

catena-Poly[[bis(2-chloropyrazine- κN^4)-cadmium]-di- μ -thiocyanato- $\kappa^2 N:S;\kappa^2 S:N$]

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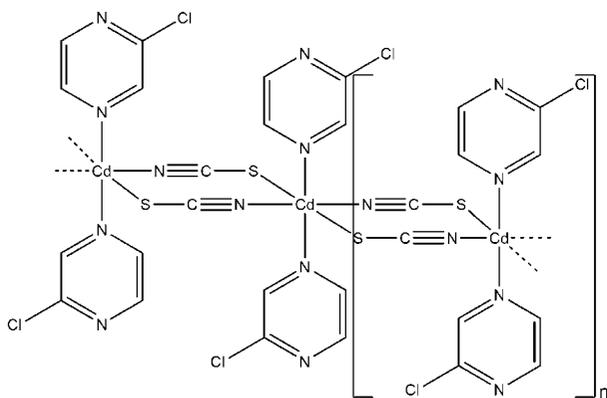
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.029; wR factor = 0.072; data-to-parameter ratio = 16.4.

Reaction of cadmium thiocyanate with 2-chloropyrazine leads to the polymeric title compound, $[Cd(NCS)_2(C_4H_3ClN_2)_2]_n$. The Cd^{II} cation, which is located on a center of inversion, is coordinated by two N -bonded and two S -bonded thiocyanate anions and by two N -bonded 2-chloropyrazine ligands within a slightly distorted octahedron. The Cd^{II} cations are linked into chains along the a axis by bridging thiocyanate anions.

Related literature

For the background to this work and the synthesis of bridging thiocyanato coordination polymers, see: Wöhlert *et al.* (2012, 2013).



Experimental

Crystal data

$[Cd(NCS)_2(C_4H_3ClN_2)_2]$
 $M_r = 457.63$
 Triclinic, $P\bar{1}$
 $a = 5.7151$ (6) Å
 $b = 6.7625$ (8) Å
 $c = 11.2915$ (13) Å
 $\alpha = 76.895$ (9)°
 $\beta = 82.639$ (9)°

$\gamma = 73.068$ (8)°
 $V = 405.70$ (8) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 1.93$ mm⁻¹
 $T = 293$ K
 $0.17 \times 0.15 \times 0.10$ mm

Data collection

Stoe IPDS-2 diffractometer
 Absorption correction: numerical
 (X -SHAPE and X -RED32; Stoe & Cie, 2008)
 $T_{min} = 0.551$, $T_{max} = 0.719$

5777 measured reflections
 1592 independent reflections
 1492 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.068$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.072$
 $S = 1.02$
 1592 reflections

97 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.56$ e Å⁻³
 $\Delta\rho_{min} = -0.49$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cd1—N1	2.287 (3)	Cd1—S1 ⁱ	2.7071 (9)
Cd1—N12	2.417 (2)		

 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, 2011); software used to prepare material for publication: $XCIF$ in $SHELXTL$ and $publCIF$ (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT6896).

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supporting information

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S1. Comment

Recently we have reported on the synthesis and characterization of cadmium(II) thiocyanato coordination polymers with different neutral N-donor co-ligands. For $[\text{Cd}(\text{NCS})_2(4\text{-ethylpyridine})_2]_n$ a one-dimensional structure was observed, in which the metal cations are octahedrally coordinated by two N and two S atoms of the thiocyanato anions and two N atoms of the co-ligands all of them in an all-*trans* coordination (Wöhlert *et al.*, 2013). In contrast, for $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$, three different modifications were obtained in which the anionic ligands are all-*trans*, all-*cis* or *cis-cis-trans* coordinated (Wöhlert *et al.*, 2012). To investigate the influence of the neutral co-ligand in more detail, 2-chloropyrazine was selected, which can act as a bidentate as well as a monodentate ligand. Therefore, cadmium(II) thiocyanate was reacted with 2-chloropyrazine in water which results in the formation of single crystals suitable for structure determination.

The crystal structure of $[\text{Cd}(\text{NCS})_2(2\text{-chloropyrazine})_2]_n$ consists of cadmium(II) cations that are located on centers of inversion as well as of thiocyanato anions and 2-chloropyrazine ligand in general position. Each cadmium(II) cation is coordinated by two *N*-bonded and two *S*-bonded thiocyanato anions as well as two 2-chloropyrazine ligands within a slightly distorted octahedral geometry (Fig. 1). The CdN_4S_2 distances ranges from 2.287 (3) Å to 2.7071 (9) Å with angles around the cadmium(II) cation between 87.75 (8) ° to 92.25 (8) ° and of 180 ° (Tab. 1). In the crystal structure the cadmium(II) cations are connected through μ -1,3 bridging thiocyanato anions into one-dimensional polymeric chains, in which all thiocyanato anions and the 2-chloropyrazine ligand are *trans*-coordinated (Fig. 2). The intrachain cadmium-cadmium separation amounts to 5.7151 (6) Å, whereas the shortest interchain Cd—Cd distance is 11.2915 (13) Å. This structural motif is frequently found in cadmium thiocyanato coordination compounds and might represent the most stable coordination. However, in this context it is noted that for $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$, the form with a *cis-cis-trans* coordination represents the thermodynamic stable form at room-temperature and this might be an exception (Wöhlert *et al.*, 2012).

