Angle dependance Spin Crossover properties in polymorphic Iron(II) complexes based on pyridine-triazole derivatives

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1– Generalities

1.1 – Chemicals

Metal salts, starting compounds and solvents were purchased from Sigma-Aldrich, Acros Organic and Fisher scientific. Deuterated solvents were purchased from Eurisotop (Cambridge Isotope Laboratories). Distilled water was obtained from MilliQ water, Millipore system.

1.2 – Physical measurements and characterizations

Powder X-ray Diffraction (PXRD) data were recorded on a high-throughput Bruker D8 Advance diffractometer working on transmission mode and equipped with a focusing Göbel mirror producing CuKα radiation (λ = 1.5418 Å) and a LynxEye detector.

Infrared spectroscopy was measured with a Nicolet iS5 FTIR ThermoFisher spectrometer at room temperature, with a resolution of 1 cm^{-1}, averaging 16 scans at 1.0 cm^{-1}·min.

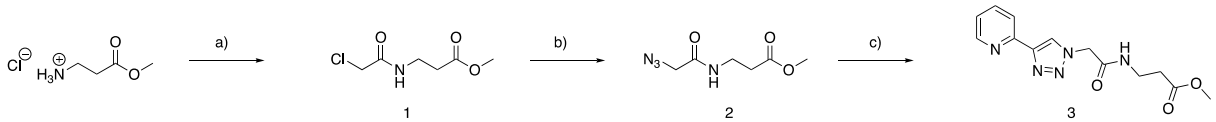
Magnetic susceptibility was recorded with a Quantum Design SQUID Magnetometer between 10 and 300 K at a sweep rate of 2 K/min under an applied field of 5 kOe. Samples of ca. 10 mg were enclosed in a diamagnetic sample holder. The data were normalized to get the magnetic susceptibility by mole of iron complex.

NMR ^{1}H and ^{13}C were measured with Bruker 300 Ultrashield spectrometer.

2– Synthesis

2.1 – Ligand synthesis: 1H-1,2,3-triazole-1-acetamide-(N-3-methoxy-3-oxopropyl)-4-(2-pyridyl) (PytaCOOMe)

The ligand name PytaCOOMe was synthesized following an already know procedure.[1]



Scheme.S1 Synthesis of the ester functionalized pyridine-triazole ligand. *Reaction conditions*: (a) chloroacetyl chloride, DIEA, dry DCM, 1h, 0°C to RT, 66%, (b) NaN_3, NaI, acetone/water (3:1 v:v), 16h, 35°C, 79%, (c) 2-ethynylpyridine, $CuSO_4$, sodium ascorbate, acetone/water (2:1 v:v), 2h, RT, 70%,.

2.1.1 – β-alanine (N-2-chloroacetyl) methyl ester (1)

β-alanine methyl ester hydrochloride salt (1.33 g, 9.5 mmol, 1.2 equiv) was suspended in dry DCM (15 mL) under argon. Dry DIEA (3.5 mL, 20 mmol, 2.5 equiv) was added, and the suspension was cooled down in an ice bath. Chloroacetyl chloride (0.64 mL, 8 mmol, 1 equiv) was added dropwise at 0°C, and the reaction mixture was stirred for one hour at room temperature. The organic layer was then diluted with DCM (15 mL), washed once with 0.1N HCl aqueous solution (30 mL), once with 10% $NaHCO_3$ aqueous solution (30 mL) and once with brine (30 mL). It was then dried over $MgSO_4$, filtered, and concentrated to yield the expected compound as a colorless oil (0.947 g, 5.3 mmol, 66%).

^{1}H-NMR (300 MHz, CDCl3): δ 7.17 (s, 1H), 4.03 (s, 2H), 3.72 (s, 3H), 3.58 (q, *J* = 6.0 Hz, 2H), 2.58 (t, *J* = 6.0 Hz, 2H).

^{13}C-NMR (101 MHz, CDCl3): δ 172.40, 166.14, 51.68, 42.40, 35.14, 33.32.

HRMS (ESI+): *m/z* calculated for $[C_6H_{10}ClNO_3+Na]^+$ 202.02414, found 202.02438 error: 1.2 ppm.

2.1.2 – β-alanine (N-2-azidoacetyl) methyl ester (2)

Compound 1 (0.947 g, 5.3 mmol, 1 equiv) was dissolved in a 3:1 v:v mixture of acetone (15.6 mL) and water (5.2 mL). Sodium azide (0.69 g g, 10.6 mmol, 2 equiv) and sodium iodide (0.079 g, 0.53 mmol, 0.1 equiv) were then added, and the mixture was stirred at 35°C (bath temperature) for 16 h. Acetone was removed by rotary evaporation and the solution was diluted with DCM (15 mL) and water (5 mL). The mixture was then decanted, the organic layer dried over $MgSO_4$, filtered and concentrated to yield compound 2 as a colorless oil (0.78 g, 4.2 mmol, 79%).

^{1}H-NMR (300 MHz, CDCl3): δ 6.87 (s, 1H), 3.97 (s, 2H), 3.72 (s, 3H), 3.57 (q, *J* = 6.0 Hz, 2H), 2.57 (t, *J* = 6.0 Hz, 2H).

^{13}C-NMR (101 MHz, CDCl3): δ 172.18, 166.94, 52.00, 51.43, 34.67, 33.26.

2.1.2 – 1H-1,2,3-triazole-1-acetamide-(N-3-methoxy-3-oxopropyl)-4-(2-pyridyl) (3),

Compound 2 (0.51 g, 2.74 mmol, 1 equiv) was dissolved in a 2:1 v:v mixture of acetone (36 mL) and water (18 mL). 2-ethynylpyridine (0.28 mL, 2.74 mmol, 1 equiv), copper sulfate (0.17 g, 0.69 mmol, 0.25 equiv) and sodium ascorbate (0.14 g, 0.69 mmol, 0.25 equiv) were then added, and the suspension was sonicated for a few minutes, during which a light brownish

precipitate formed. The reaction mixture was then stirred for 2h at room temperature (until the solution turned greenish). The solution was then poured into a 28% ammonia solution and extracted three times with DCM. The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The resulting brown solid was purified by silica gel column chromatography (DCM:EtOAc:MeOH 50:50:0 to 0:98:2 v:v:v) to yield compound 3 (0.56 g, 70%) as a white solid.

^{1}H-NMR (400 MHz, CDCl3): δ 8.56 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 8.28 (s, 1H), 8.10 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.78-7.73 (m, 1H), 7.22 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 6.88 (s, 1H), 5.11 (s, 2H), 3.62 (s, 3H), 3.53 (q, *J* = 6.2 Hz, 2H), 2.53 (t, *J* = 6.2 Hz, 2H).

^{13}C-NMR (101 MHz, CDCl3): δ 172.49, 165.19, 149.58, 136.98, 123.77, 123.16, 120.37, 53.16, 51.97, 35.42, 33.57.

HRMS (ESI+): *m/z* calculated for $[C_{13}H_{15}N_5O_3+H]^+$ 290.12477, found 290.1125527, error: 1.7 ppm.

