(13)	0.0022(13)	0.0038(15)	-0.001(2)
C(2)	0.027(2)	0.023(2)	0.024(2)	-0.006(2)	0.000(2)	0.0067(15)
C(3)	0.034(2)	0.024(2)	0.028(2)	-0.011(2)	0.001(2)	0.001(2)
C(4)	0.018(2)	0.046(2)	0.024(2)	-0.005(2)	-0.001(2)	-0.007(2)
C(5)	0.051(4)	0.076(4)	0.035(3)	-0.020(3)	0.027(2)	-0.004(3)
C(7)	0.093(6)	0.149(8)	0.031(3)	0.008(5)	-0.015(4)	0.057(4)

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table S6. Bond Lengths($\AA$) Involving Hydrogen

atom	atom	distance	atom	atom	distance
C(2)	H(1)	0.98	C(3)	H(2)	0.98
C(4)	H(3)	0.98	C(4)	H(4)	0.98
C(4)	H(5)	0.98			

Table S7. Bond Angles(°) Involving Hydrogen

atom	atom	atom	angle	atom	atom	atom	angle
N(1)	C(2)	H(1)	125.0	C(3)	C(2)	H(1)	125.0
N(2)	C(3)	H(2)	126.9	C(2)	C(3)	H(2)	126.9
N(2)	C(4)	H(3)	109.5	N(2)	C(4)	H(4)	109.5
N(2)	C(4)	H(5)	109.5	H(3)	C(4)	H(4)	109.5
H(3)	C(4)	H(5)	109.5	H(4)	C(4)	H(5)	109.5

Table S8. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Fe(1)	S(1)	C(1)	N(1)	90.3(3)	Fe(1)	S(1)	C(1)	N(2)	-87.9(2)
Fe(2)	N(1)	C(1)	S(1)	0.0(4)	Fe(2)	N(1)	C(1)	N(2)	178.4(2)
Fe(2)	N(1)	C(2)	C(3)	-177.8(2)	S(1)	Fe(1)	S(1)[a]	C(1)[a]	-61.55(10)
S(1)	Fe(1)	S(1)[b]	C(1)[b]	179.16(11)	S(1)	Fe(1)	S(1)[c]	C(1)[c]	-58.80(10)
S(1)	C(1)	N(1)	C(2)	-177.3(2)	S(1)	C(1)	N(2)	C(3)	177.2(2)
S(1)	C(1)	N(2)	C(4)	-5.1(4)	N(1)	Fe(2)	N(1)[d]	C(1)[d]	155.5(2)
N(1)	Fe(2)	N(1)[d]	C(2)[d]	-21.2(3)	N(1)	Fe(2)	N(1)[e]	C(1)[e]	-78.3(2)
N(1)	Fe(2)	N(1)[e]	C(2)[e]	105.0(3)	N(1)	Fe(2)	N(1)[c]	C(1)[c]	-38.6(2)
N(1)	Fe(2)	N(1)[c]	C(2)[c]	138.1(3)	N(1)	C(1)	N(2)	C(3)	-1.3(3)
N(1)	C(1)	N(2)	C(4)	176.5(3)	N(1)	C(2)	C(3)	N(2)	-0.2(4)
N(2)	C(1)	N(1)	C(2)	1.2(3)	C(1)	N(1)	C(2)	C(3)	-0.6(4)
C(1)	N(2)	C(3)	C(2)	0.9(4)	C(2)	C(3)	N(2)	C(4)	-176.9(3)

Table S9. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
N(2)	C(6)	3.265(14)	3	C(2)	C(3)	3.551(4)	65605
C(3)	C(6)	3.337(13)	3	C(4)	C(8)	3.31(2)	55403
C(4)	C(7)	3.514(7)	55401	C(4)	C(6)	3.566(14)	3
S(1)	H(2)	3.05	3	S(1)	H(5)	3.15	3
C(3)	H(1)	2.94	65605	C(8)	H(4)	2.88	55604
H(1)	H(2)	2.38	65605				

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one-digit numbers and one two-digit number: TA (first digit) + TB (second digit) + TC (third digit) + SN (last two digits). TA, TB and TC are the crystal lattice translation digits along cell edges a, b and c. A translation digit of 5 indicates the origin unit cell. If TA = 4, this indicates a translation of one unit cell length along the a-axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus ± 4 lattice translations from the origin (TA=5, TB=5, TC=5) can be represented.

The SN, or symmetry operator number, refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of symmetry operators relevant to this structure are given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of the atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through symmetry operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (eg. cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

(1)	x,	y,	z	(2)	1/2-x,	1/2-y,	z
(3)	1/2-y,	x,	z	(4)	y,	1/2-x,	z
(5)	-x,	-y,	-z	(6)	1/2+x,	1/2+y,	-z
(7)	1/2+y,	-x,	-z	(8)	-y,	1/2+x,	-z