

A second polymorph of *catena*-poly- [[*(1,10*-phenanthroline- κ^2 *N,N'*)- copper(II)]-di- μ -thiocyanato- κ^2 *N:S*; κ^2 *S:N*]

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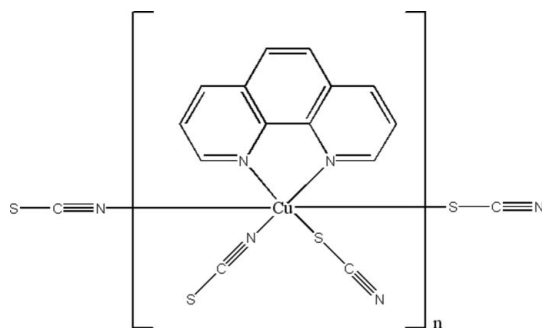
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.027; wR factor = 0.076; data-to-parameter ratio = 14.0.

In the title coordination polymer, $[\text{Cu}(\text{NCS})_2(\text{C}_{12}\text{H}_8\text{N}_2)]_n$, the Cu^{II} atom is situated on a twofold rotation axis and is coordinated by two N atoms from the bidentate 1,10-phenanthroline ligand and four thiocyanate groups to confer a CuN_4S_2 octahedral geometry and resulting in a layer structure extending parallel to (100).

Related literature

For the first polymorph of this composition, see: Breneman & Parker (1993). For related structures, see: Kulkarni *et al.* (2002); Morpurgo *et al.* (1984).



Experimental

Crystal data

$[\text{Cu}(\text{NCS})_2(\text{C}_{12}\text{H}_8\text{N}_2)]$
 $M_r = 359.90$
Monoclinic, $C2/c$
 $a = 14.0353$ (13) Å
 $b = 10.3081$ (9) Å
 $c = 10.2670$ (9) Å
 $\beta = 111.034$ (2)°

$V = 1386.4$ (2) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 1.87$ mm⁻¹
 $T = 294$ K
 $0.25 \times 0.22 \times 0.15$ mm

Data collection

Bruker SMART diffractometer
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.633$, $T_{\text{max}} = 0.755$

3938 measured reflections
1362 independent reflections
1254 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.076$
 $S = 1.08$
1362 reflections

97 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5084).

References

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supplementary materials

Acta Cryst. (2011). E67, m398 [doi:10.1107/S1600536811001759]

A second polymorph of *catena*-poly[[*(1,10-phenanthroline- κ^2N,N')copper(II)*]-di- μ -thiocyanato- $\kappa^2N:S;\kappa^2S:N$]

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Comment

Phenanthroline and its derivatives have been achieving rapidly increasing attention not only for their potential application as functional materials, but also from their intriguing variety of architectures and topologies. 1, 10-Phenanthroline, as one kind of those ligand, has usually been used to construct a great variety of structurally interesting entities, such as monomers (Breneman *et al.* 1993), polymers (Kulkarni *et al.* 2002; Morpurgo *et al.* 1984).

The structure of the title compound (I) is illustrated in Fig. 1. the Cu^{II} atom is coordinated by two N atoms from 1, 10-Phenanthroline ligand, as well as by the two N atoms and two S atoms from four thiocyanate groups to confer a distorted octahedral coordination at the metal centre. Two S atoms occupy the axial position, showing weak interaction of Cu1—S1 bond [2.952 (3)], which give rise to one-dimensional chain along (100), the crystal packing is stabilized by the intermolecular π - π stacking interaction (Fig. 2).

In contrast to the first polymorph of this composition in which the distance of Cu—S bonds are longer [3.163 (2) Å], and the S—Cu—S' angles are nearly linear [170.86 (6)°]. The S—Cu—N angles in reported complex vary from 73.8 (1) to 99.1 (1)°, which make the octahedral geometry of this compound more disordered than the title compound.

