

catena-Poly[(*E*)-4,4'-(ethane-1,2-diyl)-dipyridinium [[bis(thiocyanato- κ N)-ferrate(II)]-di- μ -thiocyanato- κ^2 N:S; κ^2 S:N]]

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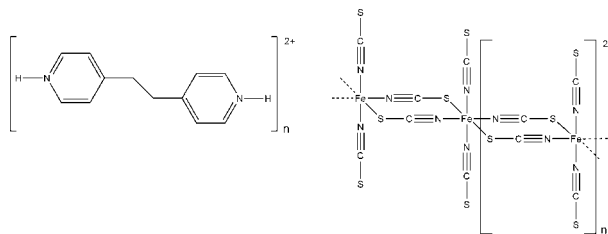
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.026; wR factor = 0.063; data-to-parameter ratio = 16.9.

In the crystal structure of the title compound, $\{(\text{C}_{12}\text{H}_{14}\text{N}_2)[\text{Fe}(\text{NCS})_4]\}_n$, the iron(II) cation is coordinated by four *N*-bonded and two *S*-bonded thiocyanate anions in a distorted octahedral coordination mode. The asymmetric unit consists of half an iron(II) cation and half a protonated (*E*)-4,4'-(ethane-1,2-diyl)dipyridinium dication, each located on a centre of inversion. In addition, there are two thiocyanate anions in general positions. The crystal structure consists of $\text{Fe}-(\text{NCS})_2-\text{Fe}$ chains in which each iron(II) cation is additionally coordinated by two terminal *N*-bonded thiocyanate anions. Non-coordinating dipyridinium dications are present between the thiocyanatoferrate(II) chains and are connected to the anions *via* $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen-bond interactions.

Related literature

For coordination polymers based on transition metal thio- and selenocyanates, see: Wöhlert *et al.* (2011); Boeckmann *et al.* (2010). For a similar structure, see: Wöhlert *et al.* (2010).



Experimental

Crystal data

$(\text{C}_{12}\text{H}_{14}\text{N}_2)[\text{Fe}(\text{NCS})_4]$
 $M_r = 474.42$
 Triclinic, $P\bar{1}$
 $a = 5.6818$ (3) Å

$b = 9.0957$ (6) Å
 $c = 10.9259$ (7) Å
 $\alpha = 105.586$ (5)°
 $\beta = 103.633$ (5)°

$\gamma = 101.383$ (5)°
 $V = 507.65$ (5) Å³
 $Z = 1$
 Mo $K\alpha$ radiation

$\mu = 1.17$ mm⁻¹
 $T = 293$ K
 $0.19 \times 0.15 \times 0.09$ mm

Data collection

Stoe IPDS-2 diffractometer
 Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2008)
 $T_{\min} = 0.806$, $T_{\max} = 0.899$

7638 measured reflections
 2101 independent reflections
 1838 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.063$
 $S = 1.03$
 2101 reflections

124 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.26$ e Å⁻³
 $\Delta\rho_{\min} = -0.40$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Fe1—N1	2.1011 (15)	Fe1—S2 ⁱ	2.6729 (5)
Fe1—N2	2.1376 (14)		
N1 ⁱⁱ —Fe1—N1	180	N2 ⁱⁱⁱ —Fe1—S2 ⁱⁱⁱ	86.73 (4)
N1 ⁱⁱ —Fe1—N2	88.06 (6)	N1—Fe1—S2 ⁱ	86.79 (4)
N1—Fe1—N2	91.94 (6)		

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N10—H10A \cdots N1	0.86	2.34	3.029 (2)	137
N10—H10A \cdots S2 ⁱ	0.86	2.73	3.4369 (15)	141

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

Data collection: *X-AREA* (Stoe & Cie, 2008); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *XCIF* in *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5657).

References

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 Wöhlert, S., Boeckmann, J., Wriedt, M. & Näther, C. (2011). *Angew. Chem. Int. Ed.* **50**, 6920–6923.
 Wöhlert, S., Wriedt, M., Jess, I. & Näther, C. (2010). *Acta Cryst.* **E66**, m1256.

supplementary materials

Acta Cryst. (2011). E67, m1503 [doi:10.1107/S1600536811039924]

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S. Wöhlert, I. Jess and C. Näther

Comment

In our current work, we are interested in the structure and properties of new coordination polymers based on transition metal thio- and selenocyanates (Wöhlert *et al.*, 2011; Boeckmann, Wriedt & Näther, 2010). In our ongoing investigation in this field we have reacted iron(II) sulfate heptahydrate, potassium thiocyanate and E-1,2-bis(4-pyridyl)-ethane in water. In this reaction red single crystals of the title compound were obtained, which were identified by single crystal X-ray diffraction.

