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Synthesis, crystal structure and stability of a new isomer of bis(ethylenethiourea)dithiocyanatocobalt(II)

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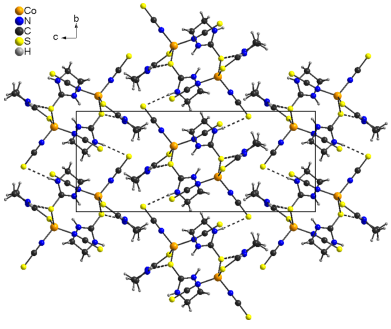
The title compound, bis(imidazolidine-2-thione-κS)dithiocyanatocobalt(II), $[Co(NCS)_2(C_3H_6N_2S)_2]$, was prepared by the reaction of cobalt thiocyanate with ethylenethiourea in ethanol solution. The asymmetric unit (space group $P2_1/c$) consists of one cobalt cation, as well as two crystallographically independent thiocyanate anions and two ethylenethiourea ligands, all of them located in general positions. The metal cations are tetrahedrally coordinated by two N-bonding anionic ligands and two ethylenethiourea ligands into discrete complexes. These complexes are linked by N—H···S hydrogen bonds into layers. The IR spectrum is in agreement with the presence of a tetrahedral coordination with N-bonding thiocyanate anions and measurements using X-ray powder diffraction indicate that a pure crystalline phase has been obtained. The title compound represents a new isomer of $Co(NCS)_2(C_3H_6N_2S)_2$, which was already reported in the literature in space group $P\overline{1}$ [Mautner *et al.*, (2018). *Polyhedron* **154**, 436–442]. In contrast to the title compound, in the triclinic isomer the cobalt cations are octahedrally coordinated and linked into chains by μ-1,3-bridging thiocyanate anions. Solvent-mediated conversion experiments starting from a mixture of both isomers show that the title complex is the thermodynamically stable form at room temperature.

1. Chemical context

Polymorphism and isomerism are widespread phenomena in coordination chemistry (Braga & Grepioni, 2000; Barnett *et al.*, 2002; Moulton & Zaworotko, 2001). Different polymorphs or isomers are frequently found in, for example, coordination compounds based on transition-metal thiocyanates with N-donor coligands, which might be traced back to the fact that this class of compounds shows a large structural variability, which originates in part from the different coordination modes of this anionic ligand but also from the fact that some transition-metal cations show variability in their coordination numbers (Krebs *et al.*, 2021*a*; Wellm *et al.*, 2020; Böhme *et al.*, 2020; Neumann *et al.*, 2018).

For many years, we and others have been especially interested in cobalt thiocyanate and selenocyanate compounds with the general composition $Co(NCX)_2(L)_2$ (X = S, Se and L = N-donor coligand) because some of them show interesting magnetic properties such as single-chain magnet (SCM) behavior (Wöhlert *et al.*, 2012, 2013). This is the case in compounds in which the cobalt cations are octahedrally coordinated by two N- and two S-bonding thiocyanate anions and two N-donor coligands and linked into chains by μ-1,3-bridging thiocyanate anions. Such a coordination represents an $MA_2B_2C_2$ system for which five isomers exist, namely one all-*trans*, three different *cis–cis–trans* and one all-*cis* isomer.



We found that for SCM behavior to be observed in compounds with linear chains, an all-*trans* coordination or a *cis–cis–trans* coordination with the coligands in *trans*-positions is needed (Böhme *et al.*, 2020). The other isomers lead to the formation of corrugated chains, for which the magnetic exchange is suppressed (Böhme *et al.*, 2020). There are a few additional compounds with this composition in which $Co(NCS)_2$ layers are observed and that show ferromagnetic ordering at low temperatures (Suckert *et al.*, 2016).

In the beginning, we focused on pyridine derivatives as coligands, for which the majority of compounds consist of linear chains. However, in the course of our systematic work we also used 4-dimethylaminopyridine as coligand, but in contrast to all other ligands investigated before, discrete tetrahedral complexes were obtained, which crystallize in different isomeric or polymorphic modifications and which represent an isomer of the compounds mentioned above (Näther *et al.*, 2018; Krebs *et al.*, 2021*b*). Such complexes are of less interest for our project because no SCM behavior can be observed. The reason why for some ligands chains and for some others discrete complexes are observed is still unknown.

In 2018, Mautner and coworkers reported on the synthesis, structure and properties of $Co(NCS)_2$(4-methoxypyridine)$_2$, which shows linear chains and SCM behavior (Mautner *et al.*, 2018; Rams *et al.*, 2020). However, under slightly different reaction conditions they were also able to prepare a second isomer with this composition that consists of discrete complexes. Unfortunately it was not determined which of the two isomers is thermodynamically stable at a given temperature.