S2. Experimental

$\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, $\text{Ba}(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$ and 2-chloropyrazine were obtained from Alfa Aesar. All chemicals were used without further purification. $\text{Cd}(\text{NCS})_2$ was prepared by the reaction of equimolar amounts of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ with $\text{Ba}(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$ in water. The resulting precipitate of BaSO_4 were filtered off and the filtrate were concentrated to complete dryness resulting in white residues of $\text{Cd}(\text{NCS})_2$. The purity was checked by XRPD and CHNS analysis. 0.1 mmol (22.0 mg) $\text{Cd}(\text{NCS})_2$ and 0.4 mmol (32.0 μL) 2-chloropyrazine were reacted in 1 ml water. Colorless single crystals of the title compound were obtained after three days.

S3. Refinement

All H atoms were located in difference map but were positioned with idealized geometry and were refined isotropic with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ using a riding model with $\text{C}-\text{H} = 0.93 \text{ \AA}$.

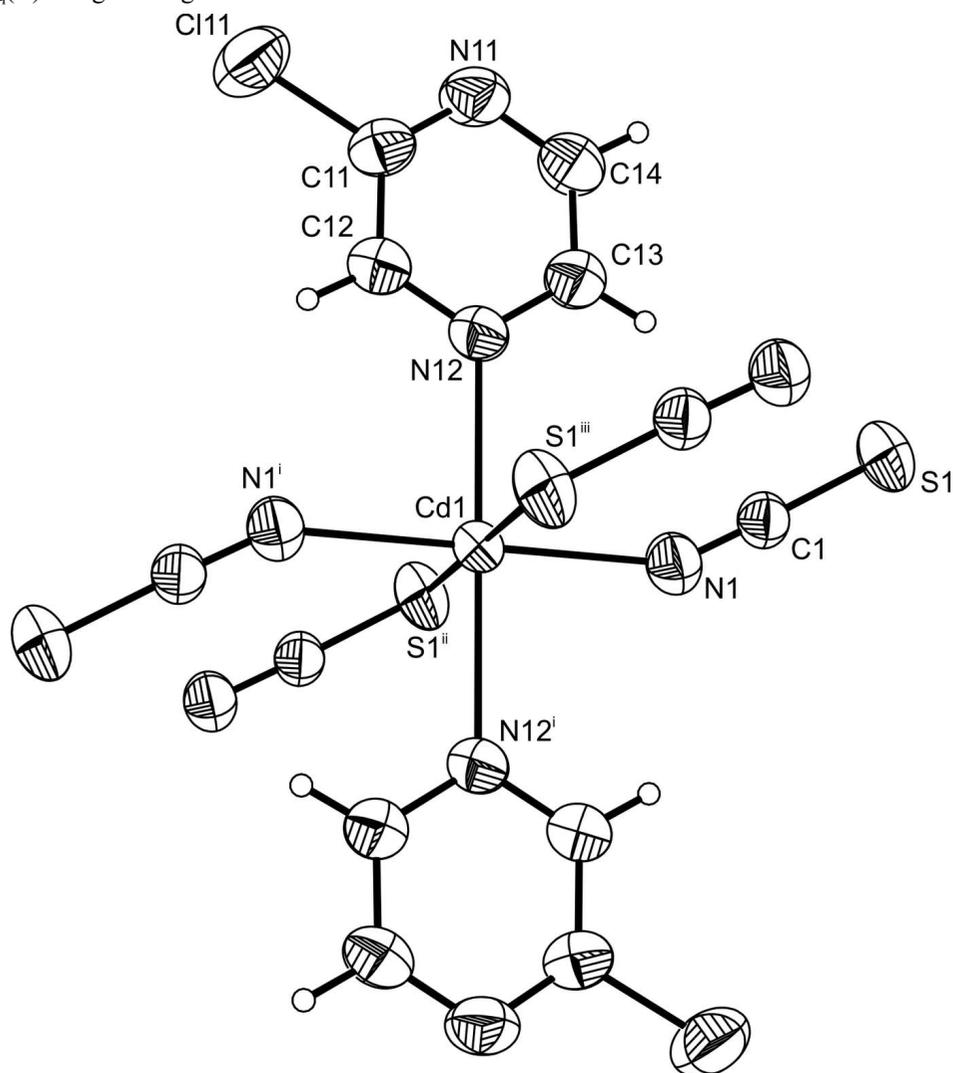


Figure 1

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

Symmetry code: $i = -x + 1, -y + 1, -z$; $ii = x - 1, y, z$; $iii = -x + 2, -y + 1, -z$.