The title compound of composition $[\text{Fe}(\text{NCS})_4]_n\text{-E-1,2-bis(4-pyridinium)-ethane}$ (Fig. 1) represents an 1-D coordination polymer, in which each iron(II) cation is connected by four μ -1,3 bridging thiocyanato anions into chains that elongate in the direction of the crystallographic *a* axis (Fig. 2). Between these chains noncoordinating protonated E-1,2-bis(4-pyridinium)-ethane ligands are found, that are linked to the anions by weak hydrogen bonding interactions (Table 1). The FeN_4S_2 octahedron is slightly distorted with two long Fe—SCN distances of 2.6729 (5) Å and short Fe—NCS distances of 2.1011 (15) and 2.1376 (14) Å. The angles around the metal cations range from 86.73 (5) to 93.27 (4) and 180° (Tab. 1). The shortest intramolecular Fe \cdots Fe distance amounts to 5.6818 (3) Å and the shortest intermolecular Fe \cdots Fe distance amounts to 9.0957 (6) Å. It must be noted that the structure is very similar but not isotypic to that of iron(II) thiocyanate and E-1,2-bis(4-pyridinium)-ethylene reported recently (Wöhlert *et al.*, 2010).

Experimental

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1,2-bis(4-pyridyl)-ethane were obtained from Sigma Aldrich. KNCS are obtained from Alfa Aesar. 0.6 mmol (168.0 mg) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 1.2 mmol (117.7 mg) KNCS and 0.15 mmol (27.2 mg) 1,2-bis(4-pyridyl)-ethane were reacted with 1 mL H_2O in closed test-tube at 120°C for three days. On cooling red block-shaped single crystals of the title compound were obtained in a mixture with a second crystalline phase that was not yet identified.

Refinement

All H atoms were located in difference map but were positioned with idealized geometry and were refined using a riding model with $U_{\text{eq}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C,N})$ with C—H = 0.93 Å and N—H = 0.86 Å.

Figures

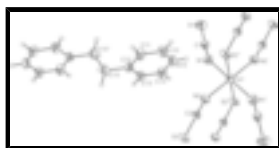


Fig. 1. Crystal structure of the title compound with labelling and displacement ellipsoids drawn at the 30% probability level. Symmetry code: i = -x + 1, -y + 1, -z + 1; ii = -x, -y + 1, -z + 1; iii = x+1, y, z; iv = -x, -y + 2, -z.

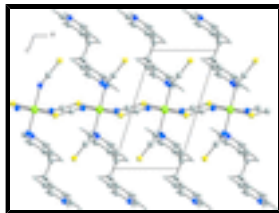


Fig. 2. : Crystal structure of the title compound viewed along the crystallographic *b* axis.

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Crystal data

(C₁₂H₁₄N₂)[Fe(NCS)₄]

M_r = 474.42

Triclinic, *P* $\bar{1}$

Hall symbol: -P 1

a = 5.6818 (3) Å

b = 9.0957 (6) Å

c = 10.9259 (7) Å

α = 105.586 (5)°

β = 103.633 (5)°

γ = 101.383 (5)°

V = 507.65 (5) Å³

Z = 1

F(000) = 242

D_x = 1.552 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 7638 reflections

θ = 2.0–26.5°

μ = 1.17 mm⁻¹

T = 293 K

Block, red

0.19 × 0.15 × 0.09 mm

Data collection

Stoe IPDS-2
diffractometer

Radiation source: fine-focus sealed tube
graphite

ω scans

Absorption correction: numerical
(*X-SHAPE* and *X-RED32*; Stoe & Cie, 2008)

T_{min} = 0.806, *T_{max}* = 0.899

7638 measured reflections

2101 independent reflections

1838 reflections with *I* > 2σ(*I*)

R_{int} = 0.030

θ_{\max} = 26.5°, θ_{\min} = 2.0°

h = -7→6

k = -11→11

l = -13→13

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.026

wR (*F*²) = 0.063

S = 1.03

2101 reflections

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0393*P*)² + 0.0464*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δσ)_{max} < 0.001