Experimental

The mixture of CuSCN (0.0244 g, 0.2 mmol), 1, 10-Phenanthroline (0.0132 g, 0.1 mmol), were placed and sealed in a 10 ml Teflon-lined stainless steel reactor and heated to 160 °C for 72 h, then cooled down to room temperature at a rate of 5 °C/ 60 min. Single crystals suitable for X-ray diffraction were obtained in the form of black bars in *ca* 35% yield.

The web of checkcif show one Alert level B (Hirshfeld Test Diff S1 – C7..8.52 su), we think this is the result of the slightly distorted S atom of the thiocyanate group for his weak interaction to the Cu atom.

Refinement

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å (aromatic) and U_{iso}(H) = 1.2 U_{eq}(C)

Figures

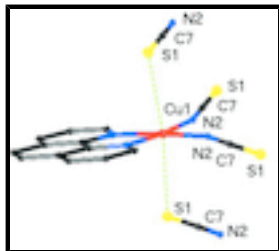


Fig. 1. The coordination environment of the title compound

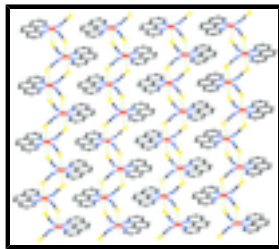


Fig. 2. The crystal packing of the title compound

catena-Poly[[*(1,10*-phenanthroline- κ^2N,N')copper(II)]- di- μ -thiocyanato- $\kappa^2N:S;\kappa^2S:N$]

Crystal data

[Cu(NCS)₂(C₁₂H₈N₂)]

$M_r = 359.90$

Monoclinic, $C2/c$

Hall symbol: $-c\ 2yc$

$a = 14.0353\ (13)\ \text{\AA}$

$b = 10.3081\ (9)\ \text{\AA}$

$c = 10.2670\ (9)\ \text{\AA}$

$\beta = 111.034\ (2)^\circ$

$V = 1386.4\ (2)\ \text{\AA}^3$

$Z = 4$

$F(000) = 724$

$D_x = 1.724\ \text{Mg m}^{-3}$

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

Cell parameters from 1647 reflections

$\theta = 2.5\text{--}27.8^\circ$

$\mu = 1.87\ \text{mm}^{-1}$

$T = 294\ \text{K}$

Block, black

$0.25 \times 0.22 \times 0.15\ \text{mm}$

Data collection

Bruker SMART
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.633$, $T_{\max} = 0.755$

3938 measured reflections

1362 independent reflections

1254 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -17 \rightarrow 17$

$k = -12 \rightarrow 5$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H-atom parameters constrained
$wR(F^2) = 0.076$	$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 0.5818P]$
$S = 1.08$	where $P = (F_o^2 + 2F_c^2)/3$
1362 reflections	$(\Delta/\sigma)_{\max} = 0.001$
97 parameters	$\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.0008 (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	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.62211 (3)	0.2500	0.03359 (15)
N2	0.43016 (13)	0.49319 (16)	0.32227 (17)	0.0407 (4)
N1	0.56960 (11)	0.77181 (16)	0.19112 (15)	0.0330 (3)
C7	0.39033 (14)	0.43783 (18)	0.38718 (19)	0.0324 (4)
C6	0.53802 (14)	0.88917 (17)	0.21873 (19)	0.0326 (4)
C1	0.64028 (15)	0.7684 (2)	0.1322 (2)	0.0426 (5)
H1	0.6632	0.6884	0.1136	0.051*
C4	0.57499 (16)	1.0064 (2)	0.1877 (2)	0.0415 (5)
C3	0.64909 (17)	0.9994 (2)	0.1252 (2)	0.0488 (6)
H3	0.6761	1.0749	0.1027	0.059*
C2	0.68083 (19)	0.8814 (2)	0.0979 (3)	0.0507 (6)
H2	0.7296	0.8759	0.0562	0.061*
S1	0.33300 (4)	0.36018 (5)	0.47588 (6)	0.04095 (18)
C5	0.5358 (2)	1.12518 (19)	0.2202 (3)	0.0548 (6)
H5	0.5599	1.2038	0.1999	0.066*

