

Poly[bis(acetonitrile- κN)di- μ -thiocyanato- $\kappa^2 N, S; \kappa^2 S, N$ -nickel(II)]

Susanne Wöhlert,* Inke Jess and Christian Näther

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Max-Eyth-Strasse 2, 24098 Kiel, Germany

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

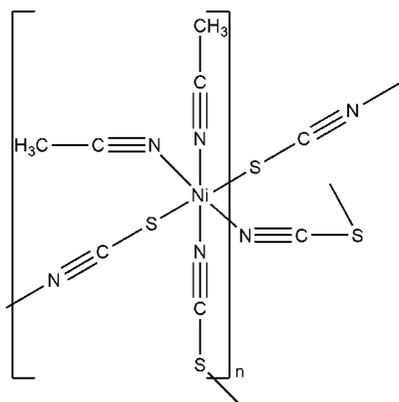
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.027; wR factor = 0.051; data-to-parameter ratio = 22.5.

In the title compound, $[\text{Ni}(\text{NCS})_2(\text{CH}_3\text{CN})_2]_n$, the Ni^{II} cation is coordinated by two N -bonded and two S -bonded thiocyanate anions, as well as two acetonitrile molecules in an octahedral NiN_4S_2 coordination mode. The asymmetric unit comprises one nickel cation, two thiocyanate anions and two acetonitrile molecules. In the crystal, the Ni^{II} cations are connected by bridging thiocyanate anions into a three-dimensional coordination network.

Related literature

For background of this work see: Boeckmann & Näther (2010); Wriedt *et al.* (2009a,b).



Experimental

Crystal data

$[\text{Ni}(\text{NCS})_2(\text{C}_2\text{H}_3\text{N})_2]$
 $M_r = 256.98$
 Orthorhombic, $P2_12_12_1$
 $a = 9.0666$ (4) Å
 $b = 9.1215$ (3) Å
 $c = 12.0696$ (6) Å

$V = 998.17$ (7) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 2.32$ mm⁻¹
 $T = 293$ K
 $0.11 \times 0.09 \times 0.06$ mm

Data collection

Stoe IPDS-2 diffractometer
 Absorption correction: numerical
 (X -SHAPE and X -RED32;
 Stoe & Cie, 2008)
 $T_{\text{min}} = 0.683$, $T_{\text{max}} = 0.772$

11157 measured reflections
 2694 independent reflections
 2479 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.051$
 $S = 1.29$
 2694 reflections
 120 parameters
 H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³
 Absolute structure: Flack (1983),
 1141 Friedel pairs
 Flack parameter: -0.003 (13)

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: IM2264).

References

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supporting information

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Poly[bis(acetonitrile- κ N)di- μ -thiocyanato- κ^2 N,S; κ^2 S,N-nickel(II)]

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S1. Comment

In recent work, we have shown that thermal decomposition reactions are an elegant route for discovering and synthesising new ligand-deficient coordination polymers with attractive magnetic properties (Boeckmann & Näther, 2010; Wriedt *et al.*, 2009a, 2009b). In our investigation on the syntheses, structures and properties of such compounds based on paramagnetic transition metals, pseudo-halides and N-donor ligands, we have reacted nickel(II) thiocyanate and *trans*-1,2-bis(4-pyridyl)-ethylene in acetonitrile. In this reaction single crystals of the title compound were obtained accidentally in a mixture with an unknown phase. To identify the reaction product the compound was investigated by single crystal X-ray diffraction.

In the crystal structure of the title compound, each nickel(II) cation is coordinated by four bridging thiocyanato anions and by two acetonitrile molecules (Fig. 1). The NiN₄S₂ octahedron is slightly distorted with two long Ni—SCN distances of 2.5305 (6) Å and 2.5341 (6) Å as well as two short Ni—NCS distances of 2.021 (2) Å and 2.023 (2) Å. The angles around the metal atom range from 87.88 (6) ° to 93.23 (6) ° and 178° (Tab. 1).

The nickel cations are linked by the thiocyanato anions into chains, that are further connected into a three-dimensional network (Fig. 2). The shortest intramolecular Ni···Ni distance amounts to 5.7052 (4) Å and the shortest intermolecular Ni···Ni distance amounts to 9.0666 (4) Å.

S2. Experimental

Ni(NCS)₂ was obtained from Alfa Aesar and *trans*-1,2-bis(4-pyridyl)-ethylene (bpe) was obtained from Sigma Aldrich. All chemicals were used without further purification. 0.6 mmol (104.7 mg) Ni(NCS)₂ and 0.15 mmol (28.2 mg) bpe were reacted with 1 ml acetonitrile in a closed test-tube at 120°C for three days. On cooling blue block-shaped single crystals of the title compound were obtained in a mixture with a unknown phase. It must be noted, that the reaction without bpe does not lead to the formation of the title compound.

