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Pyridinium bis(pyridine- κN)tetrakis(thiocyanato- κN)ferrate(III)–pyrazine-2-carbonitrile–pyridine (1/4/1)

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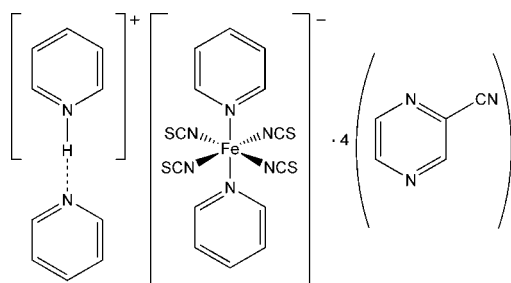
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Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.031; wR factor = 0.076; data-to-parameter ratio = 17.5.

In the title compound, $(\text{C}_5\text{H}_6\text{N})[\text{Fe}(\text{NCS})_4(\text{C}_5\text{H}_5\text{N})_2] \cdot 4\text{C}_5\text{H}_3\text{N}_3 \cdot \text{C}_5\text{H}_5\text{N}$, the Fe^{III} ion is located on an inversion centre and is six-coordinated by four N atoms of the thiocyanate ligands and two pyridine N atoms in a *trans* arrangement, forming a slightly distorted octahedral geometry. A half-occupied H atom attached to a pyridinium cation forms an $\text{N}-\text{H} \cdots \text{N}$ hydrogen bond with a centrosymmetrically-related pyridine unit. Four pyrazine-2-carbonitrile molecules crystallize per complex anion. In the crystal, $\pi-\pi$ stacking interactions are present [centroid-centroid distances = 3.6220 (9), 3.6930 (9), 3.5532 (9), 3.5803 (9) and 3.5458 (8) Å].

Related literature

For the use of molecular assemblies comprising cationic and anionic modules, see: Fritsky *et al.* (1998, 2004); Kanderl *et al.* (2005). For Fe^{II} -thiocyanate complexes with aromatic *N*-donor ligands indicating spin crossover, see: Gamez *et al.* (2009); Niel *et al.* (2001). For related structures, see: Moroz *et al.* (2010); Penkova *et al.* (2010); Petrusenko *et al.* (1997); Real *et al.* (1991).



Experimental

Crystal data

$(\text{C}_5\text{H}_6\text{N})[\text{Fe}(\text{NCS})_4(\text{C}_5\text{H}_5\text{N})_2] \cdot 4\text{C}_5\text{H}_3\text{N}_3 \cdot \text{C}_5\text{H}_5\text{N}$
 $M_r = 1025.99$
 Triclinic, $P\bar{1}$
 $a = 8.1766$ (2) Å
 $b = 11.9362$ (3) Å
 $c = 12.7519$ (3) Å
 $\alpha = 102.982$ (1)°
 $\beta = 97.799$ (1)°
 $\gamma = 97.684$ (1)°
 $V = 1184.02$ (5) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.55$ mm⁻¹
 $T = 120$ K
 $0.38 \times 0.19 \times 0.17$ mm

Data collection

Bruker Kappa APEXII DUO CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.818$, $T_{\text{max}} = 0.910$
 18588 measured reflections
 5482 independent reflections
 4470 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.076$
 $S = 1.01$
 5482 reflections
 313 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N4}-\text{H4N} \cdots \text{N4}^i$	0.88	1.80	2.677 (3)	179

Symmetry code: (i) $-x + 2, -y + 1, -z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2622).

