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catena-Poly[[iodidocopper(I)]-μ-4,4′,6,6′-tetramethyl-2,2′-(ethylenedithio)dipyrimidine-κ^2N:N']

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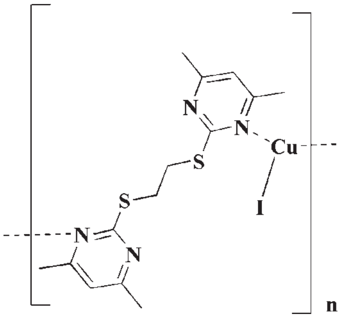
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.019; wR factor = 0.053; data-to-parameter ratio = 20.1.

In the title coordination polymer, $[\mathrm{CuI}(\mathrm{C}_{14}\mathrm{H}_{18}\mathrm{N}_4\mathrm{S}_2)]_n$, the Cu$^{\mathrm{I}}$ center is trigonally coordinated by two pyrimidine N-atom donors from two distinct dithioether ligands and one iodide anion. The Cu and I atoms are located on a twofold axis, whereas the midpoint of the central C—C bond of the dithioether ligand is located on an inversion center. Each organic ligand, acting in a bidentate mode, bridges two Cu$^{\mathrm{I}}$ ions, resulting in the formation of polymeric zigzag chains. The dihedral angle between the two pyrimidine units bonded to the metal center is 88.01 (2)°. The crystal packing is mainly stabilized by van der Waals forces and π–π stacking interactions, with an interplanar distance between the pyrimidine rings of adjacent chains of 3.638 (3) Å.

Related literature

For applications of closed-shell metal atoms or ions, see: Catalano *et al.* (2000). For applications of conjugated multi-branched molecules in optical materials, see: Nishihara *et al.* (1989); Roberto *et al.* (2000). For the structures of CuI complexes with similar ligands, see: Shi *et al.* (2008).



Experimental

Crystal data

$[\mathrm{CuI}(\mathrm{C}_{14}\mathrm{H}_{18}\mathrm{N}_4\mathrm{S}_2)]$	V = 1803.0 (14) Å^3
M_r = 496.88	Z = 4
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 14.201 (5) Å	μ = 3.16 mm^{-1}
b = 8.064 (5) Å	T = 293 K
c = 16.940 (5) Å	0.33 × 0.24 × 0.21 mm
β = 111.655 (5)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	5585 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	2070 independent reflections
$T_{\min}$ = 0.419, $T_{\max}$ = 0.515	1942 reflections with $I > 2\sigma(I)$
	R_{int} = 0.012

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.019	103 parameters
$wR(F^2)$ = 0.053	H-atom parameters constrained
S = 1.09	$\Delta\rho_{\max}$ = 0.51 e Å^{-3}
2070 reflections	$\Delta\rho_{\min}$ = −0.37 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I1—Cu1	2.5191 (16)	Cu1—N2	2.0327 (16)
N2$^{\mathrm{i}}$—Cu1—N2	118.55 (10)	N2$^{\mathrm{i}}$—Cu1—I1	120.72 (5)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We thank Professor W.-T. Yu of Shan Dong University for his assistance with the X-ray structure determinations.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2225).

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supplementary materials

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catena-Poly[[iodidocopper(I)]-μ-4,4',6,6'-tetramethyl-2,2'-(ethylenedithio)dipyrimidine-κ^2N:N']

H. B. Lu, L. Li, G. Q. Lv and J. X. Yang

Comment

Previous studies have shown that the bonding interaction between closed-shell metal atoms or ions is gaining increasing attention (Catalano *et al.*, 2000), there are a few reports of similar association in the case of alkyl copper (I) complexes. Heterocycle-based aromatic systems with conjugated multi-branched structure possess potential applications in optical image processing, all-optical switching, and integrated optical devices (Nishihara *et al.*, 1989; Roberto *et al.*, 2000). Pyrimidine is a π-electron deficient with its ionization potential value of 10.41 eV and metal complexes of such ligand has been reported (Shi *et al.*, 2008). On the other hand, pyrimidine ring has well known reactivity in the positions 4 and 6, which can easily undergo reactions with an aromatic aldehyde in solvent-free condition. Therefore we pay our attention to the pyrimidine system. As part of our ongoing investigation on d^{10} ions and pyrimidine derivatives, the title compound, has been prepared and its crystal structure is presented here.

