Poly[(μ₂-3,6-di-4-pyridyl-1,2,4,5-tetrazine)(μ₂-thiocyanato)copper(I)]

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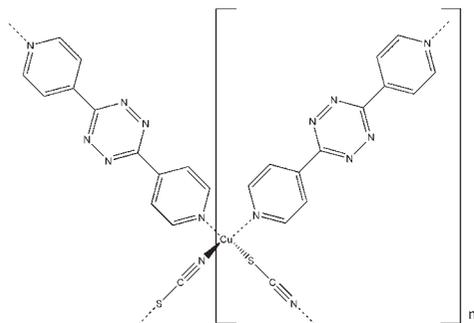Correspondence e-mail: chizhang@ujs.edu.cn

The title compound, $[Cu(NCS)(C_{12}H_8N_6)]_n$, is a self-assembled two-dimensional metal–organic network. The Cu atom is linked by two N atoms from two 3,6-di-4-pyridyl-1,2,4,5-tetrazine ligands and by the N and S atoms from two thiocyanate ligands in a distorted tetrahedral environment. The Cu atom and the thiocyanate ligand occupy a crystallographic mirror plane m, and a crystallographic inversion centre is in the middle of the tetrazine ring, generating the zigzag fashion of the two-dimensional network. The infinite –Cu—SCN—Cu—SCN– chain is due to translational symmetry along the a axis. These chains are further connected through the 3,6-di-4-pyridyl-1,2,4,5-tetrazine ligands that bridge the Cu^I centers, generating a two-dimensional network. There are π–π stacking interactions between the pyridine and tetrazine rings (perpendicular distances of 3.357 and 3.418 Å), with a centroid–centroid distance of 3.6785 (16) Å.

Related literature

For compounds with related architectures, see: Oxtoby *et al.* (2003); Dinolfo *et al.* (2004); Hsu *et al.* (2006); Xue *et al.* (2008); Withersby *et al.* (1997, 2000).

Experimental

Crystal data

$[Cu(NCS)(C_{12}H_8N_6)]$	$V = 672.7\,(2)$ Å^3
$M_r = 357.88$	$Z = 2$
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation
$a = 5.8640\,(12)$ Å	$\mu = 1.79$ mm^{-1}
$b = 18.510\,(4)$ Å	$T = 250$ K
$c = 6.3993\,(13)$ Å	$0.20 \times 0.20 \times 0.20$ mm
$\beta = 104.42\,(3)°$	

Data collection

Rigaku Mercury diffractometer	3288 measured reflections
Absorption correction: multi-scan	1373 independent reflections
(*ABSCOR*; Higashi, 1995)	1304 reflections with $I > 2\sigma(I)$
$T_{min} = 0.445$, $T_{max} = 0.738$	$R_{int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	106 parameters
$wR(F^2) = 0.069$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{max} = 0.48$ e Å^{-3}
1373 reflections	$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—N2^i	1.948 (3)	Cu1—N1	2.100 (2)
Cu1—N1^{ii}	2.100 (2)	Cu1—S1	2.2550 (13)

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

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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: *SHELXL97*.

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supporting information

Poly[(μ_2-3,6-di-4-pyridyl-1,2,4,5-tetrazine)(μ_2-thiocyanato)copper(I)]

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S1. Comment

The coordination polymers that based on metal halides and N-donor ligands are one of the most important and promising fields in magnetism, nonlinear optics, electronics, catalysis and molecular topologies (Oxtoby *et al.*, 2003; Hsu *et al.*, 2006), the title compound is an example.