References

- Brandenburg, K. (1997). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Fritsky, I. O., Kozłowski, H., Sadler, P. J., Yefetova, O. P., Świątek-Kozłowska, J., Kalibabchuk, V. A. & Głowiak, T. (1998). *J. Chem. Soc. Dalton Trans.* pp. 3269–3274.
 Fritsky, I. O., Świątek-Kozłowska, J., Dobosz, A., Sliva, T. Y. & Dudarenko, N. M. (2004). *Inorg. Chim. Acta*, **357**, 3746–3752.
 Gamez, P., Costa, J. S., Quesada, M. & Aromi, G. (2009). *Dalton Trans.* pp. 7845–7853.
 Kanderl, O. M., Kozłowski, H., Dobosz, A., Świątek-Kozłowska, J., Meyer, F. & Fritsky, I. O. (2005). *Dalton Trans.* pp. 1428–1437.
 Moroz, Y. S., Szyrweil, L., Demeshko, S., Kozłowski, H., Meyer, F. & Fritsky, I. O. (2010). *Inorg. Chem.* **49**, 4750–4752.
 Niel, V., Martínez-Agudo, J. M., Muñoz, M. C., Gaspar, A. B. & Real, J. A. (2001). *Inorg. Chem.* **40**, 3838–3839.
 Penkova, L., Demeshko, S., Pavlenko, V. A., Dechert, S., Meyer, F. & Fritsky, I. O. (2010). *Inorg. Chim. Acta*, **363**, 3036–3040.
 Petrusenko, S. R., Kokozay, V. N. & Fritsky, I. O. (1997). *Polyhedron*, **16**, 267–274.
 Real, J. A., Munno, G., Muñoz, M. C. & Julve, M. (1991). *Inorg. Chem.* **30**, 2701–2704.
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

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Pyridinium bis(pyridine- κ N)tetrakis(thiocyanato- κ N)ferrate(III)–pyrazine-2-carbonitrile–pyridine (1/4/1)

Sergii I. Shylin, Il'ya A. Gural'skiy, Matti Haukka and Irina A. Golenya

S1. Comment

Molecular assemblies comprising from cationic and anionic modules are of special interest for crystal engineering and molecular magnetism (Fritsky *et al.*, 2004). Formation of such compounds often can be mediated by different types of intermolecular interactions, such as co-ordination and hydrogen bonds, ionic and van der Waals interactions (Fritsky *et al.*, 1998; Kanderl *et al.*, 2005). Such assemblies may possess interesting functional properties and, in particular, indicate spin crossover behavior. In this regard, Fe^{II} thiocyanate complexes with aromatic N-donor ligands attract much attention considering the possible metal ion spin state modulation by variation of a ligand (Gamez *et al.*, 2009) accompanied by coordination polymer formation. Particularly, as one of the simplest bridging N-donor ligands to design coordination polymers, pyrazine (pz) is known for the construction of spin crossover Hofmann-like clathrates with general formula $[\text{Fe}^{\text{II}}\text{M}^{\text{II}}(\text{pz})(\text{CN})_4]_{\infty}$ ($M = \text{Ni}, \text{Pd}$ or Pt) (Niel *et al.*, 2001). A combination of pz and thiocyanate ligands leads to the formation of two-dimensional coordination polymer $[\text{Fe}(\text{NCS})_2(\text{pz})_2]$ with an antiferromagnetic exchange between metal centres (Real *et al.*, 1991). In this context, we attempted to synthesize Fe^{II} thiocyanate complex with pyrazine-2-carbonitrile (cnpz). However, the reaction of $[\text{Fe}^{\text{II}}(\text{NCS})_2(\text{py})_4]$ (py = pyridine) and cnpz in an organic media in air led to oxidation of Fe^{II} and to the formation of the title compound.

The compound consists of one complex anion $[\text{Fe}(\text{NCS})_4(\text{py})_2]$, one pyridinium cation, one pyridine and four pyrazine-2-carbonitrile molecules (Fig. 1). The Fe^{III} ion is located on an inversion centre and is sixfold coordinated by four N atoms of four thiocyanate anions and two N atoms of two pyridine ligands in a *trans* arrangement, forming a slightly distorted octahedral coordination geometry. The thiocyanate ligands are bound through N atoms and are quasi-linear [$\text{S1—C1—N2} = 179.41$ (14), $\text{S2—C9—N3} = 179.33$ (15) $^\circ$], while the Fe—NCS linkages are bent [$\text{Fe1—N2—C1} = 163.20$ (12), $\text{Fe1—N3—C9} = 167.56$ (12) $^\circ$]. These structural features are typical for the complexes where the NCS group is N-bound (Petrusenko *et al.*, 1997). The distances between Fe^{III} ion and N atoms of the thiocyanate anions [$\text{Fe1—N2} = 2.0424$ (13), $\text{Fe1—N3} = 2.0370$ (13) Å] are considerably shorter than those between Fe^{III} and N atoms of the pyridine ligands [$\text{Fe1—N1} = 2.1320$ (12) Å], that could be related to the higher affinity of the metal ion to negatively charged thiocyanate comparing with the neutral organic ligand. The C—N and C—C bond lengths in the coordinated pyridine ligands are normal and close to the values observed in the related structures (Moroz *et al.*, 2010; Penkova *et al.*, 2010).