The molecular structure of the title compound shows that Cu atom coordinated in a triangle-planar configuration (Fig. 1) with two equal Cu—N and one Cu—I bonds (Table 1). The dihedral angles formed by the two pyrimidine rings (N1, C2, N2, C6, C5, C3 and N1A, C2A, N2A, C6A, C5A, C3A) is 88.01 (2)°. Each ligand, acting in a bidentate mode, bridges two Cu ions, resulting in the formation of polymeric zigzag chains. The crystal packing is mainly stabilized by van der Waals forces and π-π interactions, with the shortest distance of 3.938 (3)Å along *c* axis.

Experimental

A mixture of 4,4',6,6'-tetramethyl-2,2'-(ethylenedithio)dipyrimidine (0.30 mmol) and CuI (0.30 mmol) was heated at 363 K with $CHCl_3$ (20 ml) as a solvent for 10 h. The red powder of the title compound was filtered and washed thoroughly with water and then air dried (yield 55%). Single crystals suitable for X-ray analysis were obtained by slow evaporation from a dichloromethane/2-propanol (3:1) solution.

Refinement

All H atoms were positioned geometrically with C—H =0.97 and 0.96 Å for methylene and methyl H atoms, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.5$ for methyl H and $x = 1.2$ for methylene H atoms.

Figures

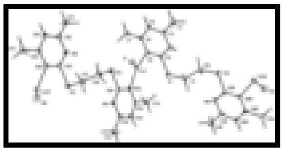


Fig. 1. : The molecular structure of the title compound showing 30% probability displacement ellipsoids. Atoms labelled with the suffixes A, B and C are at the symmetry positions (1 - *x*, *y*, 0.5 - *z*), (1 - *x*, 1 - *y*, -*z*) and (*x*, 1 - *y*, -1/2 + *z*), respectively.

catena-Poly[[iodidocopper(I)]-μ-4,4',6,6'-tetramethyl-2,2'- (ethylenedithio)dipyrimidine-κ^2*N*:*N*']

Crystal data

[CuI($C_{14}H_{18}N_4S_2$)]

M_r = 496.88

Monoclinic, *C*2/*c*

Hall symbol: -C 2yc

a = 14.201 (5) Å

b = 8.064 (5) Å

c = 16.940 (5) Å

β = 111.655 (5)°

V = 1803.0 (14) Å^3

Z = 4

F_{000} = 976

D_x = 1.830 Mg m^{-3}

Mo *K*α radiation, λ = 0.71069 Å

Cell parameters from 4275 reflections

θ = 3.0–27.5°

μ = 3.16 mm^{-1}

T = 293 K

Prism, yellow

0.33 × 0.24 × 0.21 mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: sealed tube

Monochromator: graphite

Detector resolution: 0 pixels mm^{-1}

T = 295 K

φ and ω scans

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

T_{min} = 0.419, T_{max} = 0.515

5585 measured reflections

2070 independent reflections

1942 reflections with $I > 2\sigma(I)$

R_{int} = 0.012

θ_{max} = 27.5°

θ_{min} = 3.0°

$h = -18 \rightarrow 14$

$k = -10 \rightarrow 9$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

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

$wR(F^2) = 0.053$

S = 1.09

2070 reflections

103 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 1.5073P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max}$ = 0.51 e Å^{-3}