Some time later, we became interested in such compounds with coligands other than pyridine derivatives, to study the influence of the coligand on the structural and magnetic behavior. With ethylenethiourea, we obtained a compound with the composition $Co(NCS)_2$(ethylenethiourea)$_2$ (CSD refcode ZZZFAI01, space group $P\overline{1}$; Böhme *et al.*, 2020) in which the cations are octahedrally coordinated with an all-*trans* coordination and linked into linear chains by the anionic ligands (Fig. 1). Recently we tried to synthesize this compound again for additional investigations, but instead of the known chain isomer, the title compound was obtained and we now describe its crystal structure and thermodynamic stability using solvent-mediated conversion experiments.

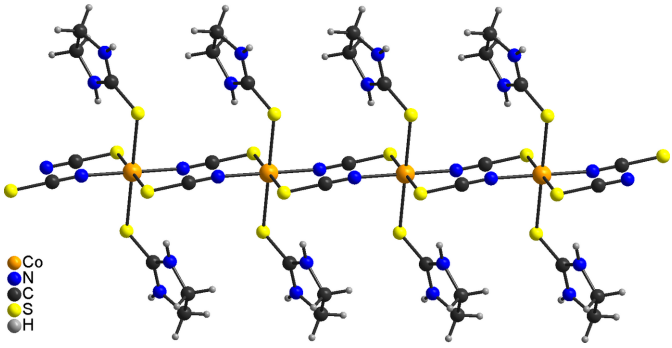
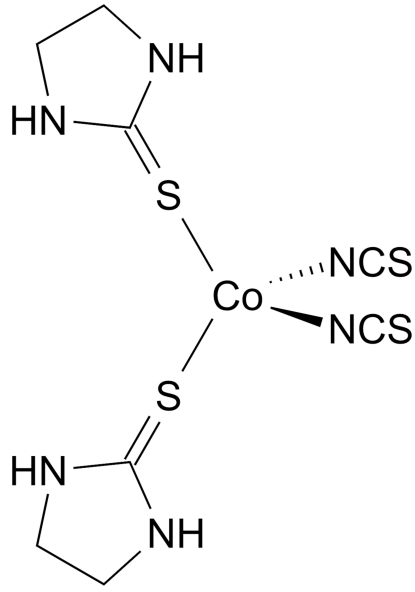


Figure 1
View of apart of a chain in the known isomer of $Co(NCS)_2$(ethylenethiourea)$_2$.



2. Structural commentary

The asymmetric unit of the title compound, $Co(NCS)_2(C_3H_6N_2S)_2$ ($C_3H_6N_2S$ = ethylenethiourea), which crystallizes in space group $P2_1/c$, consists of one crystallographically independent cobalt cation, two independent thiocyanat anions and two independent ethylenethiourea ligands with all atoms lying on general positions. The metal cations are fourfold coordinated (Table 1) by two N-bonding thiocyanate anions and two ethylenethiourea ligands in a slightly distorted tetrahedral environment (Fig. 2). The C11 ethylenethiourea ring is an envelope with atom C12 as the flap whereas the C21 ring is twisted about the C22—C23 bond. Therefore, this structure is completely different from that of the known isomer of $Co(NCS)_2$(ethylenethiourea) already reported in the literature, which consists of octahedrally cobalt cations that are linked into chains *via* pairs of μ-1,3-bridging thiocyanato anions (Fig. 1).

Even if cobalt thiocyanate compounds with an octahedral coordination and bridging anionic ligands represent the majority of structures, compounds with a tetrahedral coordination are also reported. These include, for example, $Co(NCS)_2$(4-*N*,*N*′-dimethylaminopyridine)$_2$, which crystallizes in different polymorphic modifications [Neumann *et al.*,

Table 1
Selected geometric parameters (Å, °).

Co1—N1	1.9446 (15)	Co1—S11	2.3111 (5)
Co1—N2	1.9544 (16)	Co1—S21	2.3120 (5)
N1—Co1—N2	110.32 (7)	S11—Co1—S21	113.076 (19)
N1—Co1—S11	114.80 (5)	C1—N1—Co1	167.80 (15)
N2—Co1—S11	102.29 (5)	C2—N2—Co1	171.01 (15)
N1—Co1—S21	100.61 (5)	C11—S11—Co1	102.33 (6)
N2—Co1—S21	116.30 (5)	C21—S21—Co1	110.89 (6)