In the title compound there are four solvent molecules of pyrazine-2-carbonitrile per each Fe^{III} ion that interact with one another through π – π stacking, with distances between the centroids of 3.5532 (9), 3.5803 (9) and 3.5458 (8) Å (Fig. 2). One of the uncoordinated pyridines is protonated and the N-bound H atom is disordered between two equally populated positions, forming N—H \cdots N hydrogen bonds (Table 1). Coordinated and solvent pyridine molecules also interact with one another *via* π – π contacts, with distances between the centroids of 3.6220 (9) and 3.6930 (9) Å (Fig. 3).

S2. Experimental

Crystals of the title compound were obtained by adding pyrazine-2-carbonitrile (52.5 mg, 0.5 mmol) to tetrakis(pyridine)-bis(isothiocyanato)iron(II), $[\text{Fe}(\text{NCS})_2(\text{py})_4]$, (48.8 mg, 0.1 mmol) in acetone (5 ml). The solution was left to evaporate in air. In one day this yielded red crystals that were collected, washed with water and dried in air (yield: 21 mg, 20%).

S3. Refinement

H atoms were positioned geometrically and refined as riding atoms, with $\text{C}-\text{H} = 0.95$ and $\text{N}-\text{H} = 0.88$ Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C},\text{N})$. N-bound H atom of the uncoordinated pyridine is half-occupied due to the requirement of symmetry.