2.2 – Synthesis of complex

2.2.1 – Synthesis of complex (1)

Compound **(1)** was synthesized in thin slow diffusion tubes of 25 mm long 5 mm diameter, where 2/3 of the tube was filled with 6 mL solution (water) where iron(II) tetrafluoroborate hexahydrate salt (70 mg, 0.21 mmol) was dissolved with potassium thiocyanate (36 mg, 0.42 mmol). The top layer of the tube was covered with 4 mL of a methanolic solution of PytaCOOMe (97.9 mg, 0.42 mmol). After 7 days, little yellow crystals plate appeared, with the formation of polycrystalline micro-powder. (Yield: 28%)

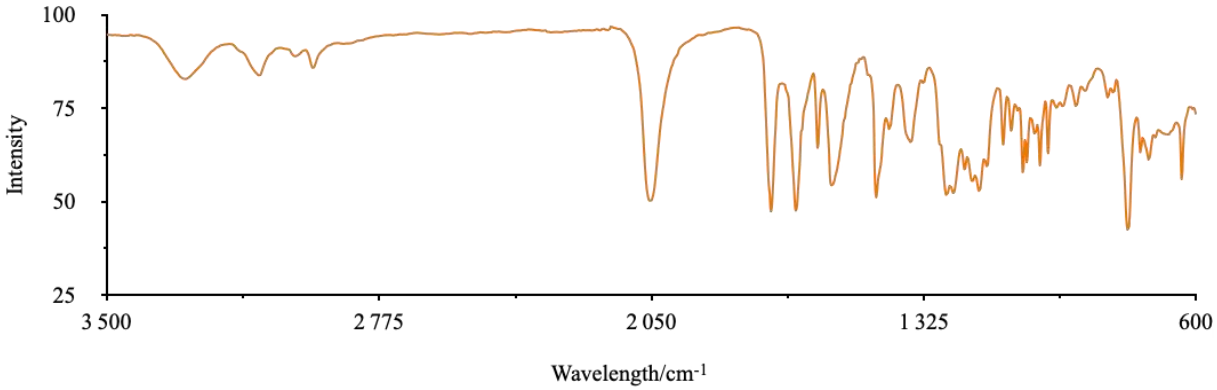


Figure.S1 Infrared spectrum of **(1).**

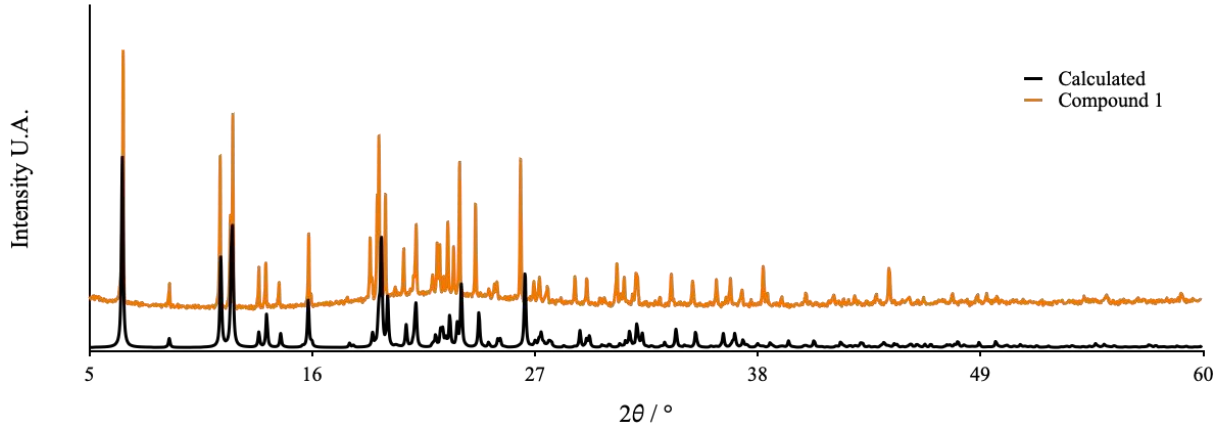


Figure.S2 Experimental (300 K) and calculated PXRD (200 K) patterns of **(1)**.

2.2.2 – Synthesis of complex (2)

Compound **(2)** was synthesized using the same solution/concentration as compound **(1)**. However, both solutions were mixed at room temperature for 10 minutes before being place in a large beaker, crystals were recovered in less than 30 minutes as yellow more needle like crystals. (Yield: 49%)

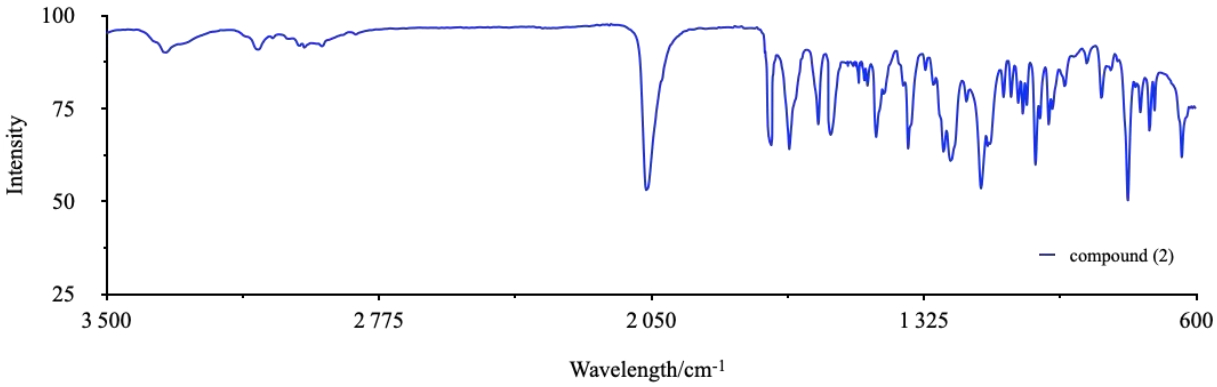


Figure.S3 Infrared spectrum of **(2).**

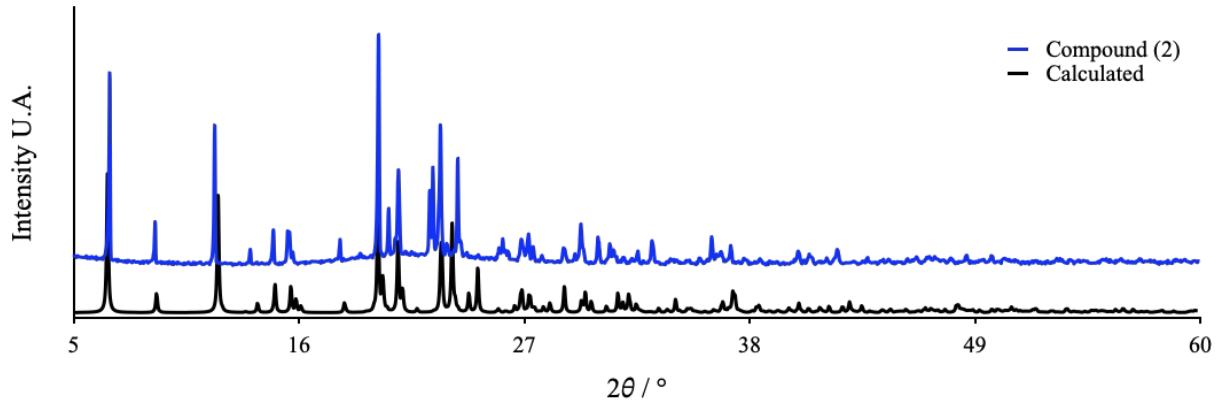


Figure.S4 Experimental and calculated PXRD patterns of **(2)**.