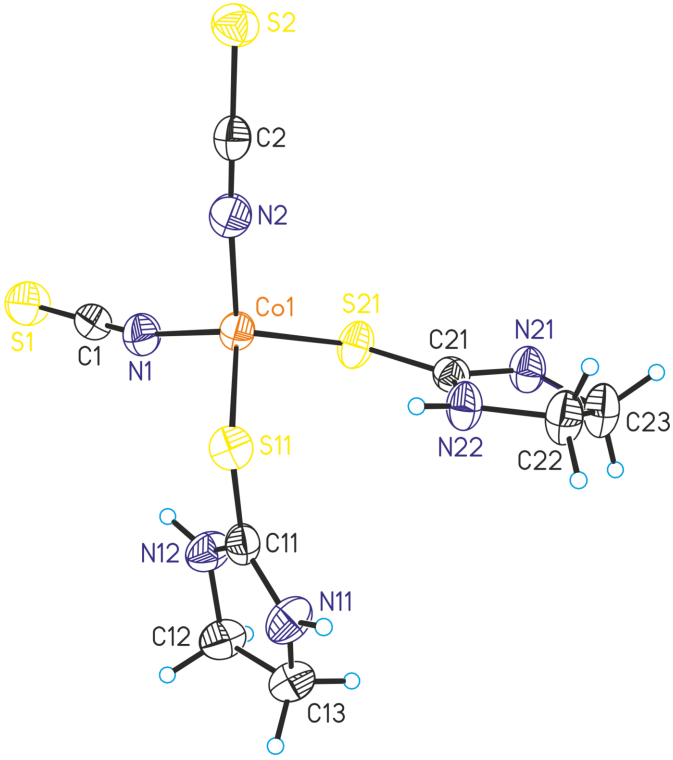


Figure 2
Crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level.

2018 (refcode GIQPEE); Krebs *et al.*, 2021*b* (GIQPEE01 and GIQPEE02)] as well as $Co(NCS)_2$(3-aminopyridine (ANUMII; Mautner *et al.*, 2021), $Co(NCS)_2$(4-aminopyridine)$_2$ (UGUWEA; Sugiyama *et al.*, 2015) $Co(NCS)_2$(4-vinylpyridine)$_2$ (BOZJUW; Foxman & Mazurek, 1982) and $Co(NCS)_2$(3-methylpyridine)$_2$ (EYARIG; Boeckmann *et al.*, 2011).

3. Supramolecular features

In the extended structure of the title compound, a number of N—H···S interactions are observed (Table 2), with some of them at relatively short H···S distances and N—H···S angles close to linearity, indicating hydrogen bonding rather than incidental contacts (Table 2). This leads to the formation of chains, which propagate in the crystallographic *a*-axis direction (Fig. 3). These chains are further connected into layers that lie parallel to the *bc* plane (Fig. 4). Additional N—H···S interactions are found between the layers, but at long distances and angles far from 180°.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···S2^{i}	0.88	2.57	3.3693 (16)	152
N12—H12···S11^{ii}	0.88	2.95	3.5571 (17)	128
N12—H12···S21^{iii}	0.88	2.97	3.4542 (15)	116
C12—H12*A*···S21^{iii}	0.99	2.91	3.4371 (19)	114
C13—H13*B*···S1^{iii}	0.99	2.95	3.816 (2)	147
N21—H21···S11^{iv}	0.88	2.74	3.5823 (16)	161
N22—H22···S2^{v}	0.88	2.83	3.3560 (16)	120
N22—H22···S11	0.88	2.73	3.5346 (15)	152
C22—H22*A*···S2^{i}	0.99	2.96	3.800 (2)	143

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

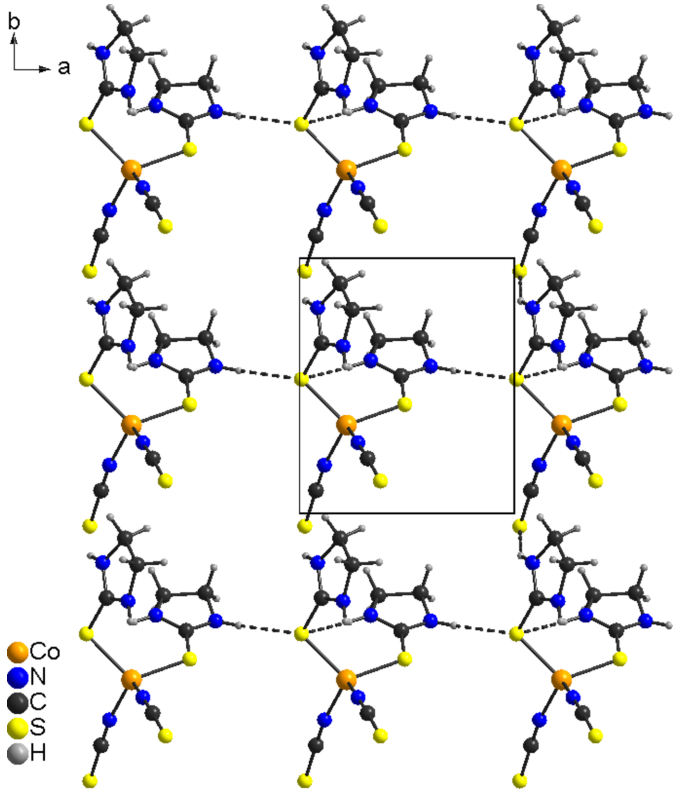


Figure 3
View onto a layer in the crystal structure of the title compound. Intermolecular N—H···S hydrogen bonding is shown as dashed lines.