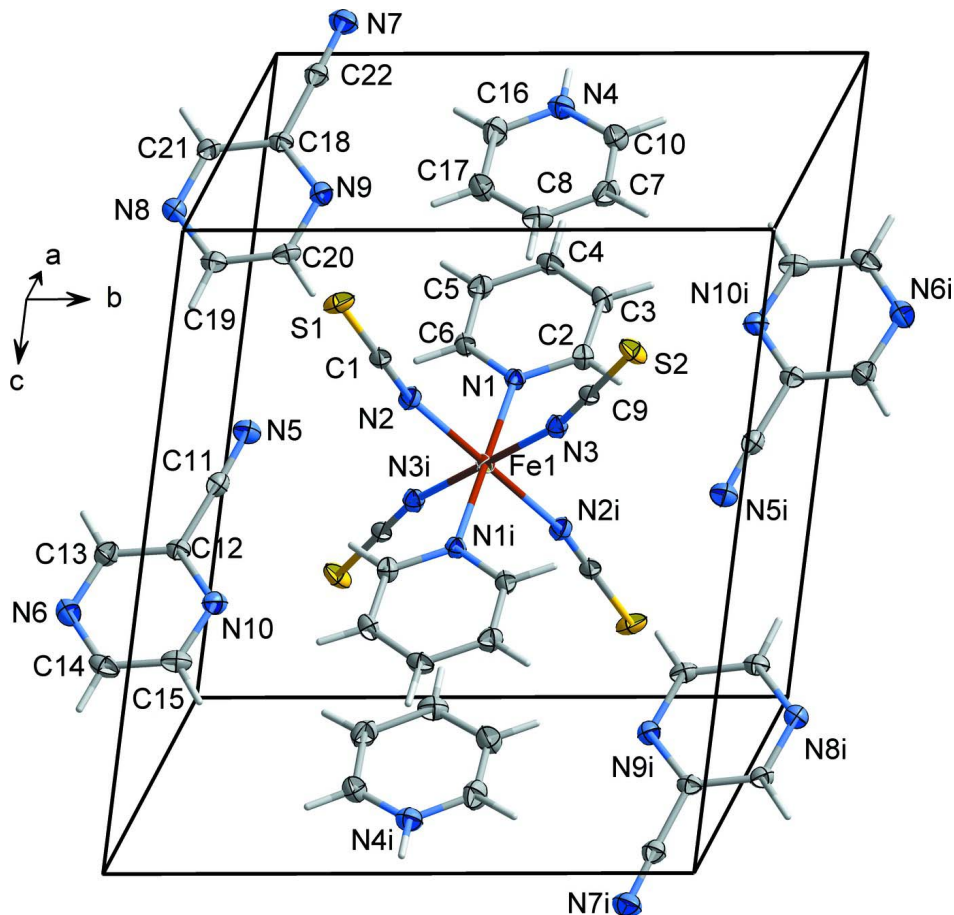
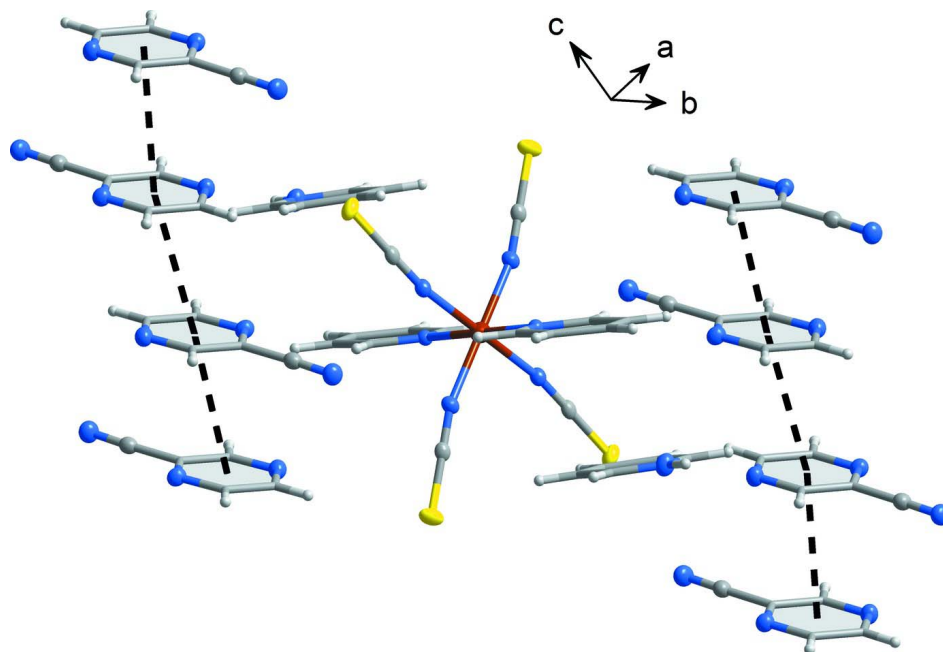
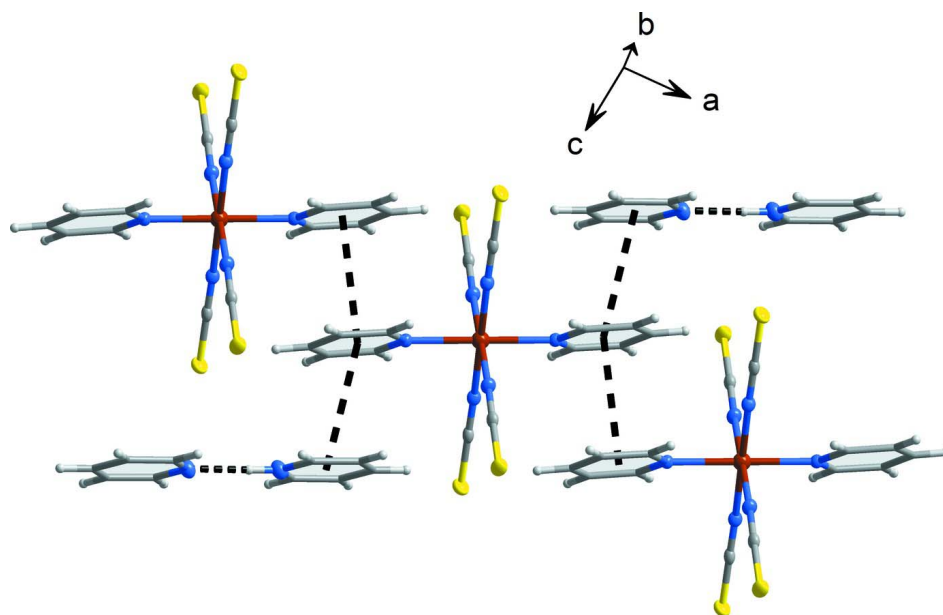


Figure 1

Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x+1, -y+1, -z+1$.]

**Figure 2**

Crystal structure of the title compound, showing π - π contacts between the cnpz molecules as dashed lines (carmine: Fe, yellow: S, blue: N, grey: C, light-grey: H).