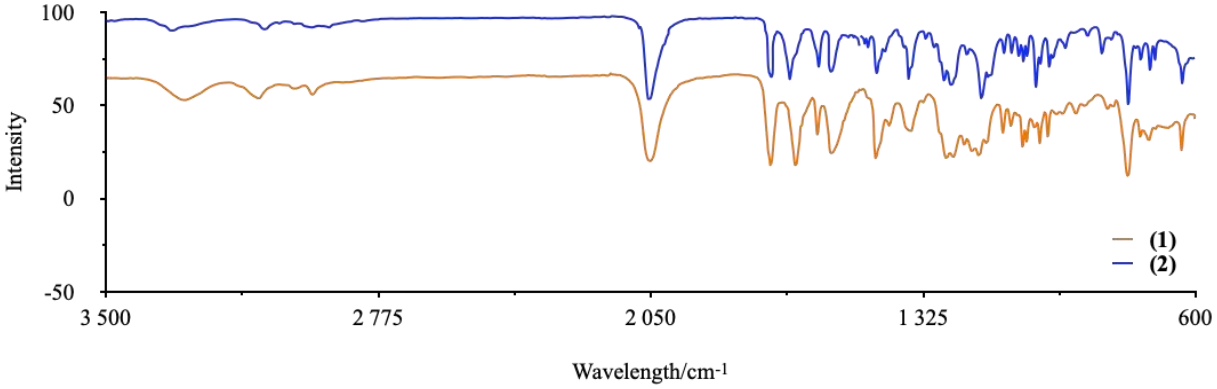


Figure.S5 Superposition of infrared spectra of **(1)** and **(2).**

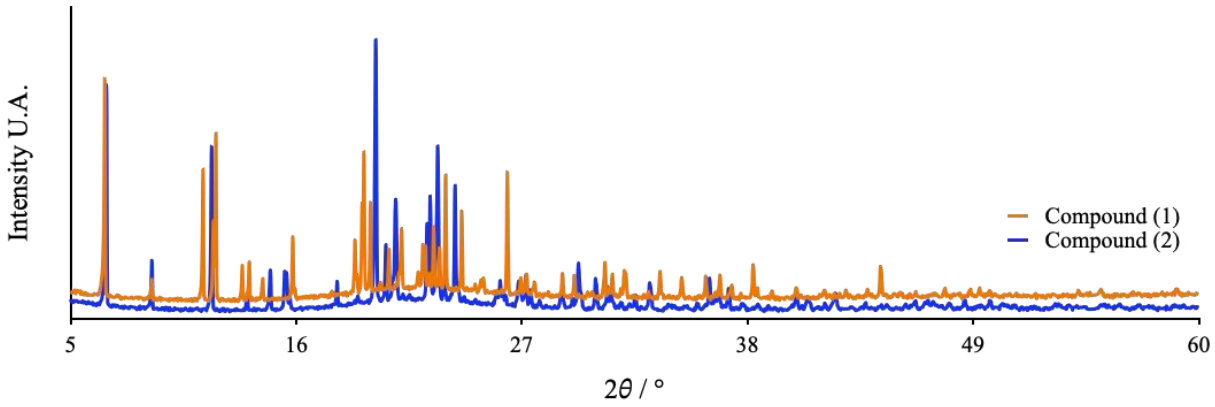


Figure.S6 Superposition of PXRD patterns of **(1)**-HS and **(2).**

3. Single crystal X-ray diffraction analysis.

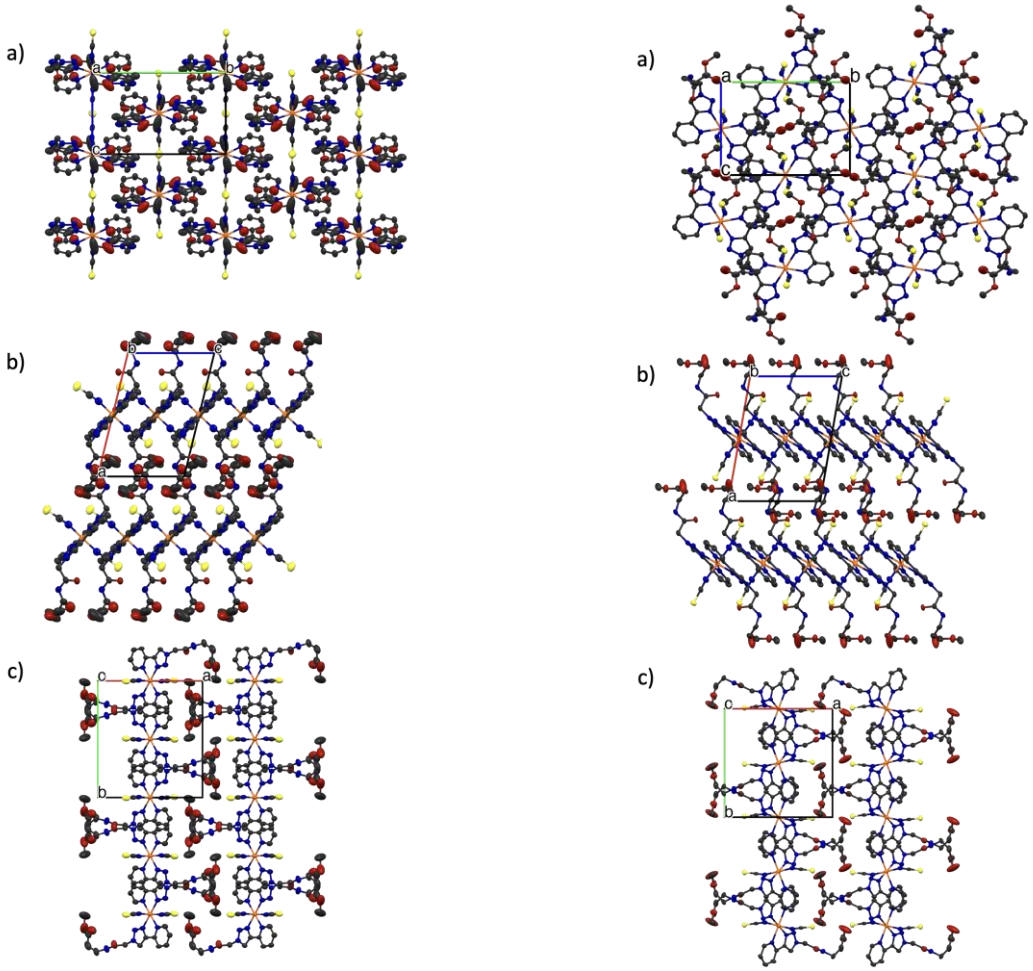


Figure.S7 Crystal packing of (left) compound **(1)** at 200 K in the a) (011), b) (101) and c) (110) plans and of (right) compound **(2)** in the a) (011), b) (101) and c) (110) plans.

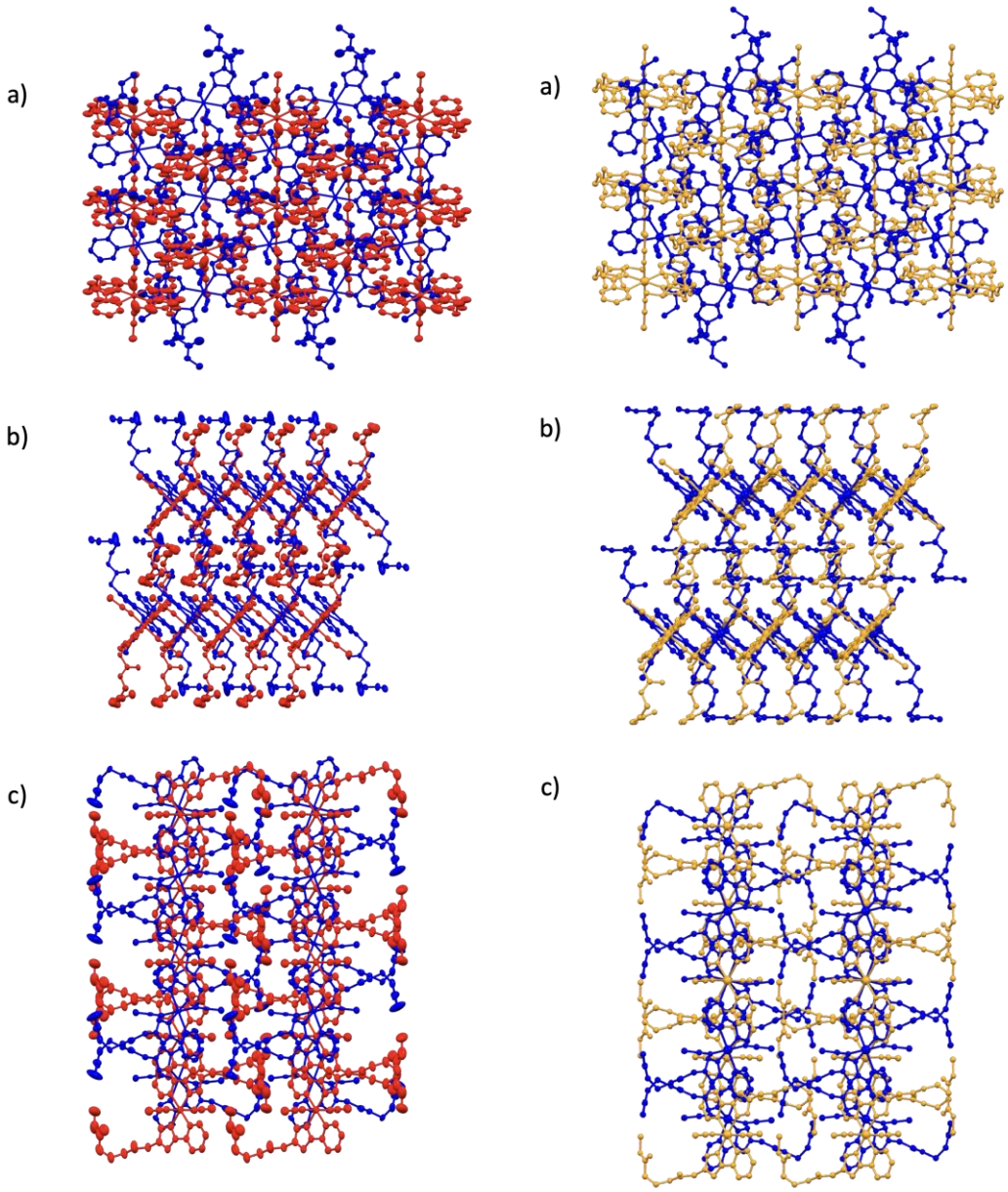


Figure.S8 Crystal packing overlay of (left) compounds **(1)** at 110 K in red and **(2)** at 200 K in blue viewed in the a) (011), b) (101) and c) (110) plans and of (right) compounds **(1)** at 200 K in orange and **(2)** at 200 K in blue viewed in the a) (011), b) (101) and c) (110) plans.