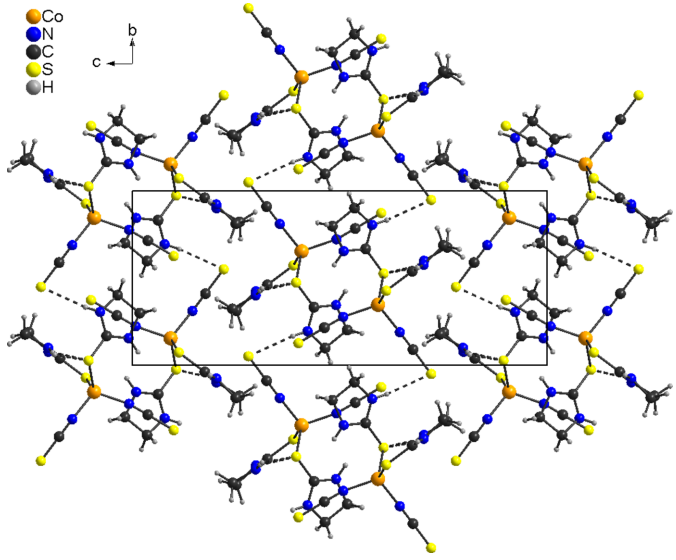


Figure 4
Crystal structure of the title compound in a view along the crystallographic *a*-axis direction. Intermolecular N—H···S hydrogen bonding is shown as dashed lines.

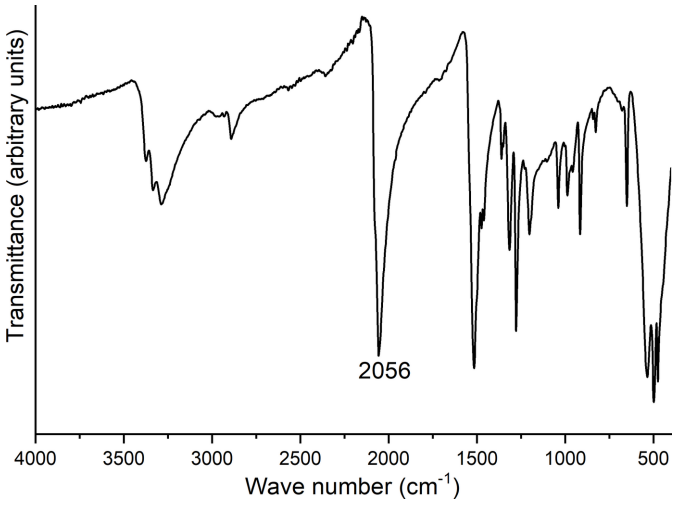


Figure 5
IR spectrum of the title compound. The value of the CN stretching vibration of the thiocyanate anions is given.

4. Physical characterization

The IR spectrum reveals that the CN stretching vibration of the thiocyanate anions occurs at 2056 cm^{-1}, in agreement with the presence of tetrahedral coordination (Fig. 5). The bands between 3000 and 3500 cm^{-1} can be assigned to the N—H stretching vibration with this group involved in intermolecular hydrogen bonding.

Comparison of the experiment X-ray powder pattern with that calculated using single crystal data reveal that a pure sample has been obtained (Fig. 6).

To investigate which of the two modifications of $Co(NCS)_2(C_3H_6N_2S)_2$ is the thermodynamically stable form at room temperature, solvent-mediated conversion experiments were performed. In this experiment, a mixture of the two isomers with excess of solid was stirred in ethanol at room temperature and these residues were investigated by X-ray powder diffraction after one and four days (Fig. 7). This shows that the reflections of the chain isomer disappear completely, which proves that the title compound represents the thermodynamically stable isomer at room temperature, where the chain isomer is metastable.

