

catena-Poly[[bis(thiocyanato- κ N)-cobalt(II)]-di- μ -thiourea- κ^4 S:S]

K. Rajarajan,^{a*} K. Sendil Kumar,^b V. Ramesh,^b
V. Shihabuddeen^b and S. Murugavel^{c*}

^aDepartment of Physics, Rajeswari Vedachalam Government Arts College, Chengalpet 603 301, India, ^bResearch and Development Center, Bharathiar University, Coimbatore 641 046, India, and ^cDepartment of Physics, Thanthai Periyar Government Institute of Technology, Vellore 632 002, India
Correspondence e-mail: drkr2007@gmail.com, smurugavel27@gmail.com

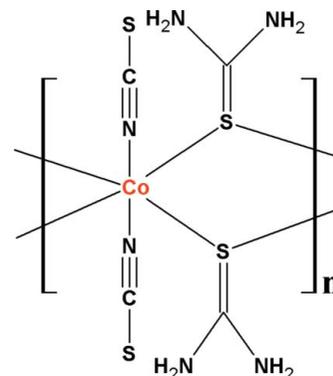
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Co}-\text{S}) = 0.002$ Å; R factor = 0.019; wR factor = 0.052; data-to-parameter ratio = 26.0.

In the title polymeric complex, $[\text{Co}(\text{NCS})_2\{\text{SC}(\text{NH}_2)_2\}_2]_n$, the asymmetric unit comprises a Co^{II} ion, which is situated on an inversion centre, an N -bound thiocyanate anion and a μ_2 -bridging thiourea molecule. The Co^{II} atom is coordinated in a distorted octahedral fashion within an N_2S_4 donor set. The bridging thiourea ligands link Co^{II} ions into a polymeric chain extending along $[100]$. The molecular conformation is stabilized by intramolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, which generate $S(6)$ ring motifs. The crystal packing is stabilized by $\text{N}-\text{H}\cdots\text{S}$ interactions, which connect the chains into a three-dimensional architecture.

Related literature

For a general introduction to thiocyanato complexes, see: Nardelli *et al.* (1957). For the crystal structure of the analogous Cd^{II} complex, see: Wang *et al.* (2002). For information on the properties of complexes incorporating these ligands, see: Yuan *et al.* (1997); Yu *et al.* (2001); Machura *et al.* (2011). For the use of Co^{II} complexes with mixed S-donor ligands as precursors to CoS , see: Kropidłowska *et al.* (2008). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$[\text{Co}(\text{NCS})_2(\text{CH}_4\text{N}_2\text{S})_2]$
 $M_r = 327.33$
Triclinic, $P\bar{1}$
 $a = 3.855$ (3) Å
 $b = 7.585$ (2) Å
 $c = 10.094$ (2) Å
 $\alpha = 92.424$ (3)°
 $\beta = 98.172$ (2)°

$\gamma = 104.166$ (2)°
 $V = 282.4$ (2) Å³
 $Z = 1$
Mo $K\alpha$ radiation
 $\mu = 2.23$ mm⁻¹
 $T = 293$ K
 $0.24 \times 0.22 \times 0.16$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.591$, $T_{\text{max}} = 0.699$

6452 measured reflections
1844 independent reflections
1764 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$
 $wR(F^2) = 0.052$
 $S = 1.07$
1844 reflections

71 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.61$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N}2-\text{H}2\text{B}\cdots\text{N}1$	0.86	2.26	3.079 (3)	159
$\text{N}2-\text{H}2\text{A}\cdots\text{S}1^{\text{i}}$	0.86	2.70	3.461 (3)	148
$\text{N}3-\text{H}3\text{A}\cdots\text{S}1^{\text{ii}}$	0.86	2.78	3.483 (3)	140
$\text{N}3-\text{H}3\text{B}\cdots\text{S}2^{\text{iii}}$	0.86	2.62	3.456 (3)	166

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

Data collection: APEX2 (Bruker, 2004); cell refinement: APEX2 and SAINT (Bruker, 2004); data reduction: SAINT and XPREP (Bruker, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia (1997)); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK5133).

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supporting information

Acta Cryst. (2012). E68, m1125–m1126 [https://doi.org/10.1107/S1600536812033193]

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S1. Comment

The interest in the coordination compounds possessing both thiourea and thiocyanato ligands dates back to the 1950's (*e.g.* Nardelli *et al.*, 1957) when the nature of coordination compounds formed by divalent cations ($M = \text{Mn, Co, Ni, Cd, Pb}$) and organic molecules containing sulfur was extensively studied. The interest in these compounds is related either to their non-linear optical properties (Yuan *et al.*, 1997, Yu *et al.*, 2001) or with their possible use as single-source precursors of semiconducting materials. Moreover, the use of SCN ligands, with bridging abilities, may lead to intriguing architectures and topologies, often generating one-dimensional chains (Machura *et al.*, 2011). For the above reasons and during our studies on new molecular precursors (Kropidłowska *et al.*, 2008), we turned our attention to systems of this type, that is, complexes containing thiourea and thiocyanate ligands connected to a cobalt center.

