# Poly[[μ3-N,N′-bis(3-pyridylmethyl)-thiourea-κ3N:N′:S]iodidocopper(I)]

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In the title coordination polymer, [CuI(C$_{13}$H$_{14}$N$_4$S)]$_n$, the Cu$^I$ atom is coordinated by two N atoms from two N,N′-bis(3-pyridylmethyl)thiourea ligands, as well as by the S atom of a third ligand and an I atom to confer a distorted tetrahedral coordination at the metal centre. The coordination bonds give rise to a layer structure parallel to (010).

## Related literature

For related literature, see: Li *et al.* (2002); Zhang *et al.* (2006).
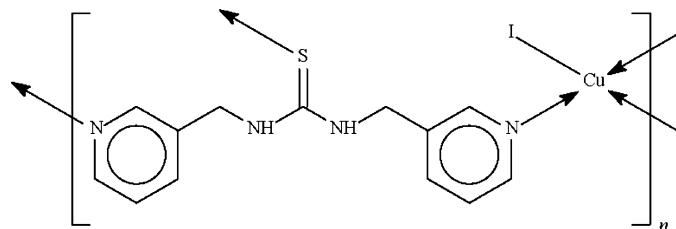


## Experimental

### Crystal data

[CuI(C$_{13}$H$_{14}$N$_4$S)]
$M_r$ = 448.78
Monoclinic, $P2_1/c$
$a$ = 13.3610 (10) Å
$b$ = 8.3673 (7) Å
$c$ = 14.2686 (11) Å
$\beta$ = 102.001 (2)°

$V$ = 1560.3 (2) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 3.51 mm$^{-1}$
$T$ = 294 (2) K
0.20 × 0.15 × 0.12 mm

### Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.541, $T_{max}$ = 0.678

8191 measured reflections
2750 independent reflections
2418 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.020

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.062
$S$ = 1.06
2750 reflections

181 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.73 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.28 e Å$^{-3}$

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; 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*.

## References

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# supporting information

# Poly[[*μ*₃-*N*,*N*′-bis(3-pyridylmethyl)thiourea-*κ*³*N*:*N*′:*S*]iodidocopper(I)]

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## S1. Comment

Flexible ligand has been considered as one of the most important type of organic ligand for their flexibility and conformational freedom allow for greater structural diversity. *N*,*N*′-bis(3-pyridylmethyl)thiurea, as one kind of those ligand, has usually been used to construct a great variety of structurally interesting entities. such as helix, macrocycle (Zhang *et al.*, 2006; Li *et al.*, 2002).

The asymmetric unit of the title compound (I) is illustrated in Fig. 1. Single-crystal X-ray diffraction shows that the asymmetric unit contains one Cu crystallographically nonequivalent atom. The Cu(I) atom coordinated by two N atoms from two N,N′-bis(3-pyridylmethyl)thiourea ligands as well as by the S atom of a third ligand to confer a tetrahedral geometry at the metal center. The Cu atom coordination by two N atoms to form a one-dimensional helix, and is then linked by the bond of Cu atom and S atom to extend to a two-dimensional structure. The crystal packing is stabilized by intermolecular $\pi$–$\pi$ stacking interaction (Fig. 2).

## S2. Experimental

a mixture of CuI (0.038 g, 0.2 nmol) and *N*,*N*′-bis(3-pyridylmethyl)thiourea (0.026 g, 0.1 nmol) in mole ratio of 2:1 in acetonitrile (6 cm³) was sealed in 15 cm³ Teflon-lined reactor and heated to 110°C for 10 h and then cooled to room temperature at a rate of 5°C/h. the yellow block crystal was obtianed in the yield of 35%.

The web of checkcif show one Alert level B (Hirshfeld Test Diff (M—*X*) I1 – Cu1.. 43.03 su), we think this is the result of the sightly distorted I atom for his unidentate coordination model.

## S3. Refinement

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å(aromatic) or 0.97 Å(aliphatic) and N—H = 0.86 Å, and with $U_{\text{iso}}(H) = 1.2U_{eq}(C,N)$
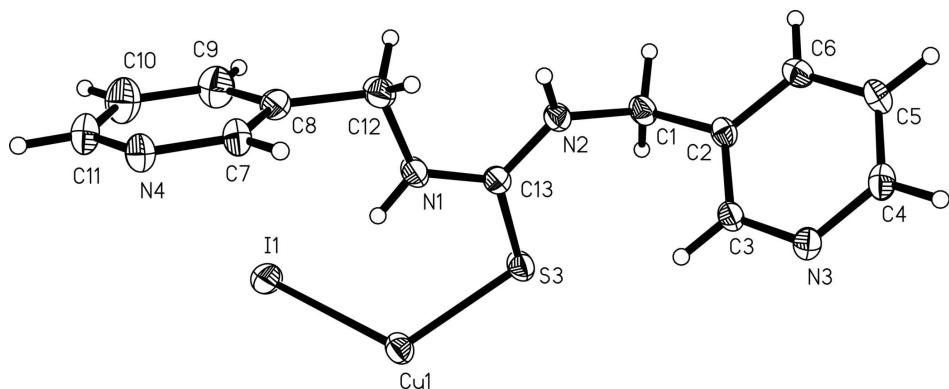
**Figure 1**

The asymmetric unit of the title compound showing 30° probability ellipsoids.