  Many different coordination modes′ polymers can be obtained by 3,6-di-4-pyridyl-1,2,4,5-tetrazine ligands because it can connect two different metal cations, and the Cu atom in CuSCN can be linked by linear spacer ligands into sheets (Dinolfo *et al.*, 2004; Hsu *et al.*, 2006). We obtained a two-dimensional metal-organic compound as the title complex, $C_{13}H_8CuN_7S$ (Fig. 1), whose structure contains single [CuSCN] ribbons as a characteristic motif. The asymmetric unit of the title compound consist of a half 3,6-di-4-pyridyl-1,2,4,5-tetrazine ligand, half a copper(I) and one SCN . group. Each Cu atom connected by three N atoms and one S atom, give rise to a distorted tetrahedron (Table 1). The layers can be described as formed by two types of perpendicular zigzag like chains crossing at the Cu^I centers. Chains of the first type run along the *b*-axis and have 3,6-di-4-pyridyl-1,2,4,5-tetrazine as a bridging ligand, while the second type extend along the *a*-axis containing bridging thiocyanate ligands. The structure is stabilized through π—π stacking interactions which can be imagined in Figure 2, with perpendicular distances between pyridine and tetrazine rings of 3.357 Å [symmetry code for Cg2$_{tetrazine}$: x, y, -1 + z), and of 3.418 Å [symmetry code for Cg1$_{pyridine}$: x, y, 1 + z); the Cg1···Cg2 distance is 3.6785 (16) Å. Cg1 and Cg2 are the centroids of rings (N1, C1, C3, C2, C6, C5) and (N3, C4, N4, N3^{iv}, C4^{iv}, N4^{iv}), symmetry code iv = -1 - x, -y, 1 - z.

S2. Experimental

CuSCN (12.2 mg) and NH$_4$SCN(1.4 mg) were added into 2.5 ml DMF and the solution were stirred for 10 min at room temperature until became clarification. Then, the resulting solution was subsequently filterated to a tube, then 2.5 ml solution of *i.*-pron and 3,6-di-4-pyridyl-1,2,4,5-tetrazine added to afford a black filtrate. Many prismatic black crystals were obtained a few weeks later.

S3. Refinement

H atoms were positioned geometrically and refined as a riding model, with U_{iso}(H) = 1.2U_{eq} (pyridyl C atoms). The C—H bond lengths are 0.93 Å.
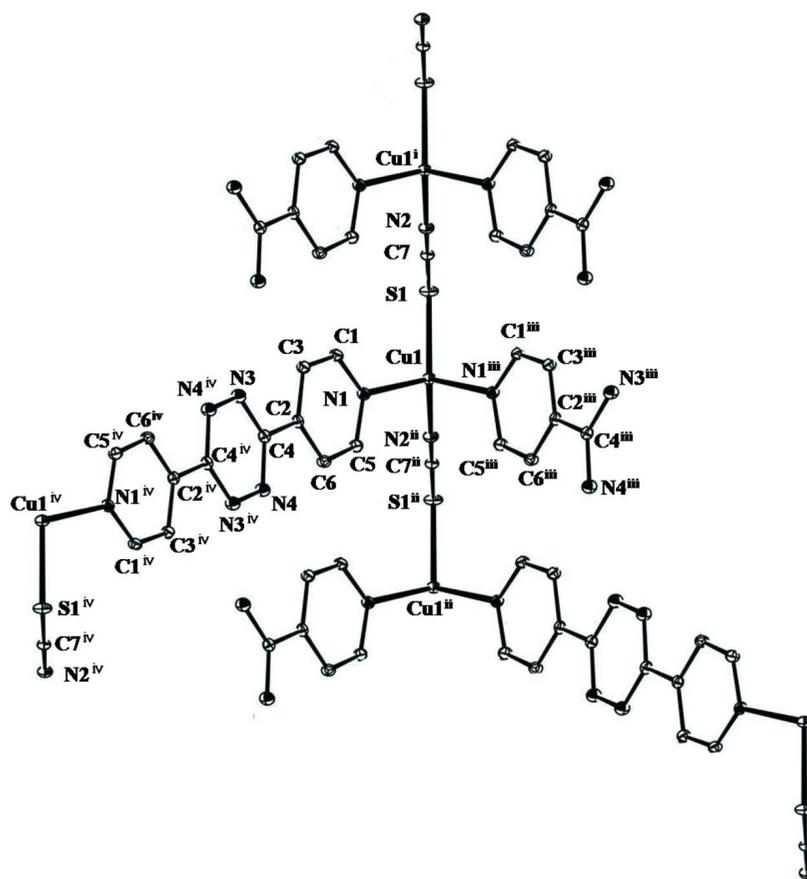
Figure 1