The title complex, Fig. 1, is isostructural with the previously reported cadmium(II) complex (Wang *et al.*, 2002). The Co^{II} atom is located at the inversion centre and is octahedrally coordinated by two N atoms from two thiocyanate groups and four S atoms from four thiourea molecules. The bridging thiourea ligands link Co^{II} ions into a one dimensional polymeric chain along [100] (Fig. 2). The $\text{Co}\cdots\text{Co}$ distance along the chain is 3.855 (3) Å. The octahedral coordination sphere of the cobalt(II) cation is slightly distorted with distances in the range of 2.016 (1) Å to 2.623 (1) Å. The angles around the cobalt(II) atom range from 83.4 (1)° to 180°. The thiocyanate group is almost linear with the $\text{N1}-\text{C1}-\text{S1}$ angle = 179.2 (1)°.

The molecular conformation is stabilized by intramolecular $\text{N2}-\text{H2B}\cdots\text{N1}$ hydrogen bond, forming an $S(6)$ ring motif (Bernstein *et al.*, 1995). In the crystal, molecules are linked by $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds into a three-dimensional architecture (Table 1).

S2. Experimental

Cobalt(II) chloride, ammonium thiocyanate and thiourea were dissolved in aqueous solution in the molar ratio 1:2:2 and stirred well for 2 h to obtain an homogeneous mixture. The dark-brown crystals of the title compound were obtained after the filtrate and had been allowed to stand at room temperature for two weeks.

S3. Refinement

H atoms were positioned geometrically, with $\text{N}-\text{H} = 0.86$ Å and constrained to ride on their parent atom, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

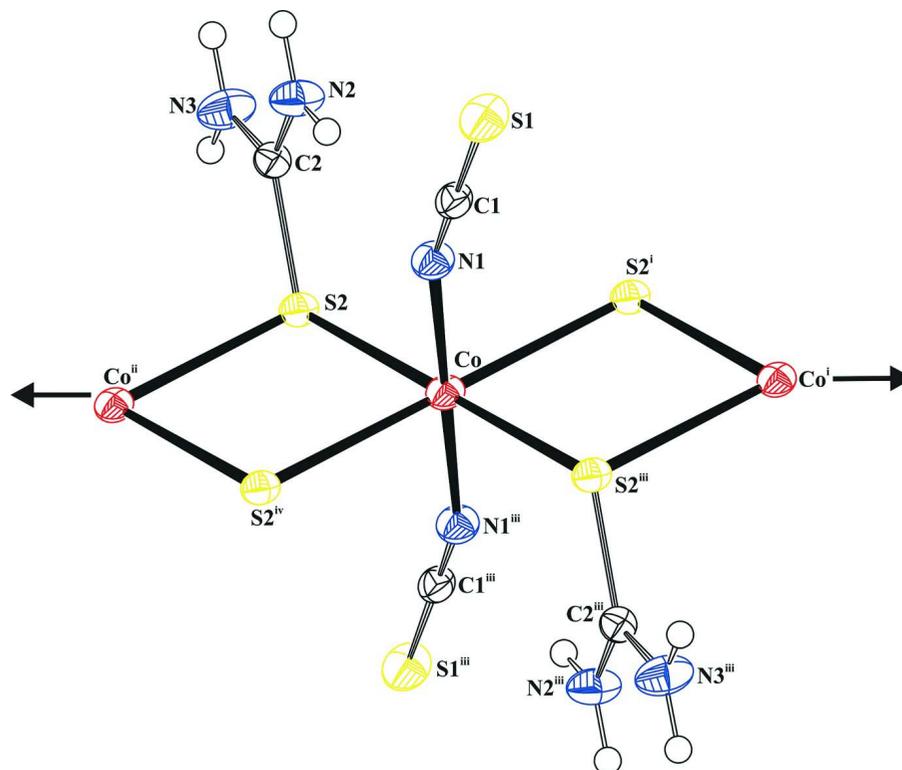


Figure 1

Asymmetric unit of the title complex expanded to show the coordination geometry of the Co^{II} atom and the polymeric connectivity. Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as a small circles of arbitrary radius. [Symmetry codes: (i) $-1 + x, y, z$; (ii) $1 + x, y, z$; (iii) $1 - x, -y, 1 - z$; (iv) $2 - x, -y, 1 - z$].