Experimental:

For **(1)**, single crystal X-ray diffraction data were recorded at 100 and 200K at Synchrotron SOLEIL using the PROXIMA2 beamline. For both structures, the low data completeness at high angle is due to geometrical constraints on the beamline that prevents measuring images at high angle.

For **(2)**, single crystal X-Ray diffraction data were measured at 180K with a four-circle kappa-axis Bruker D8 Venture diffractometer equipped with Mo wavelength X-ray microsource and photon III C14 detector. For this structure, the limited data quality at high angle is due to the limited scattered intensity (small crystal thickness).

The structural solution involved a dual-method approach, employing SHELXT for initial solving, followed by refinement using full-matrix least-squares methods against F2 conducted by XL with Olex2 and SHELXLE. Anisotropic displacement parameters were applied to refine all non-hydrogen atoms. Hydrogen atoms underwent isotropic refinement at calculated positions, employing a riding model.[2] For **(1)**, the potential disorder on the aliphatic chains was not modelled, as it resulted in a lowering of the refinement quality.

Compound **(1)** 110 K data set:

Empirical formula	$C_{28}H_{30}FeN_{12}O_6S_2$
Formula weight	750.61
Temperature/K	110.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.4990(3)
b/Å	14.2794(4)
c/Å	9.1679(3)
α/°	90
β/°	103.635(3)
γ/°	90
Volume/Å^3	1717.38(11)
Z	2
ρ_{calc}g/cm^3	1.452
μ/mm^{-1}	0.661
F(000)	776.0
Crystal size/mm^3	0.07 × 0.05 × 0.01
Radiation	synchrotron (λ = 0.72932 Å)
2Θ range for data collection/°	3.186 to 55.532
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -10 ≤ l ≤ 10
Reflections collected	17135
Independent reflections	3006 [R_{int} = 0.0652, R_{sigma} = 0.0452]
Data/restraints/parameters	3006/0/224
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0714, wR_2 = 0.2143
Final R indexes [all data]	R_1 = 0.0878, wR_2 = 0.2356
Largest diff. peak/hole / e Å^{-3}	0.96/-0.44

Table.S1 *Crystal data and structure refinement of* ***(1)*** *110 K.*

Atom	***x***	***y***	***z***	**U(eq)**
Fe1	5000	5000	5000	42.2(3)
S1	2694.1(12)	4919.1(9)	173.0(16)	70.2(5)
O1	1588(2)	2547(3)	4538(3)	68.3(10)
O2	-615(3)	3639(4)	4486(5)	102.4(14)
O3	-1318(3)	3828(5)	6516(6)	119.6(18)
N1	3962(3)	5016(2)	3070(5)	50.2(9)
N2	5715(2)	3931(2)	4148(3)	43.3(8)
N3	4313(2)	3877(3)	5651(4)	47.4(8)
N4	3582(3)	3742(3)	6347(4)	51.0(9)
N5	3440(2)	2827(3)	6391(3)	47.9(9)
N6	866(3)	2049(3)	6389(4)	63.3(11)
C1	3436(4)	4980(3)	1861(6)	51.7(11)
C2	6416(3)	4028(3)	3318(5)	51.0(10)
C3	6866(3)	3273(3)	2803(5)	51.7(11)
C4	6605(3)	2376(3)	3129(4)	52.2(11)
C5	5878(3)	2257(3)	3955(4)	47.2(10)
C6	5447(3)	3048(3)	4425(4)	42.6(9)
C7	4629(3)	3032(3)	5234(4)	43.0(9)
C8	4065(3)	2341(3)	5699(4)	47.6(10)
C9	2622(3)	2459(3)	7045(4)	50.8(11)
C10	1632(3)	2366(3)	5850(5)	54.4(11)

Atom	*x*	*y*	*z*	U(eq)
C11	-118(3)	1774(5)	5449(6)	75.0(16)
C12	-950(4)	2294(5)	5875(6)	86.2(18)
C13	-930(4)	3325(6)	5529(6)	89.8(19)
C14	-1307(8)	4897(5)	6243(14)	134(4)

Table.S2 *Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for* **(1)** at 110 K. *U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	42.1(6)	52.4(6)	37.1(5)	1.3(3)	19.6(4)	1.5(3)
S1	73.0(10)	80.6(10)	53.8(9)	4.9(6)	8.3(7)	0.1(6)
O1	49.5(18)	129(3)	29.3(15)	6.3(17)	15.7(12)	-0.8(18)
O2	104(3)	139(4)	68(3)	2(3)	30(2)	-12(3)
O3	83(3)	175(5)	104(4)	-45(3)	29(3)	-3(3)
N1	54(2)	53(2)	51(2)	0.0(15)	26.1(18)	2.5(15)
N2	39.3(17)	59(2)	33.6(17)	2.2(15)	13.6(13)	-0.1(15)
N3	42.3(18)	66(2)	37.3(18)	2.9(16)	16.7(14)	4.0(16)
N4	46.2(19)	74(3)	36.4(18)	3.1(16)	17.9(14)	1.0(17)
N5	42.6(18)	71(2)	32.4(17)	3.3(15)	14.1(13)	-3.0(17)
N6	47(2)	111(3)	33.4(18)	-0.6(19)	12.6(15)	-15(2)
C1	55(3)	53(3)	51(3)	2.1(19)	21(2)	1.7(18)
C2	45(2)	68(3)	45(2)	-1(2)	21.3(18)	-3(2)
C3	40(2)	74(3)	46(2)	-5(2)	20.6(18)	-2(2)
C4	43(2)	71(3)	45(2)	-10(2)	14.3(17)	5(2)
C5	44(2)	59(2)	39(2)	0.1(18)	9.3(17)	1.3(19)
C6	38(2)	62(3)	27.5(18)	1.5(16)	7.1(15)	1.4(17)
C7	37(2)	61(3)	30.8(19)	1.2(17)	9.2(15)	2.9(18)
C8	39(2)	68(3)	37(2)	1.5(19)	11.1(16)	1.5(19)
C9	40(2)	84(3)	33(2)	5(2)	16.1(16)	-2.7(19)
C10	50(2)	81(3)	36(2)	-5(2)	17.0(18)	-4(2)
C11	50(3)	127(5)	49(3)	-3(3)	13(2)	-12(3)
C12	68(4)	131(5)	60(3)	7(3)	15(3)	-20(3)
C13	70(4)	145(6)	58(3)	-6(4)	20(3)	-14(4)
C14	144(8)	99(6)	191(11)	-44(5)	100(8)	-23(4)

Table.S3 *Anisotropic Displacement Parameters (Å²×10³) for* ***(1)*** at 110 K. *The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.*

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe01	N1	1.981(5)	N3	C7	1.364(5)
Fe01	N1[1]	1.981(5)	N4	N5	1.323(5)
Fe01	N2	2.056(3)	N5	C8	1.359(5)
Fe01	N2[1]	2.055(3)	N5	C9	1.471(5)
Fe01	N3[1]	2.013(3)	N6	C10	1.326(5)
Fe01	N3	2.012(3)	N6	C11	1.457(6)
S1	C1	1.636(6)	C2	C3	1.374(6)
O1	C10	1.218(5)	C3	C4	1.380(7)
O2	C13	1.220(7)	C4	C5	1.385(6)
O3	C13	1.354(7)	C5	C6	1.385(6)
O3	C14	1.547(9)	C6	C7	1.468(5)
N1	C1	1.168(7)	C7	C8	1.374(6)
N2	C2	1.354(5)	C9	C10	1.521(6)
N2	C6	1.353(5)	C11	C12	1.475(8)
N3	N4	1.310(4)	C12	C13	1.507(10)