**Figure 3**

Crystal structure of the title compound, showing hydrogen bonds and π - π contacts between the pyridine molecules as dashed lines (carmine: Fe, yellow: S, blue: N, grey: C, light-grey: H).

Pyridinium bis(pyridine- κ N)tetrakis(thiocyanato- κ N)ferrate(III)–pyrazine-2-carbonitrile–pyridine (1/4/1)

Crystal data

 $(C_5H_6N)[Fe(NCS)_4(C_5H_5N)_2] \cdot 4C_5H_3N_3 \cdot C_5H_5N$ $M_r = 1025.99$ Triclinic, $P\bar{1}$

Hall symbol: -P 1

 $a = 8.1766$ (2) Å $b = 11.9362$ (3) Å $c = 12.7519$ (3) Å $\alpha = 102.982$ (1)° $\beta = 97.799$ (1)° $\gamma = 97.684$ (1)° $V = 1184.02$ (5) Å³ $Z = 1$ $F(000) = 527$ $D_x = 1.439$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7810 reflections

 $\theta = 2.6$ – 27.6 ° $\mu = 0.55$ mm⁻¹ $T = 120$ K

Block, red

 $0.38 \times 0.19 \times 0.17$ mm

Data collection

Bruker Kappa APEXII DUO CCD
diffractometer

Radiation source: fine-focus sealed tube

Curved graphite crystal monochromator

Detector resolution: 16 pixels mm⁻¹ φ and ω scans with κ offsetAbsorption correction: multi-scan
(SADABS; Sheldrick, 1996) $T_{\min} = 0.818$, $T_{\max} = 0.910$

18588 measured reflections

5482 independent reflections

4470 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.024$ $\theta_{\max} = 27.7$ °, $\theta_{\min} = 1.7$ ° $h = -10 \rightarrow 10$ $k = -15 \rightarrow 15$ $l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.031$ $wR(F^2) = 0.076$ $S = 1.01$

5482 reflections

313 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.3715P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.33$ e Å⁻³ $\Delta\rho_{\min} = -0.37$ e Å⁻³

Special details

Experimental. Hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.95 Å, N—H = 0.88 Å, and $U_{\text{iso}} = 1.2 U_{\text{eq}}(\text{parent atom})$. The highest peak is located 0.70 Å from atom C18 and the deepest hole is located 0.48 Å from atom Fe1.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Fe1	0.5000	0.5000	0.5000	0.01474 (8)	
S1	0.18557 (5)	0.25687 (4)	0.16391 (3)	0.02717 (11)	
S2	0.31797 (5)	0.74869 (4)	0.27623 (4)	0.02695 (11)	
N1	0.72282 (15)	0.50545 (11)	0.43036 (10)	0.0163 (3)	
N2	0.38008 (16)	0.37328 (11)	0.36553 (11)	0.0200 (3)	
N3	0.42809 (15)	0.62208 (11)	0.42297 (11)	0.0193 (3)	
N4	0.86353 (18)	0.50989 (12)	0.04639 (11)	0.0279 (3)	
H4N	0.9528	0.5042	0.0153	0.033*	0.50
N5	0.40216 (18)	0.10177 (12)	0.42369 (12)	0.0278 (3)	
N6	0.09833 (17)	-0.12537 (12)	0.62053 (11)	0.0271 (3)	
N7	0.90967 (18)	0.11755 (13)	-0.07429 (12)	0.0302 (3)	
N8	0.59044 (17)	-0.09046 (12)	0.13024 (11)	0.0237 (3)	
N9	0.67103 (17)	0.14539 (11)	0.12764 (11)	0.0220 (3)	
N10	0.15882 (17)	0.11284 (12)	0.62270 (11)	0.0224 (3)	
C1	0.29957 (18)	0.32456 (13)	0.28113 (12)	0.0173 (3)	
C2	0.80428 (18)	0.60594 (13)	0.41827 (12)	0.0193 (3)	
H2	0.7656	0.6766	0.4459	0.023*	
C3	0.94253 (19)	0.60979 (14)	0.36697 (13)	0.0213 (3)	
H3	0.9981	0.6821	0.3597	0.026*	
C4	0.99889 (19)	0.50744 (14)	0.32645 (13)	0.0214 (3)	
H4	1.0925	0.5080	0.2897	0.026*	
C5	0.9167 (2)	0.40386 (14)	0.34019 (13)	0.0225 (3)	
H5	0.9541	0.3323	0.3142	0.027*	
C6	0.77991 (19)	0.40658 (13)	0.39215 (12)	0.0197 (3)	
H6	0.7235	0.3354	0.4014	0.024*	
C7	0.6803 (2)	0.62600 (15)	0.12971 (14)	0.0297 (4)	
H7	0.6508	0.7007	0.1539	0.036*	
C8	0.5837 (2)	0.52690 (15)	0.14229 (13)	0.0271 (4)	
H8	0.4869	0.5328	0.1754	0.032*	
C9	0.38283 (18)	0.67553 (13)	0.36185 (12)	0.0176 (3)	
C10	0.8197 (2)	0.61399 (15)	0.08152 (14)	0.0283 (4)	
H10	0.8867	0.6817	0.0730	0.034*	
C11	0.32510 (19)	0.07281 (13)	0.48410 (13)	0.0204 (3)	
C12	0.22339 (18)	0.03216 (13)	0.55739 (12)	0.0183 (3)	
C13	0.1944 (2)	-0.08487 (14)	0.55571 (13)	0.0238 (3)	
H13	0.2437	-0.1378	0.5074	0.029*	
C14	0.0340 (2)	-0.04577 (15)	0.68615 (13)	0.0255 (4)	
H14	-0.0350	-0.0704	0.7338	0.031*	
C15	0.0642 (2)	0.07162 (15)	0.68746 (13)	0.0252 (4)	
H15	0.0157	0.1246	0.7363	0.030*	
C16	0.7703 (2)	0.41443 (15)	0.05894 (15)	0.0309 (4)	
H16	0.8024	0.3407	0.0344	0.037*	
C17	0.6293 (2)	0.42005 (15)	0.10637 (14)	0.0292 (4)	
H17	0.5645	0.3511	0.1142	0.035*	
C18	0.72593 (18)	0.05927 (13)	0.06193 (12)	0.0182 (3)	