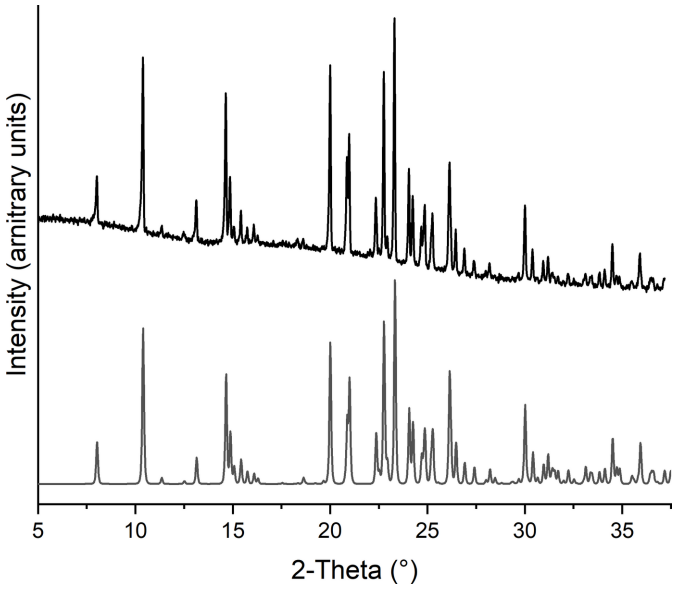


Figure 6
Experimental (top) and calculated (bottom)X-ray powder patterns of the title compound.

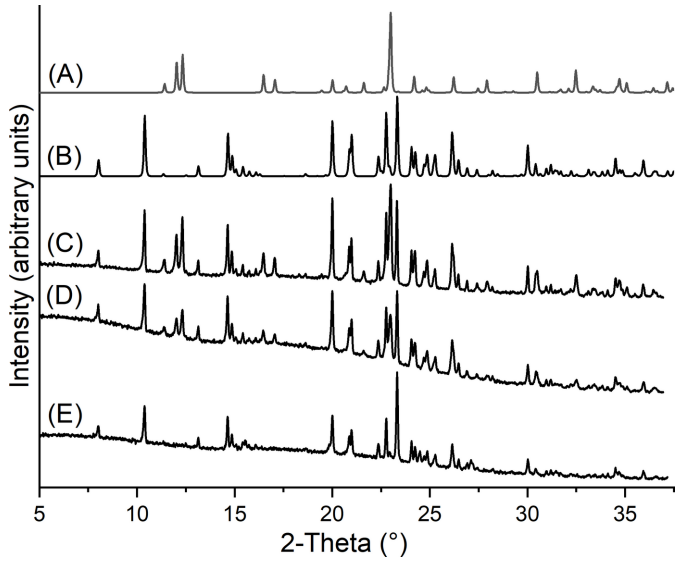


Figure 7
Calculated X-ray powder pattern of the chain isomer (A) and the title compound (B) as well as experimental pattern of a mixture of both isomers (C) and after stirring this mixture in ethanol for 1 d (D) and 4 d (E).

5. Database survey

First of all it may be mentioned that beside the chain isomer of $Co(NCS)_2(C_3H_6N_2S)_2$ (CSD refcode ZZZFAI01; Jochim *et al.*, 2020*a*), another compound with same composition is reported in the Cambridge Structural Database [CSD Version 5.43, update of May 2026 (Groom *et al.*, 2016), search with CONQUEST (Bruno *et al.*, 2002)] for which only unit-cell parameters are reported (ZZZFAI; Nardelli & Chierici, 1958). According to the entry in the CSD, this compound should consist of discrete complexes but the unit-cell parameters are very similar to the chain isomer of this compound. Moreover, it is stated that this form crystallizes in the triclinic system with $Z = 1$, in which space group $P\overline{1}$ is impossible. The same authors also reported unit-cell parameters for the corresponding Mn and Zn compounds. The unit-cell parameters for the Mn compound (ZZZEZA; Nardelli & Chierici, 1958) are also very similar to those of the chain isomer, whereas the Zn compound is isotypic to the title complex (ZZZDUE; Nardelli & Chierici, 1958). Later, Nardelli and co-workers reported the crystal structure of $Ni(NCS)_2(C_3H_6N_2S)_2$ (ESUNSC10; Nardelli *et al.*, 1966), which consists of chains and is isotypic to the chain isomer of the corresponding Co compound. The crystal structure of the Cd compound is also published and

consists of chains, but is not isotypic to the Co and Ni compounds (ETCDTH; Calvaca *et al.*, 1960).

Finally, there are some compounds with $Co(NCS)_2$ and other thiourea derivatives as ligand reported in the CSD, including $Co(NCS)_2$(tetramethylthiourea)$_2$ (WUQTIO; Jochim *et al.*, 2020*b*), $Co(NCS)_2$(*N*,*N*′-dimethylthiourea)$_2$ (QUSZAI; Jochim *et al.*, 2020*c*) and $Co(NCS)_2$(1,3-dicyclohexylthiourea)$_2$ (LAMPUO; Krebs *et al.*, 2022). All of these compounds consist of discrete complexes with a tetrahedral coordination. However, in $Co(NCS)_2$(thiourea)$_2$, the cobalt cations are linked by pairs of μ-1,3-bridging thiocyanate into chains (LEHQAS; Rajarajan *et al.*, 2012).