Table.S4 *Bond Lengths for compound* ***(1)*** at 110 K. [1]1-X,1-Y,1-Z

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	Fe01	N1[1]	180.0	N4	N5	C9	119.5(3)
N1[1]	Fe01	N2	88.04(13)	C8	N5	C9	128.0(4)
N1	Fe01	N2[1]	88.04(13)	C10	N6	C11	123.6(4)
N11	Fe01	N2[1]	91.96(13)	N1	C1	S1	179.4(4)
N1	Fe01	N2	91.96(13)	N2	C2	C3	122.5(4)
N1	Fe01	N3	90.26(14)	C2	C3	C4	119.9(4)
N1[1]	Fe01	N3[1]	90.26(14)	C3	C4	C5	118.8(4)
N1[1]	Fe01	N3	89.74(14)	C6	C5	C4	118.3(4)
N1	Fe01	N3[1]	89.74(14)	N2	C6	C5	123.5(3)
N2[1]	Fe01	N2	180.0	N2	C6	C7	112.0(3)
N3[1]	Fe01	N2	100.85(14)	C5	C6	C7	124.5(4)
N3[1]	Fe01	N2[1]	79.15(14)	N3	C7	C6	116.8(3)
N3	Fe01	N2	79.15(14)	N3	C7	C8	108.4(3)
N3	Fe01	N2[1]	100.85(14)	C8	C7	C6	134.8(4)
N3	Fe01	N3[1]	180.0	N5	C8	C7	103.2(4)
C13	O3	C14	113.3(6)	N5	C9	C10	110.8(3)
C1	N1	Fe01	172.1(4)	O1	C10	N6	125.4(4)
C2	N2	Fe01	126.2(3)	O1	C10	C9	121.5(4)
C6	N2	Fe01	116.8(2)	N6	C10	C9	113.0(4)
C6	N2	C2	117.0(3)	N6	C11	C12	110.7(5)
N4	N3	Fe01	135.6(3)	C11	C12	C13	112.5(5)
N4	N3	C7	109.2(3)	O2	C13	O3	126.1(8)
C7	N3	Fe01	115.2(2)	O2	C13	C12	123.5(6)
N3	N4	N5	106.9(3)	O3	C13	C12	110.4(5)
N4	N5	C8	112.3(3)				

Table.S5 *Bond angle for compound* ***(1)*** *at 110 K.* [1]1-X,1-Y,1-Z

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Fe01	N2	C2	C3	179.4(3)	C2	N2	C6	C7	-175.7(3)
Fe01	N2	C6	C5	-178.5(3)	C2	C3	C4	C5	1.1(6)
Fe01	N2	C6	C7	3.3(4)	C3	C4	C5	C6	-0.3(6)
Fe01	N3	N4	N5	177.3(3)	C4	C5	C6	N2	-1.6(6)
Fe01	N3	C7	C6	2.3(4)	C4	C5	C6	C7	176.5(4)
Fe01	N3	C7	C8	-177.5(3)	C5	C6	C7	N3	178.1(3)
N2	C2	C3	C4	0.0(7)	C5	C6	C7	C8	-2.2(7)
N2	C6	C7	N3	-3.6(5)	C6	N2	C2	C3	-1.7(6)
N2	C6	C7	C8	176.0(4)	C6	C7	C8	N5	179.8(4)
N3	N4	N5	C8	-1.1(4)	C7	N3	N4	N5	0.8(4)
N3	N4	N5	C9	-176.9(3)	C8	N5	C9	C10	-85.2(5)
N3	C7	C8	N5	-0.5(4)	C9	N5	C8	C7	176.3(3)
N4	N3	C7	C6	179.6(3)	C10	N6	C11	C12	-124.5(5)
N4	N3	C7	C8	-0.2(4)	C11	N6	C10	O1	6.9(8)
N4	N5	C8	C7	1.0(4)	C11	N6	C10	C9	-171.0(5)
N4	N5	C9	C10	89.9(5)	C11	C12	C13	O2	30.8(8)
N5	C9	C10	O1	2.8(6)	C11	C12	C13	O3	-150.0(5)
N5	C9	C10	N6	-179.1(4)	C14	O3	C13	O2	-1.7(10)
N6	C11	C12	C13	67.3(6)	C14	O3	C13	C12	179.2(6)
C2	N2	C6	C5	179.4(3)					

Table.S6 *Torsion Angles for* ***(1)*** *at 110 K.*

Atom	*x*	*y*	*z*	U(eq)
H6	957.24	2002.76	7369.25	76
H2	6604.81	4641	3083.46	61
H3	7354.5	3369.02	2222.73	62
H4	6919.81	1849.33	2792.29	63
H5	5679.64	1648.04	4193.04	57
H8	4103.22	1683.35	5568.99	57
H9A	2518.24	2886.79	7845.7	61
H9B	2823.62	1839.26	7501.76	61
H11A	-220.27	1093.64	5559.62	90
H11B	-129.01	1900.93	4383.87	90
H12A	-895.79	2212.42	6963.74	103
H12B	-1612.1	2028.91	5331.56	103
H14A	-997.43	5024.71	5398.5	202
H14B	-910.33	5207.41	7146.45	202
H14C	-2007.61	5136	6010.98	202

Table.S7 *Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for* ***(1)*** *at 110 K.*

Empirical formula	$C_{28}H_{30}FeN_{12}O_6S_2$
Formula weight	750.61
Temperature/K	200
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	13.5277(8)
b/Å	14.6210(7)
c/Å	9.2130(6)
α/°	90
β/°	103.732(5)
γ/°	90
Volume/$Å^3$	1770.14(18)
Z	2
$\rho_{calc}g/cm^3$	1.408
μ/mm^{-1}	0.641
F(000)	776.0
Crystal size/mm^3	0.07 × 0.05 × 0.01
Radiation	synchrotron (λ = 0.72932 Å)
2Θ range for data collection/°	3.18 to 51.988
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -10 ≤ l ≤ 11
Reflections collected	16974
Independent reflections	2920 [R_{int} = 0.1076, R_{sigma} = 0.0924]
Data/restraints/parameters	2920/0/224
Goodness-of-fit on F^2	0.862
Final R indexes [I>=2σ (I)]	R_1 = 0.0740, wR_2 = 0.1890
Final R indexes [all data]	R_1 = 0.0996, wR_2 = 0.2036
Largest diff. peak/hole / e $Å^{-3}$	0.69/-0.92

Table.S8 *Crystal data and structure refinement of* ***(1)*** *200 K.*

Atom	*x*	*y*	*z*	U(eq)
Fe01	5000	5000	5000	45.3(4)
S1	2690.1(17)	4955.9(11)	59(2)	87.4(6)
O1	8454(3)	7569(3)	5546(4)	70.3(12)
O2	10577(5)	6384(4)	5503(7)	129(2)
O3	11303(5)	6182(6)	3469(9)	160(3)
N1	3899(4)	5034(3)	2974(6)	59.5(12)
N2	4289(3)	6135(2)	5908(4)	45.2(10)
N3	5722(3)	6205(2)	4353(4)	48.0(10)
N4	6448(3)	6362(3)	3669(5)	50.9(10)
N5	6599(3)	7261(3)	3697(4)	46.7(10)
N6	9158(3)	7982(3)	3664(5)	64.6(13)
C1	3396(5)	5007(3)	1751(7)	59.2(14)
C2	3586(4)	6051(3)	6704(6)	57.1(14)
C3	3138(4)	6804(3)	7230(6)	54.2(13)
C4	3446(4)	7659(3)	6916(6)	52.6(13)
C5	4173(4)	7764(3)	6128(5)	48.1(12)
C6	4593(3)	6989(3)	5643(5)	41.9(11)
C7	5407(4)	7007(3)	4838(5)	43.0(11)
C8	5975(4)	7687(3)	4426(5)	46.2(12)
C9	7404(3)	7627(3)	3080(5)	47.9(12)
C10	8396(4)	7707(4)	4234(6)	51.9(13)
C11	10154(4)	8219(5)	4603(7)	77.5(18)
C12	10951(6)	7703(6)	4155(8)	102(3)
C13	10931(6)	6659(7)	4451(11)	115(3)
C14	11248(11)	5123(7)	3723(19)	211(8)