A section of the two-dimensional structure of the title complex, with atom labels and 30% probability displacement ellipsoids. H atoms have been omitted. [symmetry codes: i = -1 + x, y, z; ii = 1 + x, y, z; iii = x, 1/2 - y, z; iv = -1 - x, -y, 1 - z.]
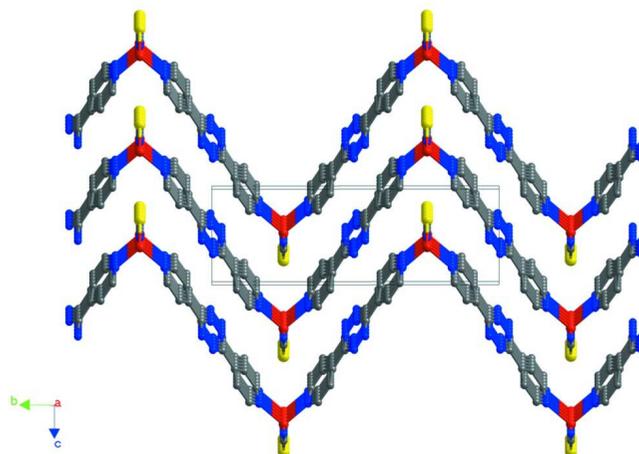
Figure 2

The unit cell packing diagram.

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Crystal data

[Cu(NCS)(C$_{12}$H$_8$N$_6$)]	$F(000) = 360$
$M_r = 357.88$	$D_x = 1.767$ Mg m^{-3}
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yb	Cell parameters from 2914 reflections
$a = 5.8640$ (12) Å	$\theta = 3.3–28.9°$
$b = 18.510$ (4) Å	$\mu = 1.79$ mm^{-1}
$c = 6.3993$ (13) Å	$T = 250$ K
$\beta = 104.42$ (3)°	Prism, black
$V = 672.7$ (2) Å^3	$0.20 \times 0.20 \times 0.20$ mm
$Z = 2$	

Data collection

Rigaku Mercury diffractometer	3288 measured reflections
Radiation source: fine-focus sealed tube	1373 independent reflections
Graphite monochromator	1304 reflections with $I > 2\sigma(I)$
Detector resolution: 28.5714 pixels mm^{-1}	$R_{int} = 0.018$
dtprofit.ref scans	$\theta_{max} = 26.4°$, $\theta_{min} = 3.3°$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$h = -7 \rightarrow 5$
$T_{min} = 0.445$, $T_{max} = 0.738$	$k = -22 \rightarrow 20$
	$l = -8 \rightarrow 7$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.033$	
$wR(F^2) = 0.069$	
$S = 1.11$	Hydrogen site location: inferred from neighbouring sites
1373 reflections	H-atom parameters constrained
106 parameters	
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 0.7211P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-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 (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Cu1	−0.50890 (7)	0.2500	−0.44195 (7)	0.03870 (15)
S1	−0.83431 (16)	0.2500	−0.71812 (15)	0.0502 (3)
N1	−0.5137 (3)	0.16473 (11)	−0.2265 (3)	0.0379 (5)
N2	−1.2068 (5)	0.2500	−0.5169 (5)	0.0454 (7)
N3	−0.7033 (4)	0.00418 (13)	0.3425 (3)	0.0465 (5)
N4	−0.3006 (4)	0.03426 (13)	0.4828 (3)	0.0467 (5)
C1	−0.7064 (4)	0.12996 (14)	−0.2042 (4)	0.0407 (6)
H1A	−0.8441	0.1346	−0.3131	0.049*
C2	−0.5081 (4)	0.07992 (13)	0.1348 (4)	0.0351 (5)
C3	−0.7118 (4)	0.08763 (14)	−0.0286 (4)	0.0407 (6)
H3A	−0.8500	0.0646	−0.0198	0.049*
C4	−0.5051 (4)	0.03705 (13)	0.3302 (4)	0.0373 (5)
C5	−0.3166 (5)	0.15430 (15)	−0.0716 (4)	0.0436 (6)
H5A	−0.1789	0.1761	−0.0871	0.052*
C6	−0.3058 (4)	0.11312 (14)	0.1092 (4)	0.0417 (6)
H6A	−0.1643	0.1077	0.2129	0.050*
C7	−1.0503 (6)	0.2500	−0.5953 (5)	0.0374 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0309 (2)	0.0500 (3)	0.0350 (2)	0.000	0.00798 (17)	0.000
S1	0.0272 (4)	0.0901 (8)	0.0326 (5)	0.000	0.0059 (3)	0.000
N1	0.0372 (11)	0.0403 (11)	0.0357 (11)	0.0029 (9)	0.0079 (9)	0.0063 (9)
N2	0.0297 (15)	0.057 (2)	0.0506 (19)	0.000	0.0111 (14)	0.000
N3	0.0462 (13)	0.0554 (14)	0.0363 (11)	−0.0009 (11)	0.0070 (9)	0.0117 (10)
N4	0.0458 (13)	0.0558 (14)	0.0369 (11)	−0.0005 (11)	0.0075 (10)	0.0097 (10)
C1	0.0349 (13)	0.0462 (14)	0.0386 (13)	0.0031 (11)	0.0047 (10)	0.0071 (11)
C2	0.0429 (13)	0.0324 (12)	0.0305 (11)	0.0032 (10)	0.0101 (10)	−0.0016 (10)
C3	0.0353 (12)	0.0444 (14)	0.0432 (14)	0.0002 (11)	0.0112 (11)	0.0081 (11)
C4	0.0430 (14)	0.0361 (13)	0.0334 (12)	0.0040 (11)	0.0105 (10)	−0.0004 (10)
C5	0.0376 (13)	0.0484 (15)	0.0426 (14)	−0.0044 (12)	0.0060 (11)	0.0072 (12)