6. Synthesis and crystallization

Cobalt thiocyanate and ethylenethiourea were purchased from Sigma-Aldrich. 87.6 mg (0.50 mmol) of $Co(NCS)_2$ and 102.4 mg (1.0 mmol) of ethylenethiourea were stirred in 3 ml of ethanol for 3 d. Then, 3 ml of *n*-heptane were added and stirred for another 10 min. The precipitate was filtered off, leading to a microcrystalline powder of the title compound. As the solvent slowly evaporated from the filtrate, blue block-shaped crystals suitable for single crystal X-ray diffraction were obtained.

The chain isomer of $Co(NCS)_2(C_3H_6N_2S)_2$ used for the solvent-mediated conversion experiments was prepared according to literature procedures (Jochim *et al.*, 2020*a*).

The IR spectroscopic measurements were performed with an ATI Mattson Genesis Series FTIR Spectrometer, control software: *WINFIRST*, from ATI Mattson in ATR mode. The PXRD measurements were performed with Cu $K\alpha_1$ radiation (λ = 1.540598 Å) using a Stoe Transmission Powder Diffraction System (STADI P) equipped with a MYTHEN 1K detector and a Johansson-type Ge(111) monochromator.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.The C-bound hydrogen atoms were positioned with idealized geometry and were refined isotropically with U_{iso}(H) = 1.2 U_{eq}(C) using a riding model. The N-bound hydrogen atoms were located in difference maps, their bond lengths set to ideal values and finally they were refined isotropically with U_{iso}(H) = 1.2 U_{eq}(N) using a riding model.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Co(NCS)_2(C_3H_6N_2S)_2]$
M_r	379.41
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	170
a, b, c (Å)	7.7636 (2), 9.1388 (3), 21.9230 (5)
β (°)	96.552 (2)
V (Å^3)	1545.28 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.65
Crystal size (mm)	0.18 × 0.11 × 0.08
Data collection	
Diffractometer	Stoe IPDS2
Absorption correction	Numerical (*X-SHAPE* and *X-RED* 32; Stoe, 2008)
T_{min}, T_{max}	0.638, 0.798
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21701, 3351, 3080
R_{int}	0.022
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.062, 1.08
No. of reflections	3351
No. of parameters	172
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.23

Computer programs: *X-AREA* and *X-RED* (Stoe, 2008), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 1999), *XP* in *SHELXTL-PC* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

Acknowledgements

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supporting information

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Christian Näther and Aleksej Jochim

Computing details

Bis(imidazolidine-2-thione-*κS*)dithiocyanatocobalt(II)