S3. Refinement

H atoms were positioned with idealized geometry, allowed to rotate but not to tip and were refined isotropically with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ and C—H distances of 0.96 Å using a riding model. The absolute structure was determined on the basis of 1127 Friedel pairs.

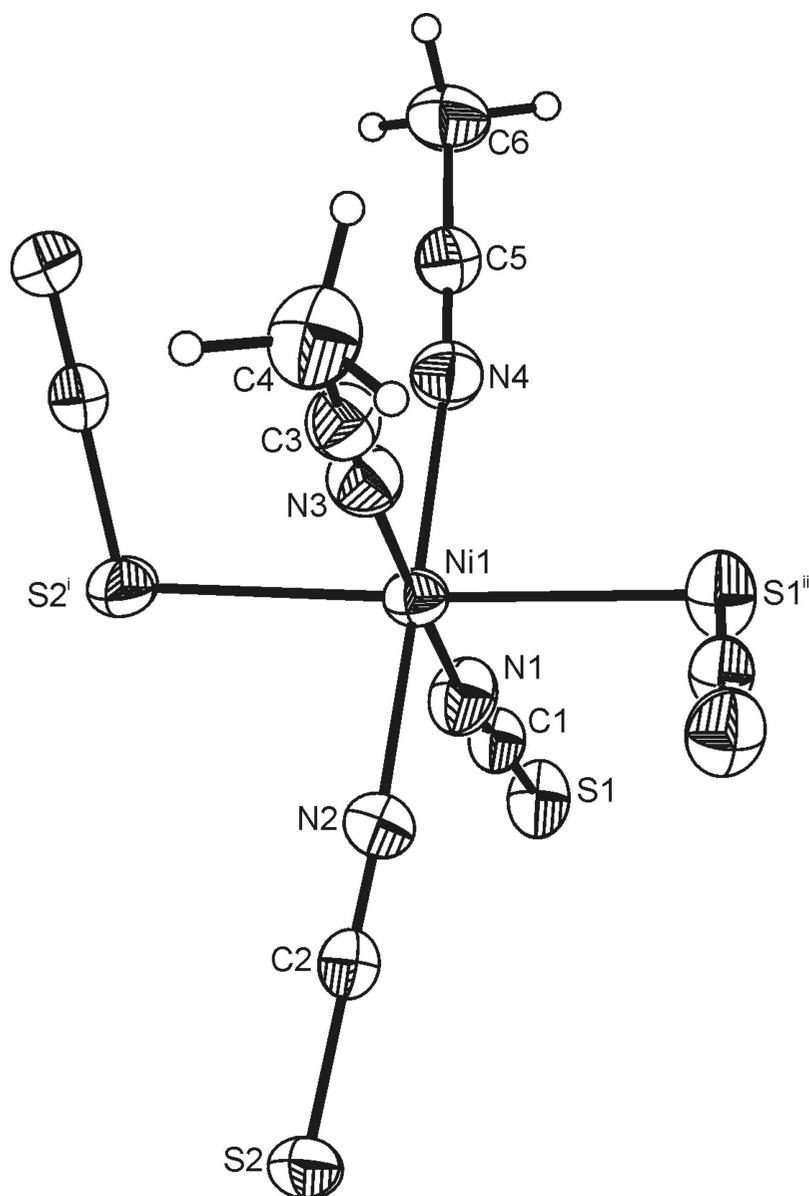


Figure 1

Crystal structure of the title compound with labelling and displacement ellipsoids drawn at the 30 % probability level. Symmetry codes: i = $x-1/2, -y+3/2, -z+1$; ii = $-x, y-1/2, -z+3/2$.