Table.S9 *Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for* **(1)** at 200 K. *U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe01	57.4(6)	25.6(5)	59.2(7)	-0.8(4)	26.0(5)	1.3(4)
S1	119.0(15)	57.6(10)	75.2(12)	5.8(8)	2.3(10)	-1.6(9)
O1	62(2)	107(3)	45(2)	9(2)	16.8(18)	-4(2)
O2	145(5)	120(5)	127(5)	11(4)	41(4)	-17(4)
O3	109(5)	190(8)	185(7)	-86(6)	40(5)	18(4)
N1	74(3)	33(2)	74(3)	1(2)	22(3)	5(2)
N2	56(3)	32(2)	53(2)	-0.4(17)	24(2)	-1.1(17)
N3	60(3)	37(2)	55(2)	1.1(19)	29(2)	3.6(18)
N4	62(3)	41(2)	56(3)	3(2)	25(2)	0.0(19)
N5	52(2)	40(2)	51(2)	2.6(19)	17(2)	-0.6(19)
N6	53(3)	93(4)	47(2)	4(2)	10(2)	-16(2)
C1	76(4)	33(3)	73(4)	8(3)	25(3)	2(3)
C2	65(4)	44(3)	68(4)	1(3)	27(3)	-4(2)
C3	56(3)	47(3)	67(3)	-4(3)	28(3)	3(2)
C4	61(3)	39(3)	61(3)	-4(2)	20(3)	5(2)
C5	59(3)	28(2)	57(3)	0(2)	14(3)	2(2)
C6	48(3)	29(2)	49(3)	-3(2)	11(2)	1.8(19)
C7	50(3)	33(2)	45(3)	1(2)	11(2)	3(2)
C8	52(3)	36(2)	54(3)	1(2)	18(2)	-3(2)
C9	48(3)	51(3)	48(3)	7(2)	18(2)	-3(2)
C10	57(3)	56(3)	47(3)	0(2)	22(3)	-4(2)
C11	55(4)	111(5)	68(4)	-4(4)	17(3)	-17(3)
C12	81(5)	138(7)	83(5)	13(5)	12(4)	-30(5)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C13	81(5)	144(9)	111(7)	38(6)	5(5)	-26(5)
C14	223(15)	104(9)	370(20)	-69(10)	195(16)	-37(8)

Table.S10 *Anisotropic Displacement Parameters ($Å^2×10^3$) for* ***(1)*** at 200 K. *The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.*

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe01	N1	2.094(5)	N3	C7	1.359(6)
Fe01	$N1^1$	2.094(5)	N4	N5	1.329(5)
Fe01	N2	2.182(4)	N5	C8	1.350(6)
Fe01	$N2^1$	2.182(4)	N5	C9	1.445(6)
Fe01	$N3^1$	2.166(4)	N6	C10	1.326(6)
Fe01	N3	2.166(4)	N6	C11	1.461(7)
S1	C1	1.624(7)	C2	C3	1.398(7)
O1	C10	1.210(6)	C3	C4	1.370(7)
O2	C13	1.245(9)	C4	C5	1.363(6)
O3	C13	1.333(11)	C5	C6	1.387(6)
O3	C14	1.570(13)	C6	C7	1.467(7)
N1	C1	1.171(7)	C7	C8	1.365(6)
N2	C2	1.337(6)	C9	C10	1.506(7)
N2	C6	1.354(5)	C11	C12	1.454(9)
N3	N4	1.307(5)	C12	C13	1.552(12)

Table.S11 *Bond Lengths for compound* ***(1)*** at 200 K. ^{1}1-X,1-Y,1-Z

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	Fe01	$N1^1$	180.0	N4	N5	C9	119.0(4)
$N1^1$	Fe01	N2	87.79(16)	C8	N5	C9	130.0(4)
N1	Fe01	$N2^1$	92.21(16)	C10	N6	C11	122.2(5)
N11	Fe01	$N2^1$	87.79(16)	N1	C1	S1	179.2(5)
N1	Fe01	N2	92.21(16)	N2	C2	C3	122.8(4)
N1	Fe01	N3	89.58(16)	C2	C3	C4	117.8(5)
$N1^1$	Fe01	$N3^1$	90.42(16)	C3	C4	C5	120.6(4)
$N1^1$	Fe01	N3	90.42(16)	C6	C5	C4	118.8(4)
N1	Fe01	$N3^1$	89.58(16)	N2	C6	C5	122.0(4)
$N2^1$	Fe01	N2	180.00(18)	N2	C6	C7	113.8(4)
$N3^1$	Fe01	N2	75.84(14)	C5	C6	C7	124.2(4)
$N3^1$	Fe01	$N2^1$	104.16(14)	N3	C7	C6	118.9(4)
N3	Fe01	N2	75.84(14)	N3	C7	C8	107.2(4)
N3	Fe01	$N2^1$	104.16(14)	C8	C7	C6	133.9(4)
N3	Fe01	$N3^1$	180.0	N5	C8	C7	105.2(4)
C13	O3	C14	112.0(9)	N5	C9	C10	112.3(4)
C1	N1	Fe01	170.1(5)	O1	C10	N6	125.1(5)
C2	N2	Fe01	125.2(3)	O1	C10	C9	121.9(4)
C6	N2	Fe01	118.0(4)	N6	C10	C9	113.0(4)
C6	N2	C2	116.9(3)	N6	C11	C12	110.6(6)
N4	N3	Fe01	135.6(3)	C11	C12	C13	114.6(7)
N4	N3	C7	109.8(4)	O2	C13	O3	129.5(10)
C7	N3	Fe01	114.4(3)	O2	C13	C12	118.8(10)
N3	N4	N5	107.0(4)	O3	C13	C12	111.7(8)
N4	N5	C8	112.2(3)				

Table.S12 *Bond angle for compound* ***(1)*** *at 200 K.* ^{1}1-X,1-Y,1-Z

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Fe01	N2	C2	C3	-178.5(4)	C2	N2	C6	C7	175.8(3)
Fe01	N2	C6	C5	178.1(4)	C2	C3	C4	C5	-1.3(6)
Fe01	N2	C6	C7	-3.1(5)	C3	C4	C5	C6	0.5(6)
Fe01	N3	N4	N5	-175.6(3)	C4	C5	C6	N2	1.5(6)
Fe01	N3	C7	C6	-3.6(5)	C4	C5	C6	C7	176.7(4)
Fe01	N3	C7	C8	176.1(3)	C5	C6	C7	N3	-0.6(8)
N2	C2	C3	C4	-0.5(8)	C5	C6	C7	C8	0.3(8)
N2	C6	C7	N3	4.5(6)	C6	N2	C2	C3	1.2(7)
N2	C6	C7	C8	-175.2(5)	C6	C7	C8	N5	-177.5(5)
N3	N4	N5	C8	0.9(5)	C7	N3	N4	N5	-176.7(4)
N3	N4	N5	C9	176.8(4)	C8	N5	C9	C10	3.6(8)
N3	C7	C8	N5	0.7(5)	C9	N5	C8	C7	1.8(8)
N4	N3	C7	C6	-179.9(4)	C10	N6	C11	C12	-179.6(5)
N4	N3	C7	C8	-0.1(5)	C11	N6	C10	O1	-0.5(5)
N4	N5	C8	C7	-1.0(5)	C11	N6	C10	C9	84.1(6)
N4	N5	C9	C10	-90.9(5)	C11	C12	C13	O2	-176.3(4)
N5	C9	C10	O1	-7.5(7)	C11	C12	C13	O3	126.1(7)
N5	C9	C10	N6	175.6(4)	C14	O3	C13	O2	-4.8(9)
N6	C11	C12	C13	-67.4(8)	C14	O3	C13	C12	171.9(5)
C2	N2	C6	C5	-2.2(7)					

