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**catena-Poly[[dichloridocopper(II)]- $\mu$ -1,4-bis(pyrimidin-2-ylsulfanylmethyl)-benzene- $\kappa^2N:N'$ ]**

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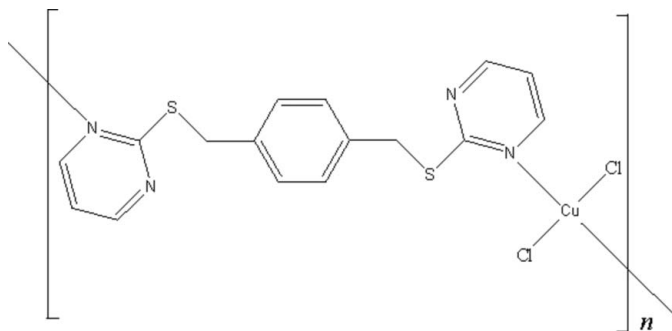
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Key indicators: single-crystal X-ray study;  $T = 295$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.047;  $wR$  factor = 0.111; data-to-parameter ratio = 17.7.

In the title complex,  $[\text{CuCl}_2(\text{C}_{16}\text{H}_{14}\text{N}_4\text{S}_2)]_n$ , the Cu atom lies on a center of inversion and is bridged by two adjacent pyrimidine N atoms and two chloride counter-ions to give a square-planar coordination geometry. The bidentate thioether ligands link adjacent Cu atoms into an infinite chain.

## Related literature

For related literature, see Peng *et al.* (2005); Caradoc-Davies & Hanton (2003); Hanton & Lee (2000); Hong *et al.* (2000). For the synthesis of the ligand, see Peng *et al.* (2006).



## Experimental

## Crystal data

 $[\text{CuCl}_2(\text{C}_{16}\text{H}_{14}\text{N}_4\text{S}_2)]$  $M_r = 460.87$ Monoclinic,  $P2_1/n$  $a = 8.9243$  (9) Å $b = 9.9867$  (9) Å $c = 10.4339$  (10) Å
 $\beta = 99.667$  (2)°  
 $V = 916.71$  (15) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation

 $\mu = 1.72$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 $0.29 \times 0.11 \times 0.09$  mm

## Data collection

 Bruker APEX CCD diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.636$ ,  $T_{\max} = 0.861$ 

 4908 measured reflections  
 2034 independent reflections  
 1517 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.032$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.111$   
 $S = 1.01$   
 2034 reflections

 115 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.60$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.43$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	2.003 (2)	Cu1—Cl1	2.2311 (8)
N1—Cu1—N1 <sup>i</sup>	180	N1—Cu1—Cl1	89.80 (7)
N1—Cu1—Cl1 <sup>i</sup>	90.20 (7)	Cl1 <sup>i</sup> —Cu1—Cl1	180

Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: publCIF (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZZ094).

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**supplementary materials**

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***catena*-Poly[[dichloridocopper(II)]- $\mu$ -1,4-bis(pyrimidin-2-ylsulfanylmethyl)benzene- $\kappa^2$ N:N']**

**R. Peng, S.-H. Lin and Y.-Y. Yang**

**Comment**

The coordination chemistry of flexible thioether ligands has attracted considerable attention recently (Caradoc-Davies & Hanton, 2003; Hanton & Lee, 2000; Hong *et al.*, 2000). We are currently involved in the synthesis and study of Cu(I) complexes of a series of N-containing heterocyclic thioether ligands. We have found that the ligand geometry and counteranions play an essential role in the framework formation of the Cu(I) complexes (Peng *et al.*, 2005; Peng *et al.*, 2006). The title compound is obtained from the solvothermal reaction of copper(I) chloride and bis(2-pyrimidinesulfanylmethyl)benzene in the presence of chloroform and acetonitrile solvents. X-ray structure analysis of the crystals shows that atom Cu1 lies on a center of inversion and is coordinated by two chloride anions and two N atoms from two adjacent thioether ligands. The bond angles about the copper atom [exactly 180° for Cl–Cu–Cl and N–Cu–N, and 89.80 (7) and 90.20 (7)° for N–Cu–Cl] confirm that it is in a regular square-planar CuCl<sub>2</sub>N<sub>2</sub> geometry. The necessity to balance charges and the geometrical preferences of metal ions indicate the divalent state of the copper ions, which result from Cu(I) being oxidized in air. The thioether ligands, acting as bidentate connectors, link adjacent Cu(II) ions into a zigzag one-dimensional chain.