C19	0.53568 (19)	-0.00576 (14)	0.19602 (12)	0.0209 (3)
H19	0.4667	-0.0256	0.2456	0.025*
C20	0.5757 (2)	0.11054 (14)	0.19485 (12)	0.0221 (3)
H20	0.5334	0.1675	0.2439	0.026*
C21	0.68690 (19)	-0.05677 (14)	0.06260 (12)	0.0211 (3)
H21	0.7296	-0.1138	0.0139	0.025*
C22	0.82945 (19)	0.09294 (14)	-0.01369 (13)	0.0219 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.01377 (15)	0.01447 (15)	0.01549 (15)	0.00130 (11)	0.00307 (11)	0.00305 (12)
S1	0.0231 (2)	0.0345 (2)	0.0178 (2)	0.00335 (17)	0.00294 (16)	-0.00485 (17)
S2	0.0290 (2)	0.0289 (2)	0.0305 (2)	0.00821 (18)	0.00977 (18)	0.01836 (18)
N1	0.0150 (6)	0.0167 (6)	0.0168 (6)	0.0016 (5)	0.0026 (5)	0.0042 (5)
N2	0.0187 (6)	0.0182 (7)	0.0213 (7)	0.0017 (5)	0.0032 (5)	0.0018 (5)
N3	0.0177 (6)	0.0178 (7)	0.0224 (7)	0.0020 (5)	0.0045 (5)	0.0050 (5)
N4	0.0315 (8)	0.0282 (8)	0.0275 (8)	0.0064 (6)	0.0127 (6)	0.0086 (6)
N5	0.0284 (8)	0.0291 (8)	0.0268 (7)	0.0039 (6)	0.0103 (6)	0.0062 (6)
N6	0.0268 (8)	0.0264 (8)	0.0279 (8)	-0.0001 (6)	0.0022 (6)	0.0108 (6)
N7	0.0279 (8)	0.0364 (9)	0.0255 (7)	-0.0008 (6)	0.0082 (6)	0.0076 (6)
N8	0.0275 (7)	0.0216 (7)	0.0223 (7)	0.0020 (6)	0.0076 (6)	0.0054 (6)
N9	0.0244 (7)	0.0212 (7)	0.0212 (7)	0.0048 (5)	0.0052 (6)	0.0054 (6)
N10	0.0244 (7)	0.0238 (7)	0.0204 (7)	0.0061 (6)	0.0061 (5)	0.0059 (6)
C1	0.0160 (7)	0.0161 (7)	0.0215 (8)	0.0043 (6)	0.0085 (6)	0.0041 (6)
C2	0.0181 (8)	0.0165 (7)	0.0228 (8)	0.0018 (6)	0.0025 (6)	0.0048 (6)
C3	0.0174 (8)	0.0209 (8)	0.0259 (8)	-0.0004 (6)	0.0037 (6)	0.0083 (7)
C4	0.0145 (7)	0.0285 (9)	0.0223 (8)	0.0026 (6)	0.0059 (6)	0.0076 (7)
C5	0.0210 (8)	0.0217 (8)	0.0257 (8)	0.0070 (6)	0.0064 (7)	0.0045 (7)
C6	0.0206 (8)	0.0166 (8)	0.0219 (8)	0.0018 (6)	0.0045 (6)	0.0054 (6)
C7	0.0383 (10)	0.0239 (9)	0.0268 (9)	0.0102 (8)	0.0048 (8)	0.0038 (7)
C8	0.0264 (9)	0.0330 (10)	0.0236 (8)	0.0089 (7)	0.0064 (7)	0.0073 (7)
C9	0.0144 (7)	0.0164 (7)	0.0219 (8)	0.0011 (6)	0.0081 (6)	0.0023 (6)
C10	0.0363 (10)	0.0226 (9)	0.0265 (9)	0.0023 (7)	0.0065 (7)	0.0081 (7)
C11	0.0201 (8)	0.0194 (8)	0.0204 (8)	0.0036 (6)	0.0017 (6)	0.0029 (6)
C12	0.0158 (7)	0.0227 (8)	0.0158 (7)	0.0024 (6)	0.0007 (6)	0.0054 (6)
C13	0.0231 (8)	0.0232 (8)	0.0238 (8)	0.0032 (7)	0.0029 (7)	0.0042 (7)
C14	0.0191 (8)	0.0380 (10)	0.0202 (8)	0.0004 (7)	0.0017 (6)	0.0124 (7)
C15	0.0238 (8)	0.0337 (10)	0.0202 (8)	0.0080 (7)	0.0072 (7)	0.0073 (7)
C16	0.0364 (10)	0.0219 (9)	0.0371 (10)	0.0087 (7)	0.0108 (8)	0.0081 (8)
C17	0.0307 (9)	0.0255 (9)	0.0337 (10)	0.0032 (7)	0.0079 (8)	0.0119 (8)
C18	0.0153 (7)	0.0238 (8)	0.0149 (7)	0.0019 (6)	0.0016 (6)	0.0049 (6)
C19	0.0179 (8)	0.0277 (9)	0.0168 (7)	0.0021 (6)	0.0038 (6)	0.0055 (6)
C20	0.0228 (8)	0.0263 (9)	0.0178 (8)	0.0085 (7)	0.0056 (6)	0.0028 (6)
C21	0.0231 (8)	0.0211 (8)	0.0187 (8)	0.0045 (6)	0.0056 (6)	0.0021 (6)
C22	0.0207 (8)	0.0235 (8)	0.0197 (8)	0.0014 (6)	0.0025 (6)	0.0039 (6)