Crystal data

$[Co(NCS)_2(C_3H_6N_2S)_2]$
M_r = 379.41
Monoclinic, $P2_1/c$
a = 7.7636 (2) Å
b = 9.1388 (3) Å
c = 21.9230 (5) Å
β = 96.552 (2)°
V = 1545.28 (7) Å^3
Z = 4
$F(000)$ = 772
D_x = 1.631 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8000 reflections
θ = 10.0–25.0°
μ = 1.65 mm^{-1}
T = 170 K
Block, blue
0.18 × 0.11 × 0.08 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: numerical (X-Shape and X-Red 32; Stoe, 2008)
T_{min} = 0.638, T_{max} = 0.798
21701 measured reflections
3351 independent reflections
3080 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 27.0°, θ_{min} = 1.9°
h = −9→9
k = −11→11
l = −28→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.062
S = 1.08
3351 reflections
172 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 0.5882P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.21856 (3)	0.34622 (2)	0.40792 (2)	0.03252 (8)
N1	0.2712 (2)	0.27718 (18)	0.49188 (7)	0.0412 (3)
C1	0.3166 (2)	0.2152 (2)	0.53726 (8)	0.0372 (4)
S1	0.37618 (8)	0.12604 (6)	0.59973 (2)	0.05231 (14)
N2	0.1156 (2)	0.18903 (18)	0.35535 (7)	0.0413 (3)
C2	0.0766 (2)	0.08932 (19)	0.32363 (7)	0.0336 (3)
S2	0.02460 (6)	−0.05075 (5)	0.27987 (2)	0.03993 (11)
S11	0.00832 (5)	0.52604 (5)	0.39459 (2)	0.03687 (11)
C11	0.1030 (2)	0.66747 (18)	0.43786 (7)	0.0321 (3)
N11	0.0839 (2)	0.80539 (18)	0.42222 (7)	0.0437 (4)
H11	0.029316	0.832996	0.386690	0.052*
N12	0.2017 (2)	0.65511 (16)	0.49075 (7)	0.0410 (3)
H12	0.213882	0.575491	0.513402	0.049*
C12	0.2443 (3)	0.7985 (2)	0.51792 (9)	0.0440 (4)
H12A	0.369897	0.807233	0.531493	0.053*
H12B	0.178507	0.817590	0.553222	0.053*
C13	0.1886 (3)	0.9017 (2)	0.46461 (9)	0.0436 (4)
H13A	0.119347	0.984540	0.477760	0.052*
H13B	0.289889	0.940337	0.446111	0.052*
S21	0.48883 (6)	0.42711 (5)	0.38813 (2)	0.03941 (11)
C21	0.4724 (2)	0.53905 (18)	0.32552 (7)	0.0311 (3)
N21	0.60888 (19)	0.57669 (18)	0.29779 (7)	0.0393 (3)
H21	0.717127	0.559478	0.312620	0.047*
N22	0.33055 (18)	0.59910 (18)	0.29709 (7)	0.0375 (3)
H22	0.229503	0.573146	0.308204	0.045*
C22	0.3662 (2)	0.6770 (2)	0.24139 (9)	0.0457 (4)
H22A	0.311627	0.775101	0.238903	0.055*
H22B	0.325286	0.620757	0.203928	0.055*
C23	0.5628 (2)	0.6878 (3)	0.25054 (9)	0.0476 (5)
H23A	0.613416	0.664837	0.212208	0.057*
H23B	0.601404	0.786424	0.264968	0.057*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.03490 (13)	0.03183 (12)	0.03132 (12)	−0.00233 (9)	0.00588 (9)	0.00202 (8)
N1	0.0486 (9)	0.0421 (8)	0.0333 (7)	−0.0018 (7)	0.0065 (6)	0.0033 (6)
C1	0.0409 (9)	0.0361 (9)	0.0356 (9)	−0.0001 (7)	0.0084 (7)	−0.0041 (7)
S1	0.0693 (3)	0.0490 (3)	0.0373 (2)	0.0069 (2)	0.0002 (2)	0.0068 (2)
N2	0.0449 (9)	0.0403 (8)	0.0390 (8)	−0.0043 (7)	0.0061 (6)	0.0006 (7)
C2	0.0322 (8)	0.0377 (9)	0.0313 (8)	0.0002 (7)	0.0048 (6)	0.0058 (7)
S2	0.0456 (2)	0.0387 (2)	0.0345 (2)	0.00118 (18)	0.00043 (17)	−0.00220 (17)
S11	0.0325 (2)	0.0404 (2)	0.0370 (2)	0.00086 (17)	0.00088 (16)	0.00048 (17)
C11	0.0289 (8)	0.0362 (8)	0.0318 (8)	0.0033 (6)	0.0070 (6)	0.0063 (6)
N11	0.0472 (9)	0.0384 (8)	0.0429 (8)	−0.0003 (7)	−0.0057 (7)	0.0120 (7)

N12	0.0519 (9)	0.0335 (8)	0.0355 (8)	0.0029 (7)	−0.0048 (6)	0.0055 (6)
C12	0.0503 (11)	0.0363 (9)	0.0436 (10)	0.0002 (8)	−0.0031 (8)	−0.0005 (8)
C13	0.0460 (10)	0.0342 (9)	0.0498 (10)	0.0016 (8)	0.0021 (8)	0.0028 (8)
S21	0.0319 (2)	0.0459 (2)	0.0396 (2)	−0.00271 (17)	0.00027 (16)	0.01317 (18)
C21	0.0307 (8)	0.0317 (8)	0.0309 (8)	−0.0011 (6)	0.0034 (6)	−0.0025 (6)
N21	0.0280 (7)	0.0483 (9)	0.0426 (8)	0.0028 (6)	0.0085 (6)	0.0102 (7)
N22	0.0280 (7)	0.0475 (8)	0.0376 (7)	0.0007 (6)	0.0065 (6)	0.0111 (6)
C22	0.0388 (10)	0.0556 (12)	0.0437 (10)	0.0054 (8)	0.0096 (8)	0.0184 (9)
C23	0.0401 (10)	0.0595 (12)	0.0447 (10)	0.0002 (9)	0.0110 (8)	0.0180 (9)

Geometric parameters (Å, º)