**Experimental**

Bis(2-pyrimidinesulfanylmethyl)benzene was synthesized using a reported procedure (Peng *et al.*, 2006). A mixture of CuCl (0.01 g, 0.1 mmol), bis(2-pyrimidinesulfanylmethyl)benzene (0.033 g, 0.1 mmol), CHCl<sub>3</sub> (2.0 ml) and acetonitrile (4.0 ml) was stirred for 15 min in air and then transferred to a 13 ml Teflon-lined reactor and sealed, then heated in an oven to 393 K for 48 h, and cooled to room temperature at a rate of 3 K 0.5 h<sup>-1</sup>. The reaction mixture was filtered to give a yellow-red solution. Black block-shaped crystals of (I) were obtained by slow diffusion of diethyl ether into the solution after one week (yield 36%, based on Cu). Analysis calculated for C<sub>16</sub>H<sub>14</sub>Cl<sub>2</sub>CuN<sub>4</sub>S<sub>2</sub>: C 41.66, H 3.04, N 12.15%; found: C 41.81, H 3.13, N 11.97%.

**Refinement**

The H atoms were placed at calculated positions [aromatic C–H = 0.93 Å and methylene C–H = 0.97 Å;  $U_{\text{iso}}(\text{H}) = 1.2$  times  $U_{\text{eq}}(\text{C})$ ].

**Figures**

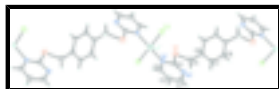


Fig. 1. View of a fragment of the chain motif in (I) showing the atom numbering scheme of the asymmetric unit and 30% displacement ellipsoids for the non-hydrogen atoms.

# supplementary materials

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## catena-Poly[[dichloridocopper(II)]- $\mu$ -1,4-bis(pyrimidin-2-ylsulfanylmethyl)benzene- $\kappa^2$ N:N']

### Crystal data

[CuCl <sub>2</sub> (C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> S <sub>2</sub> )]	$F_{000} = 466$
$M_r = 460.87$	$D_x = 1.670 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
Hall symbol: -P 2yn	$\lambda = 0.71073 \text{ \AA}$
$a = 8.9243 (9) \text{ \AA}$	Cell parameters from 1784 reflections
$b = 9.9867 (9) \text{ \AA}$	$\theta = 2.8\text{--}25.7^\circ$
$c = 10.4339 (10) \text{ \AA}$	$\mu = 1.72 \text{ mm}^{-1}$
$\beta = 99.667 (2)^\circ$	$T = 295 (2) \text{ K}$
$V = 916.71 (15) \text{ \AA}^3$	Block, black
$Z = 2$	$0.29 \times 0.11 \times 0.09 \text{ mm}$

### Data collection

Bruker APEX CCD diffractometer	2034 independent reflections
Radiation source: fine-focus sealed tube	1517 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.032$
$T = 295(2) \text{ K}$	$\theta_{\text{max}} = 27.5^\circ$
$\varphi$ and $\omega$ scans	$\theta_{\text{min}} = 2.8^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -7 \rightarrow 11$
$T_{\text{min}} = 0.636$ , $T_{\text{max}} = 0.861$	$k = -12 \rightarrow 12$
4908 measured reflections	$l = -13 \rightarrow 13$