Table.S13 *Torsion Angles for* ***(1)*** *at 200 K.*

Atom	*x*	*y*	*z*	U(eq)
H6	9059.43	8023.19	2686.79	77
H2	3382.57	5454.9	6920.6	68
H3	2635.92	6725.63	7787.44	65
H4	3149.7	8183.88	7250.5	63
H5	4388.44	8356.56	5913.71	58
H8	5938.79	8323.62	4612.8	55
H9A	7200.39	8238.67	2651.5	57
H9B	7499.95	7224.64	2260.26	57
H11A	10278.15	8882.11	4515.24	93
H11B	10167.93	8084.7	5660.23	93
H12A	11619.66	7947.73	4695.5	122
H12B	10890.07	7801.17	3073.82	122
H14A	10882.73	4829.52	2794.28	316
H14B	10887.68	5005.57	4510.42	316
H14C	11938.71	4873.45	4024.76	316

Table.S14 *Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for* ***(1)*** *at 200 K.*

Compound **(2)** data set:

Empirical formula	$C_{28}H_{30}FeN_{12}O_6S_2$
Formula weight	750.61
Temperature/K	180.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.271(3)
b/Å	13.139(3)
c/Å	9.619(2)
α/°	90
β/°	99.910(7)
γ/°	90
Volume/Å^3	1652.3(6)
Z	2
ρ_{calc}g/cm^3	1.509
μ/mm^{-1}	0.645
F(000)	776.0
Crystal size/mm^3	0.12 × 0.08 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.3 to 50.216
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -11 ≤ l ≤ 11
Reflections collected	31560
Independent reflections	2930 [R_{int} = 0.1771, R_{sigma} = 0.0739]
Data/restraints/parameters	2930/0/224
Goodness-of-fit on F^2	1.164
Final R indexes [I>=2σ (I)]	1.170
Final R indexes [all data]	R_1 = 0.0937, wR_2 = 0.1671
Largest diff. peak/hole / e Å^{-3}	R_1 = 0.1310, wR_2 = 0.1812

Table.S15 *Crystal data and structure refinement of* ***(2).***

Atom	***x***	***y***	***z***	**U(eq)**
Fe1	5000	5000	10000	29.2(3)
S1	8154.4(14)	4914.0(15)	8147.6(19)	46.3(5)
O1	1484(3)	7159(3)	6798(4)	38.7(11)
O2A	-1088(18)	5284(12)	4857(15)	102(6)
O2A	-1088(18)	5284(12)	4857(15)	102(6)
O3	-1004(4)	6234(4)	2953(5)	55.4(14)
N1	6278(5)	4701(4)	9045(6)	40.0(14)
N2	5605(4)	6571(4)	10386(5)	30.9(12)
N3	4266(4)	5853(3)	8139(5)	31.3(12)
N4	3591(4)	5657(4)	7019(5)	34.5(13)
N5	3343(4)	6564(4)	6377(5)	30.7(12)
N6	889(4)	7364(4)	4473(5)	34.6(13)
C1	7076(5)	4797(4)	8688(6)	30.0(14)
C2	6319(5)	6866(5)	11436(6)	32.7(15)
C3	6664(5)	7866(5)	11606(7)	41.6(17)
C4	6226(5)	8584(5)	10651(7)	40.2(17)
C5	5476(5)	8286(5)	9556(7)	37.1(16)
C6	5186(5)	7273(4)	9423(6)	29.1(14)
C7	4452(5)	6868(4)	8253(6)	26.8(13)
C8	3858(5)	7323(5)	7119(6)	32.1(15)
C9	2549(5)	6636(5)	5155(6)	33.7(15)

Atom	*x*	*y*	*z*	U(eq)
C10	1585(5)	7089(4)	5572(6)	30.8(14)
C11	-82(5)	7819(5)	4629(7)	41.2(17)
C12A	-749(11)	7022(11)	5149(17)	42(3)
C12B	-1000(30)	7260(30)	5010(70)	42(3)
C13A	-1020(20)	6097(15)	4290(30)	53(3)
C13B	-1010(70)	6240(40)	4310(110)	53(3)
C14	-1141(7)	5313(6)	2108(8)	59(2)

Table.S16 *Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for* ***(2)****. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	34.9(8)	20.5(6)	33.5(7)	1.1(6)	9.9(6)	0.4(6)
S1	40.5(10)	50.9(11)	50.7(11)	0.1(9)	16.6(8)	2.1(9)
O1	49(3)	47(3)	22(2)	-1.6(19)	14(2)	2(2)
O2A	174(17)	80(9)	54(7)	19(5)	23(8)	-51(9)
O2A	174(17)	80(9)	54(7)	19(5)	23(8)	-51(9)
O3	78(4)	54(3)	35(3)	0(2)	10(3)	-7(3)
N1	50(4)	28(3)	46(3)	-7(2)	17(3)	-2(2)
N2	34(3)	28(3)	33(3)	0(2)	13(2)	-1(2)
N3	39(3)	20(3)	36(3)	2(2)	8(3)	0(2)
N4	36(3)	34(3)	33(3)	1(2)	7(3)	-1(2)
N5	32(3)	29(3)	33(3)	0(2)	12(2)	3(2)
N6	38(3)	38(3)	32(3)	2(2)	18(3)	3(2)
C1	45(4)	18(3)	29(3)	-1(2)	12(3)	1(3)
C2	36(4)	32(3)	31(4)	-1(3)	10(3)	2(3)
C3	40(4)	41(4)	46(4)	-7(3)	14(3)	-14(3)
C4	52(5)	28(3)	44(4)	-5(3)	17(4)	-10(3)
C5	53(5)	26(3)	35(4)	5(3)	16(3)	-6(3)
C6	37(4)	26(3)	31(3)	2(3)	21(3)	-2(3)
C7	30(4)	21(3)	33(3)	3(3)	15(3)	2(3)
C8	41(4)	25(3)	33(4)	1(3)	14(3)	2(3)
C9	41(4)	37(4)	24(3)	0(3)	11(3)	-1(3)
C10	37(4)	30(3)	26(3)	-1(3)	7(3)	2(3)
C11	33(4)	52(4)	34(4)	-4(3)	-7(3)	13(3)
C12A	18(6)	71(8)	39(6)	-11(5)	9(6)	23(5)
C12B	18(6)	71(8)	39(6)	-11(5)	9(6)	23(5)
C13A	44(5)	76(8)	42(5)	1(6)	16(4)	-22(7)
C13B	44(5)	76(8)	42(5)	1(6)	16(4)	-22(7)
C14	75(6)	54(5)	53(5)	-6(4)	23(4)	-21(4)

Table.S17 *Anisotropic Displacement Parameters (Å²×10³) for* ***(2)****. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.*

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	N1	2.100(6)	N5	C8	1.343(8)
Fe1	N1[1]	2.100(6)	N5	C9	1.440(8)
Fe1	N2	2.222(5)	N6	C10	1.329(8)
Fe1	N2[1]	2.222(5)	N6	C11	1.451(8)
Fe1	N3	2.193(5)	C2	C3	1.391(9)
Fe1	N3[1]	2.193(5)	C3	C4	1.374(9)
S1	C1	1.611(7)	C4	C5	1.376(9)
O1	C10	1.213(7)	C5	C6	1.385(8)
O3	C14	1.452(8)	C6	C7	1.456(8)
O3	C13A	1.31(3)	C7	C8	1.369(8)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	C13B	1.31(10)	C9	C10	1.526(9)
N1	C1	1.176(8)	C11	C12A	1.511(11)
N2	C2	1.319(8)	C11	C12B	1.53(2)
N2	C6	1.357(8)	O2A	C13A	1.209(19)
N3	N4	1.303(7)	C12A	C13A	1.476(14)
N3	C7	1.357(7)	O2B	C13B	1.20(2)
N4	N5	1.357(7)	C12B	C13B	1.49(2)