Geometric parameters (Å, °)

Fe1—N3	2.0370 (13)	C6—H6	0.9500
Fe1—N2	2.0424 (13)	C7—C10	1.375 (2)
Fe1—N1	2.1320 (12)	C7—C8	1.385 (2)
S1—C1	1.6229 (16)	C7—H7	0.9500
S2—C9	1.6220 (16)	C8—C17	1.374 (2)
N1—C6	1.3412 (19)	C8—H8	0.9500
N1—C2	1.3430 (19)	C10—H10	0.9500
N2—C1	1.164 (2)	C11—C12	1.452 (2)
N3—C9	1.166 (2)	C12—N10	1.340 (2)
N4—C10	1.336 (2)	C12—C13	1.380 (2)
N4—C16	1.337 (2)	C13—H13	0.9500
N4—H4N	0.8800	C14—C15	1.386 (2)
N5—C11	1.142 (2)	C14—H14	0.9500
N6—C14	1.332 (2)	C15—N10	1.333 (2)
N6—C13	1.337 (2)	C15—H15	0.9500
N7—C22	1.141 (2)	C16—C17	1.375 (2)
N8—C19	1.330 (2)	C16—H16	0.9500
N8—C21	1.3355 (19)	C17—H17	0.9500
C2—C3	1.381 (2)	C18—N9	1.3411 (19)
C2—H2	0.9500	C19—C20	1.387 (2)
C3—C4	1.380 (2)	C19—H19	0.9500
C3—H3	0.9500	C20—N9	1.331 (2)
C4—C5	1.385 (2)	C20—H20	0.9500
C4—H4	0.9500	C21—C18	1.381 (2)
C5—C6	1.376 (2)	C21—H21	0.9500
C5—H5	0.9500	C22—C18	1.453 (2)
N3 ⁱ —Fe1—N3	179.999 (1)	N1—C6—H6	118.6
N3 ⁱ —Fe1—N2 ⁱ	88.77 (5)	C5—C6—H6	118.6
N3—Fe1—N2 ⁱ	91.23 (5)	C10—C7—C8	118.63 (16)
N3 ⁱ —Fe1—N2	91.23 (5)	C10—C7—H7	120.7
N3—Fe1—N2	88.77 (5)	C8—C7—H7	120.7
N2 ⁱ —Fe1—N2	180.0	C17—C8—C7	119.32 (16)
N3 ⁱ —Fe1—N1	90.30 (5)	C17—C8—H8	120.3
N3—Fe1—N1	89.70 (5)	C7—C8—H8	120.3
N2 ⁱ —Fe1—N1	90.58 (5)	N3—C9—S2	179.33 (15)
N2—Fe1—N1	89.42 (5)	N4—C10—C7	121.91 (16)
N3 ⁱ —Fe1—N1 ⁱ	89.70 (5)	N4—C10—H10	119.0
N3—Fe1—N1 ⁱ	90.30 (5)	C7—C10—H10	119.0
N2 ⁱ —Fe1—N1 ⁱ	89.42 (5)	N5—C11—C12	177.71 (17)
N2—Fe1—N1 ⁱ	90.58 (5)	N10—C12—C13	123.29 (14)
N1—Fe1—N1 ⁱ	180.0	N10—C12—C11	116.65 (14)
C6—N1—C2	118.34 (13)	C13—C12—C11	120.04 (14)
C6—N1—Fe1	120.20 (10)	N6—C13—C12	121.47 (15)
C2—N1—Fe1	121.37 (10)	N6—C13—H13	119.3
C1—N2—Fe1	163.20 (12)	C12—C13—H13	119.3

C9—N3—Fe1	167.56 (12)	N6—C14—C15	122.38 (15)
C10—N4—C16	119.32 (15)	N6—C14—H14	118.8
C10—N4—H4N	120.3	C15—C14—H14	118.8
C16—N4—H4N	120.3	N10—C15—C14	122.39 (15)
C14—N6—C13	115.74 (14)	N10—C15—H15	118.8
C19—N8—C21	115.86 (14)	C14—C15—H15	118.8
N2—C1—S1	179.41 (14)	C15—N10—C12	114.73 (14)
N7—C22—C18	178.82 (18)	N4—C16—C17	121.84 (16)
N8—C21—C18	121.37 (14)	N4—C16—H16	119.1
N8—C21—H21	119.3	C17—C16—H16	119.1
C18—C21—H21	119.3	C8—C17—C16	118.98 (16)
N1—C2—C3	122.04 (14)	C8—C17—H17	120.5
N1—C2—H2	119.0	C16—C17—H17	120.5
C3—C2—H2	119.0	N9—C18—C21	123.30 (14)
C4—C3—C2	119.23 (14)	N9—C18—C22	116.67 (14)
C4—C3—H3	120.4	C21—C18—C22	120.03 (14)
C2—C3—H3	120.4	N8—C19—C20	122.36 (14)
C3—C4—C5	118.89 (14)	N8—C19—H19	118.8
C3—C4—H4	120.6	C20—C19—H19	118.8
C5—C4—H4	120.6	N9—C20—C19	122.46 (14)
C6—C5—C4	118.72 (15)	N9—C20—H20	118.8
C6—C5—H5	120.6	C19—C20—H20	118.8
C4—C5—H5	120.6	C20—N9—C18	114.64 (13)
N1—C6—C5	122.77 (14)		

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H4N \cdots N4 ⁱⁱ	0.88	1.80	2.677 (3)	179

Symmetry code: (ii) $-x+2, -y+1, -z$.