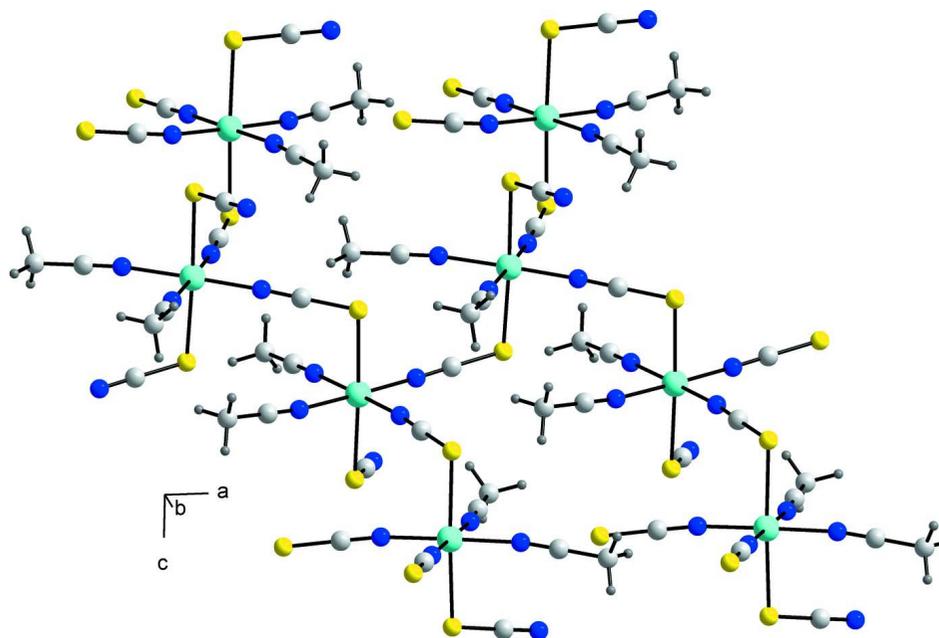


Figure 2

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

Poly[bis(acetonitrile- κ N)di- μ -thiocyanato- κ^2 N,S; κ^2 S,N-nickel(II)]

Crystal data

[Ni(NCS)₂(C₂H₃N)₂]

M_r = 256.98

Orthorhombic, *P*2₁2₁2₁

Hall symbol: P 2ac 2ab

a = 9.0666 (4) Å

b = 9.1215 (3) Å

c = 12.0696 (6) Å

V = 998.17 (7) Å³

Z = 4

F(000) = 520

D_x = 1.710 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 11157 reflections

θ = 2.8–29.2°

μ = 2.32 mm⁻¹

T = 293 K

Block, blue

0.11 × 0.09 × 0.06 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_{min} = 0.683, *T_{max}* = 0.772

11157 measured reflections

2694 independent reflections

2479 reflections with *I* > 2σ(*I*)

R_{int} = 0.023

θ_{max} = 29.2°, θ_{min} = 2.8°

h = -12→10

k = -12→12

l = -16→16

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.027

wR(*F*²) = 0.051

S = 1.29

2694 reflections

120 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

$$w = 1/[\sigma^2(F_o^2) + (0.0221P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), **1127 Friedel pairs**

Absolute structure parameter: -0.003 (13)

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 $F^2 > 2\sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	-0.10172 (3)	0.83322 (3)	0.62898 (2)	0.02615 (6)
N1	-0.0070 (2)	1.0335 (2)	0.63730 (18)	0.0388 (4)
C1	0.0391 (2)	1.1504 (3)	0.64845 (15)	0.0307 (4)
S1	0.10459 (8)	1.31745 (6)	0.66142 (4)	0.03781 (12)
N2	0.0983 (2)	0.7362 (2)	0.61691 (15)	0.0356 (4)
C2	0.2172 (2)	0.6972 (2)	0.60194 (15)	0.0283 (4)
S2	0.38867 (6)	0.64753 (7)	0.58006 (4)	0.03776 (13)
N3	-0.2036 (2)	0.6293 (2)	0.62176 (17)	0.0341 (4)
C3	-0.2491 (2)	0.5139 (3)	0.6242 (2)	0.0335 (4)
C4	-0.3109 (3)	0.3669 (3)	0.6278 (3)	0.0468 (6)
H4A	-0.4134	0.3723	0.6472	0.070*
H4B	-0.2593	0.3098	0.6823	0.070*
H4C	-0.3007	0.3215	0.5565	0.070*
N4	-0.3065 (2)	0.9326 (2)	0.63801 (17)	0.0365 (4)
C5	-0.4170 (2)	0.9893 (2)	0.63197 (19)	0.0344 (4)
C6	-0.5579 (3)	1.0633 (3)	0.6230 (3)	0.0452 (5)
H6A	-0.5743	1.1215	0.6881	0.068*
H6B	-0.6351	0.9920	0.6161	0.068*
H6C	-0.5575	1.1256	0.5589	0.068*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.02348 (10)	0.02426 (11)	0.03072 (11)	-0.00044 (11)	-0.00046 (11)	-0.00142 (9)
N1	0.0458 (11)	0.0336 (10)	0.0371 (9)	-0.0091 (8)	-0.0039 (10)	-0.0018 (9)
C1	0.0340 (9)	0.0322 (11)	0.0258 (9)	-0.0008 (9)	-0.0008 (7)	0.0003 (8)
S1	0.0523 (3)	0.0278 (3)	0.0333 (2)	-0.0104 (3)	-0.0001 (2)	0.00087 (19)
N2	0.0288 (7)	0.0434 (9)	0.0346 (9)	0.0041 (9)	0.0021 (10)	-0.0025 (7)
C2	0.0318 (9)	0.0280 (10)	0.0252 (8)	-0.0010 (8)	-0.0010 (7)	-0.0013 (7)
S2	0.0262 (2)	0.0527 (3)	0.0343 (2)	0.0089 (3)	0.0010 (2)	0.0033 (2)