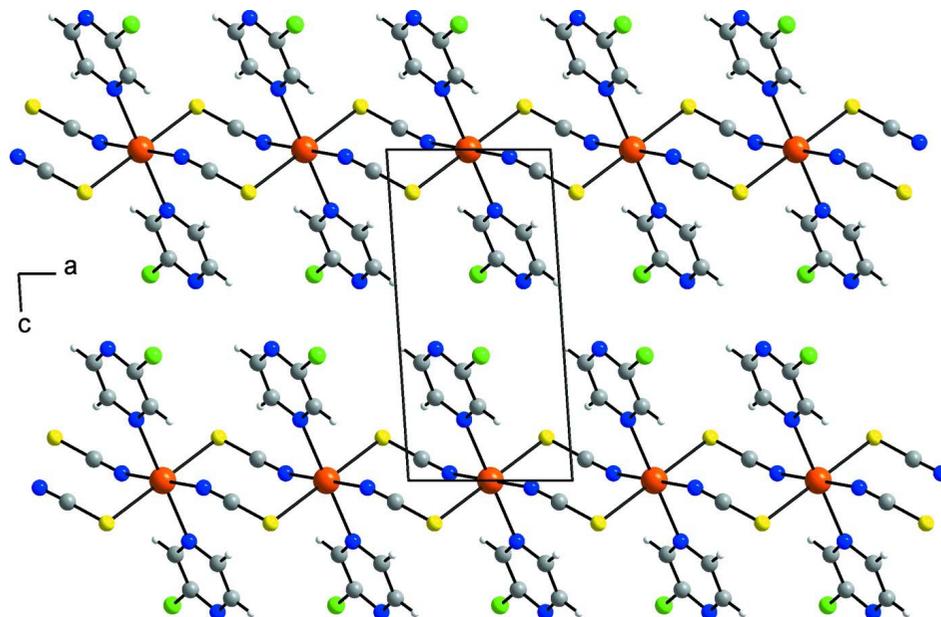


Figure 2

Crystal structure of the title compound with view along the b -axis (orange = cadmium, blue = nitrogen, yellow = sulfur, green = chloro, grey = carbon, white = hydrogen).

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Crystal data

$[\text{Cd}(\text{NCS})_2(\text{C}_4\text{H}_3\text{ClN}_2)_2]$

$M_r = 457.63$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 5.7151\ (6)\ \text{\AA}$

$b = 6.7625\ (8)\ \text{\AA}$

$c = 11.2915\ (13)\ \text{\AA}$

$\alpha = 76.895\ (9)^\circ$

$\beta = 82.639\ (9)^\circ$

$\gamma = 73.068\ (8)^\circ$

$V = 405.70\ (8)\ \text{\AA}^3$

$Z = 1$

$F(000) = 222$

$D_x = 1.873\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 5777 reflections

$\theta = 1.9\text{--}26.0^\circ$

$\mu = 1.93\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colourless

$0.17 \times 0.15 \times 0.10\ \text{mm}$

Data collection

Stoe IPDS-2
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scan

Absorption correction: numerical

(*X-SHAPE* and *X-RED32*; Stoe & Cie, 2008)

$T_{\min} = 0.551$, $T_{\max} = 0.719$

5777 measured reflections

1592 independent reflections

1492 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.068$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -7 \rightarrow 7$