124 parameters

$$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$$

0 restraints

$$\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.5000	0.5000	0.5000	0.02833 (10)
N1	0.4723 (3)	0.45516 (18)	0.29744 (15)	0.0398 (3)
C1	0.5464 (3)	0.40682 (18)	0.20845 (16)	0.0311 (3)
S1	0.64953 (10)	0.33771 (7)	0.08533 (5)	0.04980 (14)
N2	0.2339 (3)	0.63622 (17)	0.48892 (15)	0.0356 (3)
C2	0.0753 (3)	0.69028 (18)	0.51257 (15)	0.0283 (3)
S2	-0.14718 (8)	0.76903 (5)	0.54918 (5)	0.03592 (12)
N10	0.4056 (3)	0.77059 (17)	0.27628 (15)	0.0384 (3)
H10A	0.4891	0.7200	0.3178	0.046*
C10	0.5213 (3)	0.9178 (2)	0.28629 (19)	0.0413 (4)
H10	0.6894	0.9642	0.3374	0.050*
C11	0.3919 (4)	1.0005 (2)	0.22104 (18)	0.0399 (4)
H11	0.4724	1.1029	0.2273	0.048*
C12	0.1399 (3)	0.9314 (2)	0.14537 (16)	0.0333 (4)
C13	0.0289 (3)	0.7782 (2)	0.13838 (18)	0.0390 (4)
H13	-0.1393	0.7289	0.0886	0.047*
C14	0.1652 (4)	0.6990 (2)	0.20418 (19)	0.0410 (4)
H14	0.0905	0.5958	0.1986	0.049*
C15	-0.0056 (4)	1.0190 (2)	0.07142 (17)	0.0416 (4)
H15A	0.0637	1.1324	0.1177	0.050*
H15B	-0.1800	0.9896	0.0701	0.050*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.02747 (17)	0.03565 (18)	0.03103 (17)	0.01680 (13)	0.01363 (13)	0.01564 (13)
N1	0.0459 (9)	0.0434 (8)	0.0355 (8)	0.0179 (7)	0.0150 (7)	0.0153 (6)
C1	0.0323 (8)	0.0272 (7)	0.0324 (8)	0.0078 (6)	0.0059 (7)	0.0116 (6)
S1	0.0492 (3)	0.0540 (3)	0.0424 (3)	0.0118 (2)	0.0221 (2)	0.0048 (2)
N2	0.0292 (7)	0.0391 (7)	0.0465 (8)	0.0149 (6)	0.0158 (6)	0.0192 (6)

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C2	0.0246 (7)	0.0288 (7)	0.0327 (8)	0.0073 (6)	0.0078 (6)	0.0130 (6)
S2	0.0281 (2)	0.0341 (2)	0.0472 (2)	0.01455 (16)	0.01351 (18)	0.01003 (18)
N10	0.0410 (8)	0.0391 (8)	0.0416 (8)	0.0172 (6)	0.0088 (7)	0.0226 (6)
C10	0.0339 (9)	0.0418 (9)	0.0442 (10)	0.0083 (7)	0.0028 (8)	0.0173 (8)
C11	0.0460 (10)	0.0306 (8)	0.0422 (9)	0.0093 (7)	0.0082 (8)	0.0161 (7)
C12	0.0414 (9)	0.0376 (8)	0.0270 (7)	0.0192 (7)	0.0115 (7)	0.0135 (7)
C13	0.0336 (9)	0.0424 (9)	0.0391 (9)	0.0082 (7)	0.0061 (7)	0.0165 (8)
C14	0.0449 (10)	0.0343 (9)	0.0450 (10)	0.0072 (7)	0.0115 (8)	0.0198 (8)
C15	0.0517 (11)	0.0469 (10)	0.0369 (9)	0.0292 (9)	0.0128 (8)	0.0204 (8)

Geometric parameters (\AA , $^\circ$)