Table.S18 *Bond Lengths for compound* ***(2)****.* [1]*1-X,1-Y,2-Z*

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	Fe1	N1[1]	180.0	C10	N6	C11	122.5(5)
N1	Fe1	N2	87.22(19)	N1	C1	S1	178.1(6)
N1[1]	Fe1	N2	92.79(19)	N2	C2	C3	123.1(6)
N1[1]	Fe1	N2[1]	87.21(19)	C4	C3	C2	118.5(6)
N1	Fe1	N2[1]	92.78(19)	C3	C4	C5	118.9(6)
N1	Fe1	N3[1]	89.0(2)	C4	C5	C6	119.8(6)
N1[1]	Fe1	N3[1]	91.0(2)	N2	C6	C5	121.0(6)
N1	Fe1	N3	91.0(2)	N2	C6	C7	114.9(5)
N1[1]	Fe1	N3	89.0(2)	C5	C6	C7	124.1(6)
N2[1]	Fe1	N2	180.0	N3	C7	C6	120.6(5)
N3	Fe1	N2[1]	103.96(18)	N3	C7	C8	107.0(5)
N3	Fe1	N2	76.04(18)	C8	C7	C6	132.4(5)
N3[1]	Fe1	N2	103.96(18)	N5	C8	C7	105.7(5)
N3[1]	Fe1	N2[1]	76.04(18)	N5	C9	C10	109.9(5)
N3[1]	Fe1	N3	180.0	O1	C10	N6	125.1(6)
C13A	O3	C14	114.6(9)	O1	C10	C9	121.5(6)
C13B	O3	C14	123(2)	N6	C10	C9	113.3(5)
C1	N1	Fe1	160.8(5)	N6	C11	C12A	109.2(8)
C2	N2	Fe1	126.3(4)	N6	C11	C12B	126.0(19)
C2	N2	C6	118.6(5)	C13A	C12A	C11	119.0(12)
C6	N2	Fe1	115.1(4)	O3	C13A	C12A	113.2(15)
N4	N3	Fe1	136.0(4)	O2A	C13A	O3	125.5(18)
N4	N3	C7	110.6(5)	O2A	C13A	C12A	121(2)
C7	N3	Fe1	112.8(4)	C13B	C12B	C11	105(3)
N3	N4	N5	106.3(5)	O3	C13B	C12B	117(6)
N4	N5	C9	121.0(5)	O2B	C13B	O3	104(7)
C8	N5	N4	110.4(5)	O2B	C13B	C12B	121(6)
C8	N5	C9	128.2(5)				

Table.S19 *Bond angles for compound* ***(2)****.* [1]1-X,1-Y,2-Z

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Fe1	N2	C2	C3	179.6(5)	C3	C4	C5	C6	-0.8(10)
Fe1	N2	C6	C5	178.5(5)	C4	C5	C6	N2	2.3(10)
Fe1	N2	C6	C7	-3.3(6)	C4	C5	C6	C7	-175.7(6)
Fe1	N3	N4	N5	170.5(4)	C5	C6	C7	N3	174.8(6)
Fe1	N3	C7	C6	8.1(7)	C5	C6	C7	C8	-4.0(11)
Fe1	N3	C7	C8	-172.8(4)	C6	N2	C2	C3	0.1(9)
N2	C2	C3	C4	1.3(10)	C6	C7	C8	N5	179.0(6)
N2	C6	C7	N3	-3.3(8)	C7	N3	N4	N5	0.9(6)
N2	C6	C7	C8	177.8(6)	C8	N5	C9	C10	-68.9(8)
N3	N4	N5	C8	-0.9(6)	C9	N5	C8	C7	174.1(5)
N3	N4	N5	C9	-175.0(5)	C10	N6	C11	C12A	-70.8(10)
N3	C7	C8	N5	0.1(7)	C10	N6	C11	C12B	-76(3)

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
N4	N3	C7	C6	-179.7(5)	C11	N6	C10	O1	2.0(10)
N4	N3	C7	C8	-0.6(7)	C11	N6	C10	C9	-179.5(5)
N4	N5	C8	C7	0.5(7)	C11	C12A	C13A	O3	-26(3)
N4	N5	C9	C10	104.1(6)	C11	C12A	C13A	O2A	144.2(18)
N5	C9	C10	O1	-13.8(8)	C11	C12B	C13B	O3	-54(9)
N5	C9	C10	N6	167.6(5)	C11	C12B	C13B	O2B	176(9)
N6	C11	C12A	C13A	-59(2)	C14	O3	C13A	O2A	3(4)
N6	C11	C12B	C13B	-36(6)	C14	O3	C13A	C12A	172.9(15)
C2	N2	C6	C5	-1.9(9)	C14	O3	C13B	O2B	-35(9)
C2	N2	C6	C7	176.2(5)	C14	O3	C13B	C12B	-172(4)
C2	C3	C4	C5	-0.9(10)					

Table.S20 *Torsion Angles for* ***(2).***

Atom	*x*	*y*	*Z*	U(eq)
H6	1021.58	7265.64	3617.24	42
H2	6611.86	6372.99	12108.42	39
H3	7190.33	8047.72	12364.4	50
H4	6438.03	9275.02	10745.01	48
H5	5158.69	8772.99	8892.01	45
H8	3818.98	8028.19	6900.68	39
H9A	2396.19	5950.66	4744.14	40
H9B	2782.47	7071	4433.35	40
H11A	-426.49	8092.21	3709.66	49
H11B	35.89	8389.35	5310.37	49
H11C	-334	8169	3723.96	49
H11D	85.61	8362.12	5345.02	49
H14A	-548.52	4866.02	2378.25	89
H14B	-1205.95	5489.76	1106.96	89
H14C	-1761.94	4960.33	2268.73	89
H12A	-403.57	6803.23	6096.5	51
H12B	-1396.2	7356.56	5271.18	51
H12C	-933.08	7177.03	6048.21	51
H12D	-1644.21	7632.69	4663.09	51

Table.S21 *Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³)* ***(2).***

	(1)		**(2)**
T/K	**110**	**200**	**180**
Fe1-N1	1.981(5)	1.971(4)	2.100(6)
Fe1-N2	2.056(3)	2.045(3)	2.222(5)
Fe1-N3	2.055(3)	2.094(5)	2.193(5)
<d(Fe-N)>	2.0165(5)	2.1489 (5)	2.1720(6)
N1-Fe1-N2	88.04(13)	87.79(16)	87.21(19)
N1-Fe1-N3	89.74(14)	89.58(16)	89.0(2)
N2-Fe1-N3	79.15(14)	75.84(14)	76.03(18)
Σ <N-Fe-N>	52.2956	67.4108	70.8659
θ <N-Fe-N>	201.2079	262.0193	260.0641

Table S.22 *Fe–N Bond Distances (Å) and Distortion Parameters (∑ and Θ in deg) for (**1**) and (**2**)*

Compounds	Spin state	<Fe1-N-C>	d<Fe1-N> (Å)	Σ <N-Fe1-N>	Θ<N-Fe1-N>
$[Fe(FTP)_2(NCS)_2]CHCl_3$[3]	$T_{1/2}$ = 85 K, T_{LIESST} = 47 K	*167.60*	2.1571	75.29	265.39
$Fe(FTP)_2(NCSe)_2]CHCl_3$[3]	$T_{1/2}$ = 168 K, T_{LIESST} = 39 K	166.08	2.1577	72.13	261.60
$Fe(FTP)_2(NCSe)_2]CHCl_3$[3]		*172.45*	*1.9955*	*58.33*	*175.84*
$[Fe^{II}(FTP)_2(NCS)_2]$ [4]	*HS*	*145.70*	*2.1686*	*73.14*	*257.44*
$[Fe(tzpy\text{-}py)_2(NCSe)_2]$ [5]	$T_{1/2}$ = 250 K	*168.73*	*2.1458*	*72.40*	*259.48*
$[Fe(tzpy\text{-}py)_2(NCSe)_2]$ [5]	$T_{1/2}$ = 250 K	*171.20*	*1.9807*	*53.59*	*176.57*
$[Fe(tzpy)_2(NCS)_2]\cdot 2CHCl_3$[6]	incomplete HS ↔ LS	*178.89*	*2.1757*	*70.26*	*275.15*
$Fe(tzpy\text{-}py)_2(NCS)2]$ A[7]	$T_{1/2}$ = 150 K	*174.46*	*2.1652*	*74.84*	*271.78*
$Fe(tzpy\text{-}py)_2(NCS)_2]$ A[7]	$T_{1/2}$ = 150 K	*174.98*	*1.9762*	*51.99*	*171.67*
$Fe(tzpy\text{-}py)_2(NCS)_2]$ A'[7]	$T_{1/2}$ = 150 K	*177.53*	*2.1576*	*72.69*	*172.05*
$Fe(tzpy\text{-}py)_2(NCS)_2]$ B'[7]	$T_{1/2}$ = 110 K	*175.40*	*2.1548*	*76.91*	*267.03*

Table.S23 *Angle and bond length, theta and zeta for related compounds[3] (HS LS)*

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