| C6 | 0.0391 (13) | 0.0483 (15) | 0.0340 (13) | −0.0009 (11) | 0.0024 (10) | 0.0035 (11) |
| C7 | 0.0297 (17) | 0.046 (2) | 0.0330 (17) | 0.000 | 0.0008 (14) | 0.000 |

Geometric parameters (Å, º)

Cu1—N2^i	1.948 (3)	N4—N3^{iv}	1.321 (3)
Cu1—N1^{ii}	2.100 (2)	N4—C4	1.346 (3)
Cu1—N1	2.100 (2)	C1—C3	1.377 (3)
Cu1—S1	2.2550 (13)	C1—H1A	0.9300
S1—C7	1.648 (4)	C2—C6	1.381 (3)
N1—C5	1.336 (3)	C2—C3	1.385 (3)
N1—C1	1.339 (3)	C2—C4	1.477 (3)
N2—C7	1.150 (4)	C3—H3A	0.9300
N2—Cu1^{iii}	1.948 (3)	C5—C6	1.374 (3)
N3—N4^{iv}	1.321 (3)	C5—H5A	0.9300
N3—C4	1.332 (3)	C6—H6A	0.9300
N2^i—Cu1—N1^{ii}	108.87 (8)	C6—C2—C3	118.0 (2)
N2^i—Cu1—N1	108.87 (8)	C6—C2—C4	120.7 (2)
N1^{ii}—Cu1—N1	97.43 (11)	C3—C2—C4	121.4 (2)
N2^i—Cu1—S1	116.81 (10)	C1—C3—C2	119.0 (2)
N1^{ii}—Cu1—S1	111.55 (6)	C1—C3—H3A	120.5
N1—Cu1—S1	111.55 (6)	C2—C3—H3A	120.5
C7—S1—Cu1	103.11 (12)	N3—C4—N4	125.0 (2)
C5—N1—C1	116.6 (2)	N3—C4—C2	118.0 (2)
C5—N1—Cu1	116.43 (17)	N4—C4—C2	117.1 (2)
C1—N1—Cu1	125.52 (16)	N1—C5—C6	123.7 (2)
C7—N2—Cu1^{iii}	168.8 (3)	N1—C5—H5A	118.1
N4^{iv}—N3—C4	117.7 (2)	C6—C5—H5A	118.1
N3^{iv}—N4—C4	117.3 (2)	C5—C6—C2	119.1 (2)
N1—C1—C3	123.5 (2)	C5—C6—H6A	120.5
N1—C1—H1A	118.2	C2—C6—H6A	120.5
C3—C1—H1A	118.2	N2—C7—S1	177.5 (3)

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