metal-organic compounds

catena-Poly[(E)-4,4′-(ethane-1,2-diyl)-dipyridinium [[bis(thiocyanato-κN)-ferrate(II)]-di-μ-thiocyanato-κ²N:S;κ²S:N]]

Susanne Wöhlert,* Inke Jess and Christian Näther

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Max-Eyth-Strasse 2, 24118 Kiel, Germany

Correspondence e-mail: swoehlert@ac.uni-kiel.de

In the crystal structure of the title compound, $\{(C_{12}H_{14}N_2)[Fe(NCS)_4]\}_n$, 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 Fe—(NCS)₂—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* N—H···N and N—H···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

$(C_{12}H_{14}N_2)[Fe(NCS)_4]$	b = 9.0957 (6) Å
M_r = 474.42	c = 10.9259 (7) Å
Triclinic, $P\bar{1}$	α = 105.586 (5)°
a = 5.6818 (3) Å	β = 103.633 (5)°

γ = 101.383 (5)°	μ = 1.17 mm⁻¹
V = 507.65 (5) Å³	T = 293 K
Z = 1	0.19 × 0.15 × 0.09 mm
Mo $K\alpha$ radiation	

Data collection

Stoe IPDS-2 diffractometer	7638 measured reflections
Absorption correction: numerical	2101 independent reflections
(*X-SHAPE* and *X-RED32*; Stoe	1838 reflections with $I > 2\sigma(I)$
& Cie, 2008)	R_{int} = 0.030
T_{min} = 0.806, T_{max} = 0.899	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026	124 parameters
$wR(F^2)$ = 0.063	H-atom parameters constrained
S = 1.03	$\Delta\rho_{max}$ = 0.26 e Å⁻³
2101 reflections	$\Delta\rho_{min}$ = −0.40 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Fe1—N1	2.1011 (15)	Fe1—S2ⁱ	2.6729 (5)
Fe1—N2	2.1376 (14)		
N1ⁱⁱ—Fe1—N1	180	N2ⁱⁱ—Fe1—S2ⁱⁱⁱ	86.73 (4)
N1ⁱⁱ—Fe1—N2	88.06 (6)	N1—Fe1—S2ⁱ	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—H···A	D—H	H···A	D···A	D—H···A
N10—H10A···N1	0.86	2.34	3.029 (2)	137
N10—H10A···S2ⁱ	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*.

References

Boeckmann, J., Wriedt, M. & Näther, C. (2010). *Eur. J. Inorg. Chem.* **12**, 1820–1828.

Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Stoe & Cie (2008). *X-AREA*, *X-RED32* and *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.

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.* E**66**, m1256.

supporting information

catena-Poly[(*E*)-4,4′-(ethane-1,2-diyl)dipyridinium [[bis(thiocyanato-*κN*)ferrate(II)]-di-*μ*-thiocyanato-*κ²N:S;κ²S:N*]]

Susanne Wöhlert, Inke Jess and Christian Näther

S1. 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 $[Fe(NCS)_4]_n$-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 arround the metal cations range from 86.73 (5) to 93.27 (4) and 180° (Tab. 1). The shortest intramolecular Fe···Fe distance amounts to 5.6818 (3) Å and the shortest intermolecular Fe···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).

S2. Experimental

$FeSO_4·7H_2O$ and 1,2-bis(4-pyridyl)-ethane were obtained from Sigma Aldrich. KNCS are obtained from Alfa Aesar. 0.6 mmol (168.0 mg) $FeSO_4·7H_2O$, 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.

S3. Refinement

All H atoms were located in difference map but were positioned with idealized geometry and were refined using a riding model with $U_{eq}(H) = 1.2\ U_{eq}(C,N)$ with C—H = 0.93 Å and N—H = 0.86 Å.
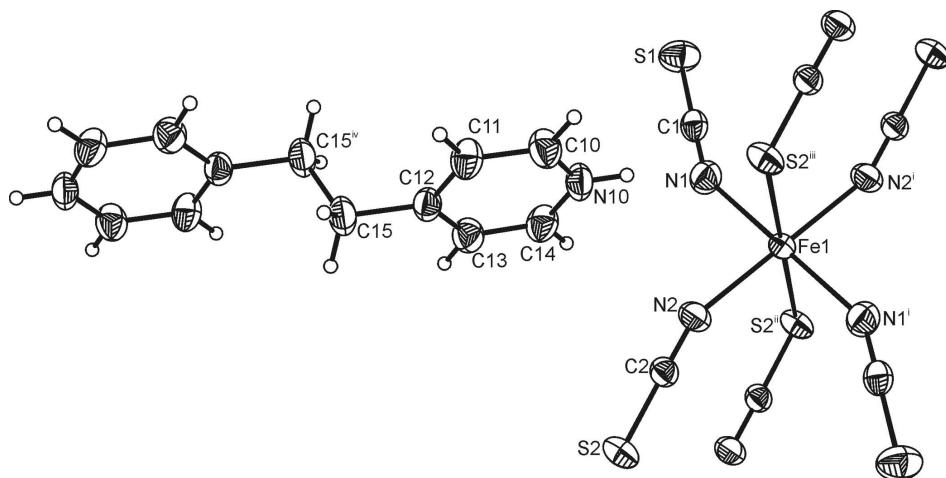
Figure 1