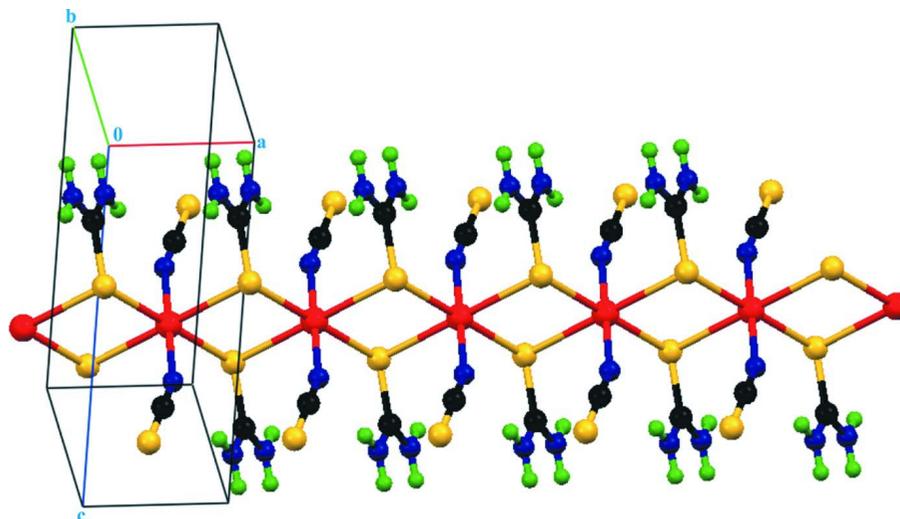


Figure 2

A view of the linear polymeric chain aligned along $[100]$ in the title complex. Colour code: Co, red; N, blue; S, yellow; C, black; H, green.

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$M_r = 327.33$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 3.855$ (3) Å

$b = 7.585$ (2) Å

$c = 10.094$ (2) Å

$\alpha = 92.424$ (3)°

$\beta = 98.172$ (2)°

$\gamma = 104.166$ (2)°

$V = 282.4$ (2) Å³

$Z = 1$

$F(000) = 165$

$D_x = 1.925$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2298 reflections

$\theta = 2.0$ – 34.1 °

$\mu = 2.23$ mm⁻¹

$T = 293$ K

Block, brown

$0.24 \times 0.22 \times 0.16$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 10.0 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.591$, $T_{\max} = 0.699$

6452 measured reflections

1844 independent reflections

1764 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 34.1$ °, $\theta_{\min} = 2.0$ °

$h = -5 \rightarrow 5$

$k = -11 \rightarrow 10$

$l = -14 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.052$

$S = 1.07$

1844 reflections

71 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

$w = 1/[\sigma^2(F_o^2) + (0.0264P)^2 + 0.0757P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.61$ e Å⁻³

$\Delta\rho_{\min} = -0.33$ e Å⁻³

Extinction correction: *SHELXL97* (Sheldrick,

2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.203 (7)

Special details

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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5577 (3)	0.18192 (15)	0.78972 (10)	0.01952 (19)

C2	0.9805 (3)	-0.29358 (15)	0.69572 (11)	0.02016 (19)
N1	0.5889 (3)	0.10262 (13)	0.69282 (9)	0.02280 (18)
N2	0.9447 (3)	-0.19551 (16)	0.80075 (10)	0.0295 (2)
H2A	0.9899	-0.2301	0.8800	0.035*
H2B	0.8759	-0.0966	0.7903	0.035*
N3	1.0858 (3)	-0.44519 (15)	0.71126 (11)	0.0324 (2)
H3A	1.1313	-0.4801	0.7904	0.039*
H3B	1.1091	-0.5092	0.6423	0.039*
S1	0.51233 (9)	0.29477 (5)	0.92362 (3)	0.03241 (9)
S2	0.89332 (7)	-0.22779 (3)	0.53449 (2)	0.01878 (8)
Co	0.5000	0.0000	0.5000	0.01874 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0193 (4)	0.0231 (5)	0.0165 (4)	0.0073 (4)	0.0011 (3)	0.0004 (3)
C2	0.0189 (4)	0.0209 (5)	0.0200 (4)	0.0033 (4)	0.0031 (3)	0.0046 (4)
N1	0.0259 (4)	0.0256 (4)	0.0169 (4)	0.0078 (4)	0.0022 (3)	-0.0016 (3)
N2	0.0430 (6)	0.0313 (5)	0.0173 (4)	0.0147 (4)	0.0056 (4)	0.0040 (4)
N3	0.0484 (6)	0.0269 (5)	0.0256 (5)	0.0173 (5)	0.0027 (4)	0.0072 (4)
S1	0.03586 (17)	0.0469 (2)	0.01841 (14)	0.02104 (14)	0.00223 (11)	-0.00877 (12)
S2	0.02254 (13)	0.01991 (13)	0.01566 (12)	0.00861 (9)	0.00307 (9)	0.00202 (8)
Co	0.02202 (11)	0.02291 (12)	0.01230 (10)	0.00862 (8)	0.00200 (7)	-0.00215 (7)