$\Delta\rho_{min}$ = −0.37 e Å^{-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 ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}
I1	0.5000	−0.19054 (3)	0.2500	0.04737 (8)
Cu1	0.5000	0.12185 (4)	0.2500	0.03416 (9)
S1	0.52076 (4)	0.34963 (8)	0.11434 (3)	0.04371 (14)
N1	0.32885 (12)	0.4555 (2)	0.05807 (11)	0.0342 (3)
N2	0.38109 (11)	0.2506 (2)	0.16787 (9)	0.0290 (3)
C5	0.21161 (14)	0.3484 (3)	0.11508 (12)	0.0344 (4)
H5	0.1466	0.3468	0.1161	0.041*
C3	0.23460 (14)	0.4530 (2)	0.06006 (12)	0.0340 (4)
C6	0.28616 (14)	0.2463 (3)	0.16853 (11)	0.0317 (4)
C1	0.52381 (15)	0.5214 (3)	0.04659 (12)	0.0366 (4)
H1A	0.4881	0.6149	0.0584	0.044*
H1B	0.5936	0.5545	0.0597	0.044*
C2	0.39619 (13)	0.3559 (2)	0.11190 (11)	0.0298 (3)
C4	0.15807 (18)	0.5669 (3)	0.00052 (16)	0.0505 (5)
H4A	0.1729	0.6791	0.0202	0.076*
H4B	0.0916	0.5374	−0.0017	0.076*
H4C	0.1605	0.5575	−0.0552	0.076*
C7	0.26594 (15)	0.1282 (3)	0.22824 (14)	0.0437 (5)
H7A	0.2754	0.0165	0.2128	0.066*
H7B	0.1975	0.1419	0.2252	0.066*
H7C	0.3119	0.1500	0.2851	0.066*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.04987 (13)	0.03860 (12)	0.05587 (13)	0.000	0.02211 (9)	0.000
Cu1	0.03150 (16)	0.0412 (2)	0.03022 (16)	0.000	0.01191 (12)	0.000
S1	0.0306 (2)	0.0610 (3)	0.0444 (3)	0.0086 (2)	0.0194 (2)	0.0221 (2)
N1	0.0331 (8)	0.0374 (9)	0.0338 (8)	0.0040 (6)	0.0144 (6)	0.0047 (6)
N2	0.0270 (7)	0.0335 (7)	0.0272 (7)	−0.0021 (6)	0.0107 (5)	0.0004 (6)
C5	0.0261 (8)	0.0388 (10)	0.0398 (10)	−0.0015 (7)	0.0138 (7)	−0.0044 (8)
C3	0.0315 (9)	0.0344 (10)	0.0346 (9)	0.0022 (7)	0.0106 (7)	−0.0033 (7)

C6	0.0305 (8)	0.0352 (9)	0.0308 (8)	−0.0052 (7)	0.0130 (7)	−0.0036 (7)
C1	0.0331 (9)	0.0444 (11)	0.0337 (10)	−0.0086 (8)	0.0141 (8)	0.0027 (8)
C2	0.0292 (8)	0.0343 (9)	0.0283 (8)	−0.0006 (7)	0.0133 (7)	−0.0001 (7)
C4	0.0399 (11)	0.0518 (13)	0.0563 (13)	0.0140 (10)	0.0136 (10)	0.0122 (11)
C7	0.0338 (10)	0.0531 (13)	0.0470 (11)	−0.0064 (9)	0.0183 (8)	0.0099 (10)

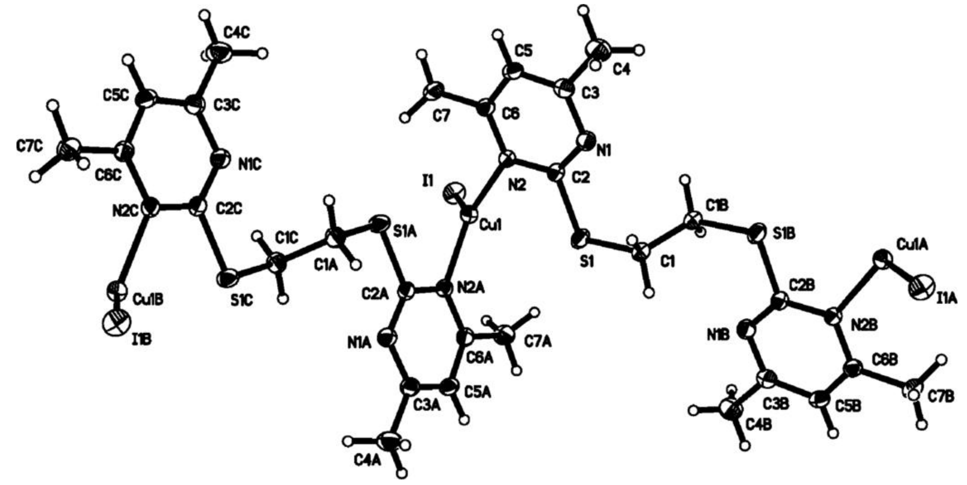
Geometric parameters (Å, °)