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.
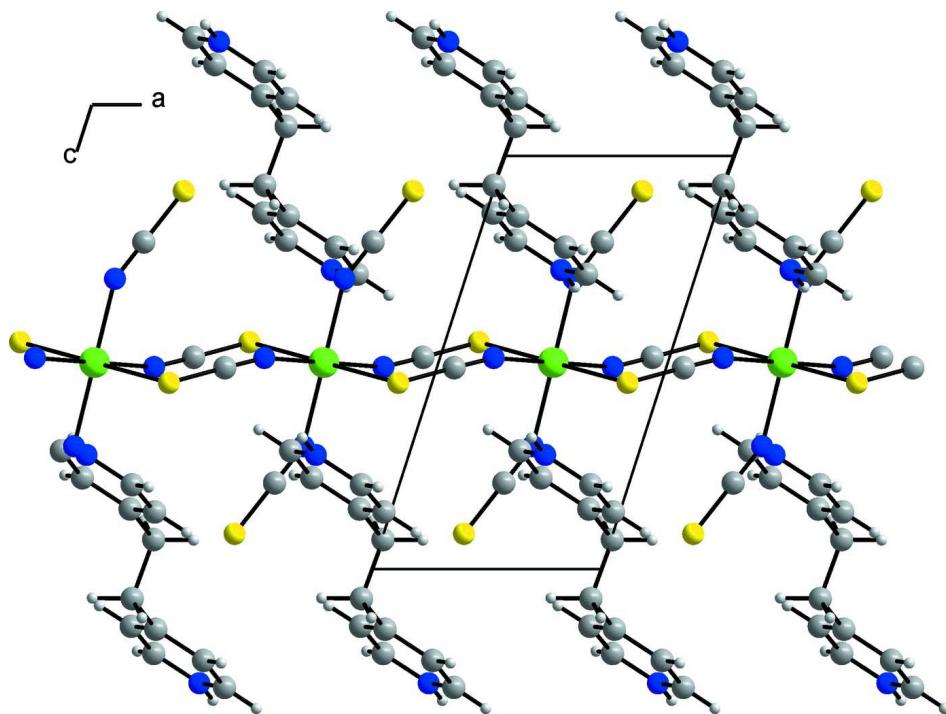
Figure 2

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

***catena*-Poly[(*E*)-4,4′-(ethane-1,2-diyl)dipyridinium [[bis(thiocyanato-*κN*)ferrate(II)]-di-*μ*-thiocyanato-*κ²N:S;κ²S:N*]]**

Crystal data
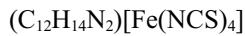
$(C_{12}H_{14}N_2)[Fe(NCS)_4]$
$M_r = 474.42$
Triclinic, $P\overline{1}$

Hall symbol: -P 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) Å^3
$Z = 1$
$F(000) = 242$
$D_{\text{x}} = 1.552$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7638 reflections
$\theta = 2.0$–26.5°
$\mu = 1.17$ mm^{-1}
$T = 293$ K
Block, red
$0.19 \times 0.15 \times 0.09$ mm

Data collection

Stoe IPDS-2
    diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: numerical
    (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2008)
$T_{\text{min}} = 0.806$, $T_{\text{max}} = 0.899$

7638 measured reflections
2101 independent reflections
1838 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.030$
$\theta_{\text{max}} = 26.5°$, $\theta_{\text{min}} = 2.0°$
$h = -7\rightarrow6$
$k = -11\rightarrow11$
$l = -13\rightarrow13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.063$
$S = 1.03$
2101 reflections
124 parameters
0 restraints
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
$w = 1/[\sigma^2(F_\text{o}^2) + (0.0393P)^2 + 0.0464P]$
    where $P = (F_\text{o}^2 + 2F_\text{c}^2)/3$
$(\Delta/\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 0.26$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.40$ e Å^{-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 > 2sigma(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 (Å^2)

	x	y	z	U_{iso}*/U_{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 (Å²)

	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)
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 (Å, º)

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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10—H10*A*···N1	0.86	2.34	3.029 (2)	137
N10—H10*A*···S2^{iii}	0.86	2.73	3.4369 (15)	141

Symmetry code: (iii) *x*+1, *y*, *z*.