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.047$	H-atom parameters constrained
$wR(F^2) = 0.111$	$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
2034 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
115 parameters	$\Delta\rho_{\text{max}} = 0.60 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
	Extinction correction: none

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.5000	0.5000	0.0398 (2)
Cl1	0.57709 (10)	0.70107 (9)	0.44428 (9)	0.0612 (3)
S1	0.20657 (10)	0.64387 (9)	0.57216 (8)	0.0565 (3)
N1	0.3033 (3)	0.5254 (2)	0.3782 (3)	0.0411 (6)
N2	0.0592 (3)	0.6232 (3)	0.3285 (2)	0.0518 (7)
C1	0.2880 (4)	0.4759 (3)	0.2575 (3)	0.0504 (8)
H1	0.3661	0.4249	0.2338	0.060*
C2	0.1601 (4)	0.4987 (4)	0.1686 (3)	0.0633 (11)
H2	0.1487	0.4636	0.0849	0.076*
C3	0.0499 (4)	0.5753 (4)	0.2079 (3)	0.0625 (10)
H3	-0.0363	0.5953	0.1477	0.075*
C4	0.1860 (3)	0.5945 (3)	0.4089 (3)	0.0391 (7)
C5	0.0246 (4)	0.7224 (3)	0.5817 (3)	0.0485 (8)
H5B	-0.0553	0.6716	0.5286	0.058*
H5A	0.0072	0.7180	0.6709	0.058*
C6	0.0134 (3)	0.8652 (3)	0.5382 (3)	0.0404 (7)
C7	-0.0903 (3)	0.9039 (3)	0.4302 (3)	0.0439 (7)
H7	-0.1515	0.8397	0.3826	0.053*
C8	-0.1037 (3)	1.0371 (3)	0.3923 (3)	0.0445 (8)
H8	-0.1739	1.0612	0.3197	0.053*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0352 (3)	0.0342 (3)	0.0486 (3)	-0.0014 (2)	0.0032 (2)	-0.0005 (2)
Cl1	0.0574 (5)	0.0444 (6)	0.0783 (6)	-0.0115 (4)	0.0015 (4)	0.0115 (4)
S1	0.0658 (6)	0.0556 (6)	0.0436 (5)	0.0203 (4)	-0.0035 (4)	-0.0068 (4)
N1	0.0394 (13)	0.0373 (15)	0.0459 (14)	-0.0035 (11)	0.0052 (11)	0.0001 (11)
N2	0.0468 (15)	0.0571 (18)	0.0479 (15)	0.0075 (13)	-0.0025 (12)	-0.0003 (13)
C1	0.0462 (18)	0.057 (2)	0.0504 (19)	-0.0045 (15)	0.0162 (15)	-0.0070 (16)
C2	0.060 (2)	0.092 (3)	0.0366 (17)	-0.011 (2)	0.0051 (16)	-0.0100 (17)
C3	0.054 (2)	0.083 (3)	0.0458 (19)	-0.0016 (19)	-0.0043 (15)	0.0035 (19)