Fe1—N1 ⁱ	2.1011 (15)	N10—H10A	0.8600
Fe1—N1	2.1011 (15)	C10—C11	1.369 (2)
Fe1—N2 ⁱ	2.1376 (14)	C10—H10	0.9300
Fe1—N2	2.1376 (14)	C11—C12	1.391 (3)
Fe1—S2 ⁱⁱ	2.6729 (5)	C11—H11	0.9300
Fe1—S2 ⁱⁱⁱ	2.6729 (5)	C12—C13	1.385 (2)
N1—C1	1.163 (2)	C12—C15	1.504 (2)
C1—S1	1.6157 (18)	C13—C14	1.368 (3)
N2—C2	1.156 (2)	C13—H13	0.9300
C2—S2	1.6472 (16)	C14—H14	0.9300
S2—Fe1 ^{iv}	2.6729 (5)	C15—C15 ^v	1.525 (4)
N10—C14	1.333 (2)	C15—H15A	0.9700
N10—C10	1.333 (2)	C15—H15B	0.9700
N1 ⁱ —Fe1—N1	180.000 (1)	C10—N10—H10A	118.8
N1 ⁱ —Fe1—N2 ⁱ	91.94 (6)	N10—C10—C11	119.77 (16)
N1—Fe1—N2 ⁱ	88.06 (6)	N10—C10—H10	120.1
N1 ⁱ —Fe1—N2	88.06 (6)	C11—C10—H10	120.1
N1—Fe1—N2	91.94 (6)	C10—C11—C12	120.07 (16)
N2 ⁱ —Fe1—N2	180.000 (1)	C10—C11—H11	120.0
N1 ⁱ —Fe1—S2 ⁱⁱ	86.79 (4)	C12—C11—H11	120.0
N1—Fe1—S2 ⁱⁱ	93.21 (4)	C13—C12—C11	117.78 (15)
N2 ⁱ —Fe1—S2 ⁱⁱ	86.73 (4)	C13—C12—C15	121.12 (16)
N2—Fe1—S2 ⁱⁱ	93.27 (4)	C11—C12—C15	121.09 (16)
N1 ⁱ —Fe1—S2 ⁱⁱⁱ	93.21 (4)	C14—C13—C12	120.42 (16)
N1—Fe1—S2 ⁱⁱⁱ	86.79 (4)	C14—C13—H13	119.8
N2 ⁱ —Fe1—S2 ⁱⁱⁱ	93.27 (4)	C12—C13—H13	119.8
N2—Fe1—S2 ⁱⁱⁱ	86.73 (4)	N10—C14—C13	119.63 (16)
S2 ⁱⁱ —Fe1—S2 ⁱⁱⁱ	180.000 (13)	N10—C14—H14	120.2
C1—N1—Fe1	149.29 (13)	C13—C14—H14	120.2
N1—C1—S1	179.28 (15)	C12—C15—C15 ^v	111.35 (18)
C2—N2—Fe1	158.76 (13)	C12—C15—H15A	109.4
N2—C2—S2	178.92 (16)	C15 ^v —C15—H15A	109.4

C2—S2—Fe1 ^{iv}	98.29 (6)	C12—C15—H15B	109.4
C14—N10—C10	122.34 (15)	C15 ^v —C15—H15B	109.4
C14—N10—H10A	118.8	H15A—C15—H15B	108.0

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z+1$; (iii) $x+1, y, z$; (iv) $x-1, y, z$; (v) $-x, -y+2, -z$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N10—H10A \cdots N1	0.86	2.34	3.029 (2)	137.
N10—H10A \cdots S2 ⁱⁱⁱ	0.86	2.73	3.4369 (15)	141.

Symmetry codes: (iii) $x+1, y, z$.

Fig. 1

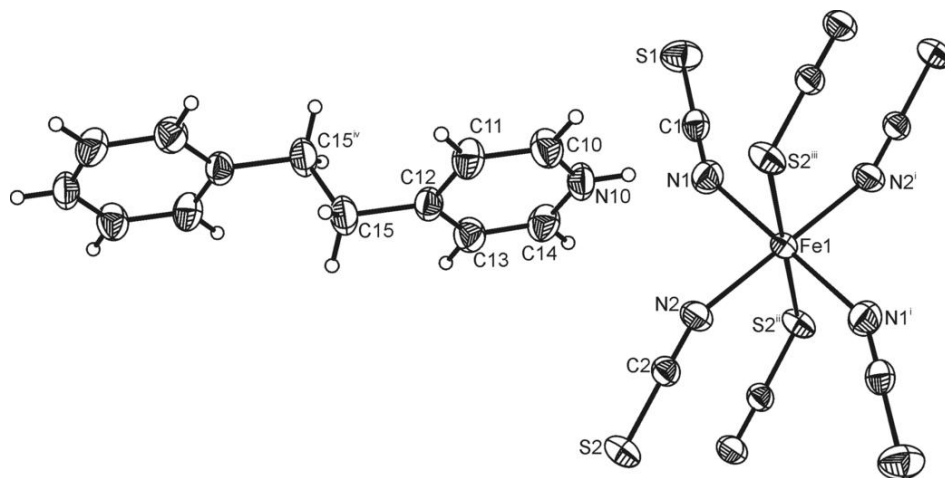


Fig. 2