N3	0.0339 (8)	0.0314 (10)	0.0369 (9)	-0.0033 (7)	0.0016 (9)	-0.0011 (9)
C3	0.0351 (9)	0.0332 (11)	0.0322 (9)	-0.0013 (8)	-0.0007 (9)	0.0025 (9)
C4	0.0585 (15)	0.0327 (12)	0.0492 (13)	-0.0105 (11)	-0.0028 (14)	-0.0001 (12)
N4	0.0334 (9)	0.0379 (10)	0.0382 (9)	0.0053 (8)	-0.0016 (9)	-0.0003 (9)
C5	0.0333 (10)	0.0368 (10)	0.0332 (9)	-0.0002 (9)	0.0007 (10)	-0.0034 (9)
C6	0.0326 (10)	0.0485 (13)	0.0547 (14)	0.0061 (10)	0.0018 (12)	-0.0008 (13)

Geometric parameters (Å, °)

Ni1—N1	2.0210 (19)	S2—Ni1 ^{iv}	2.5305 (6)
Ni1—N2	2.0231 (18)	N3—C3	1.131 (3)
Ni1—N4	2.0685 (19)	C3—C4	1.454 (3)
Ni1—N3	2.0782 (18)	C4—H4A	0.9600
Ni1—S2 ⁱ	2.5305 (6)	C4—H4B	0.9600
Ni1—S1 ⁱⁱ	2.5341 (6)	C4—H4C	0.9600
N1—C1	1.154 (3)	N4—C5	1.130 (3)
C1—S1	1.643 (2)	C5—C6	1.449 (3)
S1—Ni1 ⁱⁱⁱ	2.5341 (6)	C6—H6A	0.9600
N2—C2	1.149 (3)	C6—H6B	0.9600
C2—S2	1.641 (2)	C6—H6C	0.9600
N1—Ni1—N2	91.02 (8)	N2—C2—S2	178.0 (2)
N1—Ni1—N4	89.02 (8)	C2—S2—Ni1 ^{iv}	100.02 (7)
N2—Ni1—N4	178.89 (9)	C3—N3—Ni1	173.7 (2)
N1—Ni1—N3	178.69 (9)	N3—C3—C4	178.7 (3)
N2—Ni1—N3	90.23 (8)	C3—C4—H4A	109.5
N4—Ni1—N3	89.73 (8)	C3—C4—H4B	109.5
N1—Ni1—S2 ⁱ	90.09 (6)	H4A—C4—H4B	109.5
N2—Ni1—S2 ⁱ	89.40 (5)	C3—C4—H4C	109.5
N4—Ni1—S2 ⁱ	89.50 (6)	H4A—C4—H4C	109.5
N3—Ni1—S2 ⁱ	90.29 (6)	H4B—C4—H4C	109.5
N1—Ni1—S1 ⁱⁱ	90.35 (6)	C5—N4—Ni1	173.2 (2)
N2—Ni1—S1 ⁱⁱ	93.23 (6)	N4—C5—C6	179.2 (3)
N4—Ni1—S1 ⁱⁱ	87.88 (6)	C5—C6—H6A	109.5
N3—Ni1—S1 ⁱⁱ	89.22 (6)	C5—C6—H6B	109.5
S2 ⁱ —Ni1—S1 ⁱⁱ	177.34 (2)	H6A—C6—H6B	109.5
C1—N1—Ni1	174.6 (2)	C5—C6—H6C	109.5
N1—C1—S1	178.77 (19)	H6A—C6—H6C	109.5
C1—S1—Ni1 ⁱⁱⁱ	98.29 (7)	H6B—C6—H6C	109.5
C2—N2—Ni1	170.90 (18)		

Symmetry codes: (i) $x-1/2, -y+3/2, -z+1$; (ii) $-x, y-1/2, -z+3/2$; (iii) $-x, y+1/2, -z+3/2$; (iv) $x+1/2, -y+3/2, -z+1$.