$k = -8 \rightarrow 8$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.072$
 $S = 1.02$
 1592 reflections
 97 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
 $w = 1/[\sigma^2(F_o^2) + (0.0411P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	0.5000	0.5000	0.0000	0.04055 (12)
N1	0.7466 (5)	0.7003 (4)	0.0217 (3)	0.0512 (6)
N12	0.6360 (5)	0.2497 (4)	0.1840 (2)	0.0457 (6)
C12	0.5473 (6)	0.0818 (5)	0.2234 (3)	0.0485 (7)
H12	0.4340	0.0591	0.1794	0.058*
C11	0.6252 (7)	-0.0574 (5)	0.3298 (3)	0.0502 (8)
C14	0.8718 (8)	0.1294 (6)	0.3560 (3)	0.0623 (9)
H14	0.9856	0.1502	0.4005	0.075*
C13	0.8027 (7)	0.2699 (6)	0.2508 (3)	0.0545 (8)
H13	0.8726	0.3819	0.2247	0.065*
N11	0.7817 (7)	-0.0377 (5)	0.3977 (3)	0.0590 (7)
Cl11	0.5080 (2)	-0.27337 (15)	0.37726 (10)	0.0755 (3)
S1	1.14072 (16)	0.73906 (13)	0.12925 (8)	0.0535 (2)
C1	0.9108 (6)	0.7182 (4)	0.0647 (3)	0.0404 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.03692 (19)	0.04198 (17)	0.04287 (19)	-0.01361 (12)	-0.01125 (13)	-0.00014 (12)
N1	0.0460 (16)	0.0474 (13)	0.0632 (17)	-0.0154 (12)	-0.0118 (13)	-0.0089 (12)
N12	0.0451 (15)	0.0484 (13)	0.0416 (14)	-0.0117 (11)	-0.0087 (11)	-0.0031 (11)
C12	0.0487 (18)	0.0482 (15)	0.0459 (16)	-0.0095 (13)	-0.0086 (14)	-0.0057 (13)
C11	0.060 (2)	0.0455 (15)	0.0418 (16)	-0.0124 (14)	-0.0037 (15)	-0.0052 (12)
C14	0.071 (3)	0.071 (2)	0.0480 (18)	-0.0249 (19)	-0.0237 (18)	-0.0015 (16)
C13	0.059 (2)	0.0546 (17)	0.0511 (19)	-0.0204 (15)	-0.0145 (16)	-0.0011 (14)

N11	0.072 (2)	0.0601 (16)	0.0431 (14)	-0.0183 (15)	-0.0143 (14)	0.0004 (12)
Cl11	0.1033 (9)	0.0591 (5)	0.0665 (6)	-0.0365 (5)	-0.0086 (6)	0.0031 (4)
S1	0.0426 (5)	0.0638 (5)	0.0620 (5)	-0.0142 (4)	-0.0100 (4)	-0.0250 (4)
C1	0.0381 (16)	0.0394 (13)	0.0452 (16)	-0.0123 (11)	-0.0033 (13)	-0.0088 (12)

Geometric parameters (Å, °)

Cd1—N1	2.287 (3)	C12—H12	0.9300
Cd1—N1 ⁱ	2.287 (3)	C11—N11	1.303 (5)
Cd1—N12 ⁱ	2.417 (2)	C11—Cl11	1.730 (3)
Cd1—N12	2.417 (2)	C14—N11	1.341 (5)
Cd1—S1 ⁱⁱ	2.7071 (9)	C14—C13	1.364 (5)
Cd1—S1 ⁱⁱⁱ	2.7071 (9)	C14—H14	0.9300
N1—C1	1.158 (4)	C13—H13	0.9300
N12—C12	1.338 (4)	S1—C1	1.636 (3)
N12—C13	1.342 (4)	S1—Cd1 ^{iv}	2.7071 (9)
C12—C11	1.381 (4)		
N1—Cd1—N1 ⁱ	180.0	C12—N12—Cd1	120.7 (2)
N1—Cd1—N12 ⁱ	88.62 (10)	C13—N12—Cd1	122.4 (2)
N1 ⁱ —Cd1—N12 ⁱ	91.38 (10)	N12—C12—C11	119.6 (3)
N1—Cd1—N12	91.38 (10)	N12—C12—H12	120.2
N1 ⁱ —Cd1—N12	88.62 (10)	C11—C12—H12	120.2
N12 ⁱ —Cd1—N12	180.00 (15)	N11—C11—C12	124.5 (3)
N1—Cd1—S1 ⁱⁱ	92.25 (8)	N11—C11—Cl11	117.2 (2)
N1 ⁱ —Cd1—S1 ⁱⁱ	87.75 (8)	C12—C11—Cl11	118.2 (3)
N12 ⁱ —Cd1—S1 ⁱⁱ	91.06 (7)	N11—C14—C13	122.5 (4)
N12—Cd1—S1 ⁱⁱ	88.94 (7)	N11—C14—H14	118.7
N1—Cd1—S1 ⁱⁱⁱ	87.75 (8)	C13—C14—H14	118.7
N1 ⁱ —Cd1—S1 ⁱⁱⁱ	92.25 (8)	N12—C13—C14	121.3 (3)
N12 ⁱ —Cd1—S1 ⁱⁱⁱ	88.94 (7)	N12—C13—H13	119.4
N12—Cd1—S1 ⁱⁱⁱ	91.06 (7)	C14—C13—H13	119.4
S1 ⁱⁱ —Cd1—S1 ⁱⁱⁱ	180.00 (4)	C11—N11—C14	115.1 (3)
C1—N1—Cd1	150.2 (2)	C1—S1—Cd1 ^{iv}	96.53 (11)
C12—N12—C13	116.9 (3)	N1—C1—S1	178.3 (3)

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