Geometric parameters (Å, °)

C1—N1	1.1627 (14)	N3—H3A	0.8600
C1—S1	1.6226 (11)	N3—H3B	0.8600
C2—N2	1.3121 (15)	S2—Co	2.5668 (10)
C2—N3	1.3182 (15)	S2—Co ⁱ	2.6231 (14)
C2—S2	1.7338 (11)	Co—N1 ⁱⁱ	2.0158 (10)
N1—Co	2.0158 (10)	Co—S2 ⁱⁱ	2.5668 (10)
N2—H2A	0.8600	Co—S2 ⁱⁱⁱ	2.6231 (14)
N2—H2B	0.8600	Co—S2 ^{iv}	2.6231 (14)
N1—C1—S1	179.17 (10)	N1—Co—S2 ⁱⁱ	83.37 (3)
N2—C2—N3	120.18 (11)	N1 ⁱⁱ —Co—S2 ⁱⁱ	96.63 (3)
N2—C2—S2	121.31 (9)	N1—Co—S2	96.63 (3)
N3—C2—S2	118.50 (9)	N1 ⁱⁱ —Co—S2	83.37 (3)
C1—N1—Co	160.34 (9)	S2 ⁱⁱ —Co—S2	180.000 (11)
C2—N2—H2A	120.0	N1—Co—S2 ⁱⁱⁱ	88.73 (3)
C2—N2—H2B	120.0	N1 ⁱⁱ —Co—S2 ⁱⁱⁱ	91.27 (3)
H2A—N2—H2B	120.0	S2 ⁱⁱ —Co—S2 ⁱⁱⁱ	95.93 (5)
C2—N3—H3A	120.0	S2—Co—S2 ⁱⁱⁱ	84.07 (5)
C2—N3—H3B	120.0	N1—Co—S2 ^{iv}	91.27 (3)
H3A—N3—H3B	120.0	N1 ⁱⁱ —Co—S2 ^{iv}	88.73 (3)
C2—S2—Co	117.06 (4)	S2 ⁱⁱ —Co—S2 ^{iv}	84.07 (5)
C2—S2—Co ⁱ	104.64 (4)	S2—Co—S2 ^{iv}	95.93 (5)

Co—S2—Co ⁱ	95.93 (5)	S2 ⁱⁱⁱ —Co—S2 ^{iv}	180.000 (11)
N1—Co—N1 ⁱⁱ	180.0		
S1—C1—N1—Co	-33 (7)	C2—S2—Co—N1	21.76 (5)
N2—C2—S2—Co	-19.76 (11)	Co ⁱ —S2—Co—N1	-88.02 (3)
N3—C2—S2—Co	160.47 (8)	C2—S2—Co—N1 ⁱⁱ	-158.24 (5)
N2—C2—S2—Co ⁱ	84.92 (10)	Co ⁱ —S2—Co—N1 ⁱⁱ	91.98 (3)
N3—C2—S2—Co ⁱ	-94.85 (10)	C2—S2—Co—S2 ⁱⁱ	-117 (100)
C1—N1—Co—N1 ⁱⁱ	-140 (100)	Co ⁱ —S2—Co—S2 ⁱⁱ	133 (100)
C1—N1—Co—S2 ⁱⁱ	12.8 (3)	C2—S2—Co—S2 ⁱⁱⁱ	109.79 (4)
C1—N1—Co—S2	-167.2 (3)	Co ⁱ —S2—Co—S2 ⁱⁱⁱ	0.0
C1—N1—Co—S2 ⁱⁱⁱ	108.9 (3)	C2—S2—Co—S2 ^{iv}	-70.21 (4)
C1—N1—Co—S2 ^{iv}	-71.1 (3)	Co ⁱ —S2—Co—S2 ^{iv}	180.0

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N2—H2B...N1	0.86	2.26	3.079 (3)	159
N2—H2A...S1 ^v	0.86	2.70	3.461 (3)	148
N3—H3A...S1 ^{vi}	0.86	2.78	3.483 (3)	140
N3—H3B...S2 ^{vii}	0.86	2.62	3.456 (3)	166

Symmetry codes: (v) $-x+2, -y, -z+2$; (vi) $x+1, y-1, z$; (vii) $-x+2, -y-1, -z+1$.