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Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0418 (2)	0.0268 (2)	0.0433 (2)	0.000	0.02887 (17)	0.000
N2	0.0479 (10)	0.0375 (9)	0.0432 (9)	-0.0075 (8)	0.0242 (8)	0.0008 (7)
N1	0.0348 (8)	0.0338 (8)	0.0351 (8)	-0.0009 (6)	0.0182 (6)	0.0016 (6)
C7	0.0353 (9)	0.0279 (9)	0.0358 (9)	-0.0008 (8)	0.0148 (8)	-0.0027 (7)
C6	0.0359 (10)	0.0312 (9)	0.0302 (9)	-0.0021 (7)	0.0111 (8)	0.0015 (7)
C1	0.0424 (10)	0.0461 (12)	0.0487 (11)	-0.0017 (9)	0.0280 (9)	0.0019 (9)
C4	0.0451 (11)	0.0366 (11)	0.0391 (10)	-0.0057 (9)	0.0107 (9)	0.0052 (8)
C3	0.0515 (12)	0.0467 (13)	0.0501 (12)	-0.0150 (10)	0.0206 (10)	0.0097 (10)
C2	0.0481 (12)	0.0637 (16)	0.0498 (13)	-0.0116 (10)	0.0293 (11)	0.0039 (10)
S1	0.0430 (3)	0.0442 (3)	0.0433 (3)	-0.0070 (2)	0.0249 (2)	0.0026 (2)
C5	0.0705 (17)	0.0301 (11)	0.0589 (15)	-0.0062 (9)	0.0174 (12)	0.0025 (9)

Geometric parameters (\AA , $^\circ$)

Cu1—N2	1.9492 (16)	C1—C2	1.397 (3)
Cu1—N2 ⁱ	1.9492 (16)	C1—H1	0.9300
Cu1—N1	2.0310 (15)	C4—C3	1.406 (3)
Cu1—N1 ⁱ	2.0310 (15)	C4—C5	1.430 (3)
N2—C7	1.162 (3)	C3—C2	1.359 (3)
N1—C1	1.335 (2)	C3—H3	0.9300
N1—C6	1.353 (2)	C2—H2	0.9300
C7—S1	1.6259 (19)	C5—C5 ⁱ	1.351 (6)
C6—C4	1.397 (3)	C5—H5	0.9300
C6—C6 ⁱ	1.430 (4)		
N2—Cu1—N2 ⁱ	94.04 (10)	N1—C1—H1	119.0
N2—Cu1—N1	173.03 (6)	C2—C1—H1	119.0
N2 ⁱ —Cu1—N1	92.49 (7)	C6—C4—C3	117.1 (2)
N2—Cu1—N1 ⁱ	92.49 (7)	C6—C4—C5	118.8 (2)
N2 ⁱ —Cu1—N1 ⁱ	173.03 (6)	C3—C4—C5	124.1 (2)
N1—Cu1—N1 ⁱ	81.10 (9)	C2—C3—C4	119.4 (2)
C7—N2—Cu1	164.69 (16)	C2—C3—H3	120.3
C1—N1—C6	118.10 (17)	C4—C3—H3	120.3
C1—N1—Cu1	129.05 (15)	C3—C2—C1	120.1 (2)
C6—N1—Cu1	112.85 (12)	C3—C2—H2	120.0
N2—C7—S1	179.12 (18)	C1—C2—H2	120.0
N1—C6—C4	123.34 (18)	C5 ⁱ —C5—C4	121.13 (13)
N1—C6—C6 ⁱ	116.59 (10)	C5 ⁱ —C5—H5	119.4
C4—C6—C6 ⁱ	120.07 (12)	C4—C5—H5	119.4
N1—C1—C2	121.9 (2)		

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

Fig. 2