I1—Cu1	2.5191 (16)	C3—C4	1.495 (3)
Cu1—N2^{i}	2.0327 (16)	C6—C7	1.492 (3)
Cu1—N2	2.0327 (16)	C1—C1^{ii}	1.510 (4)
S1—C2	1.7550 (19)	C1—H1A	0.9700
S1—C1	1.809 (2)	C1—H1B	0.9700
N1—C2	1.322 (2)	C4—H4A	0.9600
N1—C3	1.351 (2)	C4—H4B	0.9600
N2—C2	1.348 (2)	C4—H4C	0.9600
N2—C6	1.353 (2)	C7—H7A	0.9600
C5—C3	1.382 (3)	C7—H7B	0.9600
C5—C6	1.383 (3)	C7—H7C	0.9600
C5—H5	0.9300		
N2^{i}—Cu1—N2	118.55 (10)	S1—C1—H1A	109.1
N2^{i}—Cu1—I1	120.72 (5)	C1^{ii}—C1—H1B	109.1
N2—Cu1—I1	120.72 (5)	S1—C1—H1B	109.1
C2—S1—C1	102.87 (9)	H1A—C1—H1B	107.8
C2—N1—C3	116.41 (16)	N1—C2—N2	127.28 (16)
C2—N2—C6	116.10 (16)	N1—C2—S1	120.02 (13)
C2—N2—Cu1	119.73 (12)	N2—C2—S1	112.69 (13)
C6—N2—Cu1	124.04 (13)	C3—C4—H4A	109.5
C3—C5—C6	119.38 (17)	C3—C4—H4B	109.5
C3—C5—H5	120.3	H4A—C4—H4B	109.5
C6—C5—H5	120.3	C3—C4—H4C	109.5
N1—C3—C5	120.57 (17)	H4A—C4—H4C	109.5
N1—C3—C4	117.01 (18)	H4B—C4—H4C	109.5
C5—C3—C4	122.42 (18)	C6—C7—H7A	109.5
N2—C6—C5	120.24 (17)	C6—C7—H7B	109.5
N2—C6—C7	117.63 (17)	H7A—C7—H7B	109.5
C5—C6—C7	122.13 (17)	C6—C7—H7C	109.5
C1^{ii}—C1—S1	112.45 (19)	H7A—C7—H7C	109.5
C1^{ii}—C1—H1A	109.1	H7B—C7—H7C	109.5
N2^{i}—Cu1—N2—C2	59.68 (13)	C3—C5—C6—N2	1.1 (3)
I1—Cu1—N2—C2	−120.32 (13)	C3—C5—C6—C7	−178.78 (19)
N2^{i}—Cu1—N2—C6	−115.97 (16)	C2—S1—C1—C1^{ii}	−79.7 (2)
I1—Cu1—N2—C6	64.03 (16)	C3—N1—C2—N2	0.9 (3)
C2—N1—C3—C5	−1.1 (3)	C3—N1—C2—S1	179.92 (14)
C2—N1—C3—C4	179.03 (19)	C6—N2—C2—N1	0.3 (3)
C6—C5—C3—N1	0.2 (3)	Cu1—N2—C2—N1	−175.69 (15)
C6—C5—C3—C4	−179.9 (2)	C6—N2—C2—S1	−178.79 (13)

C2—N2—C6—C5	−1.3 (3)	Cu1—N2—C2—S1	5.22 (18)
Cu1—N2—C6—C5	174.53 (14)	C1—S1—C2—N1	9.16 (18)
C2—N2—C6—C7	178.58 (18)	C1—S1—C2—N2	−171.68 (14)
Cu1—N2—C6—C7	−5.6 (2)		

Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2; (ii) −*x*+1, −*y*+1, −*z*.

Fig. 1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