## supplementary materials

C4	0.0429 (15)	0.0329 (17)	0.0398 (15)	-0.0017 (13)	0.0018 (12)	0.0014 (13)
C5	0.058 (2)	0.038 (2)	0.0535 (19)	0.0023 (15)	0.0204 (15)	-0.0011 (15)
C6	0.0402 (16)	0.0373 (18)	0.0482 (16)	0.0029 (13)	0.0205 (13)	-0.0008 (14)
C7	0.0395 (15)	0.041 (2)	0.0527 (18)	-0.0059 (13)	0.0105 (13)	-0.0082 (15)
C8	0.0414 (17)	0.044 (2)	0.0485 (17)	0.0021 (14)	0.0082 (13)	-0.0012 (15)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Cu1—N1	2.003 (2)	C2—C3	1.363 (5)
Cu1—N1 <sup>i</sup>	2.003 (2)	C2—H2	0.9300
Cu1—Cl1 <sup>i</sup>	2.2311 (8)	C3—H3	0.9300
Cu1—Cl1	2.2311 (8)	C5—C6	1.495 (4)
S1—C4	1.754 (3)	C5—H5B	0.9700
S1—C5	1.821 (3)	C5—H5A	0.9700
N1—C4	1.336 (4)	C6—C7	1.387 (4)
N1—C1	1.339 (4)	C6—C8 <sup>ii</sup>	1.390 (4)
N2—C4	1.322 (4)	C7—C8	1.387 (4)
N2—C3	1.335 (4)	C7—H7	0.9300
C1—C2	1.364 (5)	C8—C6 <sup>ii</sup>	1.390 (4)
C1—H1	0.9300	C8—H8	0.9300
N1—Cu1—N1 <sup>i</sup>	180.0	C2—C3—H3	118.3
N1—Cu1—Cl1 <sup>i</sup>	90.20 (7)	N2—C4—N1	125.6 (3)
N1 <sup>i</sup> —Cu1—Cl1 <sup>i</sup>	89.80 (7)	N2—C4—S1	119.6 (2)
N1—Cu1—Cl1	89.80 (7)	N1—C4—S1	114.8 (2)
N1 <sup>i</sup> —Cu1—Cl1	90.20 (7)	C6—C5—S1	114.2 (2)
Cl1 <sup>i</sup> —Cu1—Cl1	180.0	C6—C5—H5B	108.7
C4—S1—C5	103.02 (14)	S1—C5—H5B	108.7
C4—N1—C1	117.1 (3)	C6—C5—H5A	108.7
C4—N1—Cu1	123.5 (2)	S1—C5—H5A	108.7
C1—N1—Cu1	119.4 (2)	H5B—C5—H5A	107.6
C4—N2—C3	115.5 (3)	C7—C6—C8 <sup>ii</sup>	118.5 (3)
N1—C1—C2	121.4 (3)	C7—C6—C5	120.9 (3)
N1—C1—H1	119.3	C8 <sup>ii</sup> —C6—C5	120.5 (3)
C2—C1—H1	119.3	C8—C7—C6	120.8 (3)
C3—C2—C1	116.9 (3)	C8—C7—H7	119.6
C3—C2—H2	121.6	C6—C7—H7	119.6
C1—C2—H2	121.6	C7—C8—C6 <sup>ii</sup>	120.6 (3)
N2—C3—C2	123.4 (3)	C7—C8—H8	119.7
N2—C3—H3	118.3	C6 <sup>ii</sup> —C8—H8	119.7
Cl1 <sup>i</sup> —Cu1—N1—C4	97.7 (2)	Cu1—N1—C4—N2	174.1 (2)
Cl1—Cu1—N1—C4	-82.3 (2)	C1—N1—C4—S1	174.6 (2)
Cl1 <sup>i</sup> —Cu1—N1—C1	-85.0 (2)	Cu1—N1—C4—S1	-8.0 (3)
Cl1—Cu1—N1—C1	95.0 (2)	C5—S1—C4—N2	2.1 (3)
C4—N1—C1—C2	2.0 (5)	C5—S1—C4—N1	-175.9 (2)
Cu1—N1—C1—C2	-175.4 (2)	C4—S1—C5—C6	-82.9 (3)
N1—C1—C2—C3	0.7 (5)	S1—C5—C6—C7	116.1 (3)

C4—N2—C3—C2	1.7 (6)	S1—C5—C6—C8 <sup>ii</sup>	-65.9 (3)
C1—C2—C3—N2	-2.7 (6)	C8 <sup>ii</sup> —C6—C7—C8	0.0 (5)
C3—N2—C4—N1	1.4 (5)	C5—C6—C7—C8	178.0 (3)
C3—N2—C4—S1	-176.4 (2)	C6—C7—C8—C6 <sup>ii</sup>	0.0 (5)
C1—N1—C4—N2	-3.3 (4)		

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