Co1—N1	1.9446 (15)	C12—H12A	0.9900
Co1—N2	1.9544 (16)	C12—H12B	0.9900
Co1—S11	2.3111 (5)	C13—H13A	0.9900
Co1—S21	2.3120 (5)	C13—H13B	0.9900
N1—C1	1.164 (2)	S21—C21	1.7050 (17)
C1—S1	1.6153 (18)	C21—N22	1.321 (2)
N2—C2	1.165 (2)	C21—N21	1.326 (2)
C2—S2	1.6228 (18)	N21—C23	1.466 (2)
S11—C11	1.7182 (18)	N21—H21	0.8800
C11—N11	1.310 (2)	N22—C22	1.467 (2)
C11—N12	1.320 (2)	N22—H22	0.8801
N11—C13	1.459 (2)	C22—C23	1.520 (3)
N11—H11	0.8800	C22—H22A	0.9900
N12—C12	1.462 (2)	C22—H22B	0.9900
N12—H12	0.8799	C23—H23A	0.9900
C12—C13	1.526 (3)	C23—H23B	0.9900
N1—Co1—N2	110.32 (7)	N11—C13—H13A	111.4
N1—Co1—S11	114.80 (5)	C12—C13—H13A	111.4
N2—Co1—S11	102.29 (5)	N11—C13—H13B	111.4
N1—Co1—S21	100.61 (5)	C12—C13—H13B	111.4
N2—Co1—S21	116.30 (5)	H13A—C13—H13B	109.3
S11—Co1—S21	113.076 (19)	C21—S21—Co1	110.89 (6)
C1—N1—Co1	167.80 (15)	N22—C21—N21	110.04 (15)
N1—C1—S1	178.59 (18)	N22—C21—S21	127.65 (13)
C2—N2—Co1	171.01 (15)	N21—C21—S21	122.30 (13)
N2—C2—S2	179.20 (17)	C21—N21—C23	111.12 (15)
C11—S11—Co1	102.33 (6)	C21—N21—H21	124.3
N11—C11—N12	110.46 (16)	C23—N21—H21	122.1
N11—C11—S11	123.40 (13)	C21—N22—C22	111.61 (14)
N12—C11—S11	126.14 (13)	C21—N22—H22	118.6
C11—N11—C13	112.06 (15)	C22—N22—H22	128.3
C11—N11—H11	122.4	N22—C22—C23	101.74 (14)
C13—N11—H11	124.6	N22—C22—H22A	111.4
C11—N12—C12	111.27 (15)	C23—C22—H22A	111.4
C11—N12—H12	125.5	N22—C22—H22B	111.4

C12—N12—H12	120.4	C23—C22—H22B	111.4
N12—C12—C13	102.19 (15)	H22A—C22—H22B	109.3
N12—C12—H12A	111.3	N21—C23—C22	102.05 (14)
C13—C12—H12A	111.3	N21—C23—H23A	111.4
N12—C12—H12B	111.3	C22—C23—H23A	111.4
C13—C12—H12B	111.3	N21—C23—H23B	111.4
H12A—C12—H12B	109.2	C22—C23—H23B	111.4
N11—C13—C12	101.73 (15)	H23A—C23—H23B	109.2
Co1—S11—C11—N11	143.67 (14)	Co1—S21—C21—N22	12.57 (18)
Co1—S11—C11—N12	−37.17 (16)	Co1—S21—C21—N21	−166.68 (13)
N12—C11—N11—C13	5.1 (2)	N22—C21—N21—C23	7.9 (2)
S11—C11—N11—C13	−175.63 (13)	S21—C21—N21—C23	−172.69 (14)
N11—C11—N12—C12	5.5 (2)	N21—C21—N22—C22	4.9 (2)
S11—C11—N12—C12	−173.74 (14)	S21—C21—N22—C22	−174.42 (14)
C11—N12—C12—C13	−12.9 (2)	C21—N22—C22—C23	−14.7 (2)
C11—N11—C13—C12	−12.6 (2)	C21—N21—C23—C22	−16.5 (2)
N12—C12—C13—N11	14.3 (2)	N22—C22—C23—N21	17.5 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···S2^{i}	0.88	2.57	3.3693 (16)	152
N12—H12···S11^{ii}	0.88	2.95	3.5571 (17)	128
N12—H12···S21^{iii}	0.88	2.97	3.4542 (15)	116
C12—H12*A*···S21^{iii}	0.99	2.91	3.4371 (19)	114
C13—H13*B*···S1^{iii}	0.99	2.95	3.816 (2)	147
N21—H21···S11^{iv}	0.88	2.74	3.5823 (16)	161
N22—H22···S2^{v}	0.88	2.83	3.3560 (16)	120
N22—H22···S11	0.88	2.73	3.5346 (15)	152
C22—H22*A*···S2^{i}	0.99	2.96	3.800 (2)	143

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*+1, *y*, *z*; (v) −*x*, *y*+1/2, −*z*+1/2.