**Figure 2**

The crystal packing of the title compound.

**Poly[[μ₃-*N*,*N*′-bis(3-pyridylmethyl)thiourea-*κ³N*:*N*′:*S*]iodidocopper(I)]**

*Crystal data*

| | |
|---|---|
| [CuI(C₁₃H₁₄N₄S)] | $F(000) = 872$ |
| $M_r = 448.78$ | $D_x = 1.910$ Mg m⁻³ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 3234 reflections |
| $a = 13.361$ (1) Å | $\theta = 2.8–27.7°$ |
| $b = 8.3673$ (7) Å | $\mu = 3.51$ mm⁻¹ |
| $c = 14.2686$ (11) Å | $T = 294$ K |
| $\beta = 102.001$ (2)° | Block, yellow |
| $V = 1560.3$ (2) Å³ | $0.20 \times 0.15 \times 0.12$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD diffractometer | 8191 measured reflections |
| Radiation source: fine-focus sealed tube | 2750 independent reflections |
| Graphite monochromator | 2418 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{\text{int}} = 0.020$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $\theta_{\text{max}} = 25.0°$, $\theta_{\text{min}} = 2.8°$ |
| | $h = -12 \rightarrow 15$ |
| | $k = -9 \rightarrow 9$ |
| $T_{\text{min}} = 0.541$, $T_{\text{max}} = 0.678$ | $l = -15 \rightarrow 16$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.026$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.062$ | |
| $S = 1.06$ | H-atom parameters constrained |
| 2750 reflections | $w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 0.8144P]$ |
| 181 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\text{max}} = 0.73$ e Å$^{-3}$ |
| | $\Delta\rho_{\text{min}} = -0.28$ 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$^2$)*

| | $x$ | $y$ | $z$ | $U_{\text{iso}}$*/$U_{\text{eq}}$ |
|---|---|---|---|---|
| C1 | 0.4137 (2) | 0.8305 (4) | 0.3317 (2) | 0.0340 (7) |
| H1A | 0.4469 | 0.7269 | 0.3368 | 0.041* |
| H1B | 0.4581 | 0.9036 | 0.3739 | 0.041* |
| C2 | 0.4006 (2) | 0.8893 (3) | 0.2301 (2) | 0.0290 (6) |
| C3 | 0.3491 (2) | 1.0308 (3) | 0.2012 (2) | 0.0315 (7) |
| H3 | 0.3220 | 1.0879 | 0.2460 | 0.038* |
| C4 | 0.3768 (2) | 1.0054 (4) | 0.0489 (2) | 0.0361 (7) |
| H4 | 0.3685 | 1.0441 | −0.0134 | 0.043* |
| C5 | 0.4292 (2) | 0.8663 (4) | 0.0718 (2) | 0.0402 (7) |
| H5 | 0.4565 | 0.8122 | 0.0260 | 0.048* |
| C6 | 0.4415 (2) | 0.8065 (4) | 0.1630 (2) | 0.0376 (7) |
| H6 | 0.4770 | 0.7115 | 0.1795 | 0.045* |
| C7 | −0.0360 (2) | 0.7596 (4) | 0.4500 (2) | 0.0379 (7) |
| H7 | −0.0490 | 0.7921 | 0.3863 | 0.045* |
| C8 | 0.0621 (2) | 0.7151 (4) | 0.4916 (2) | 0.0372 (7) |
| C9 | 0.0813 (3) | 0.6670 (5) | 0.5858 (3) | 0.0521 (9) |

| | | | |
|---|---|---|---|
| H9 | 0.1469 | 0.6365 | 0.6166 | 0.063* |
| C10 | 0.0020 (3) | 0.6648 (5) | 0.6337 (3) | 0.0571 (10) |
| H10 | 0.0130 | 0.6307 | 0.6970 | 0.068* |
| C11 | −0.0934 (3) | 0.7134 (4) | 0.5874 (2) | 0.0445 (8) |
| H11 | −0.1460 | 0.7147 | 0.6210 | 0.053* |
| C12 | 0.1456 (2) | 0.7225 (4) | 0.4347 (3) | 0.0413 (8) |
| H12A | 0.1909 | 0.6314 | 0.4502 | 0.050* |
| H12B | 0.1157 | 0.7194 | 0.3667 | 0.050* |
| C13 | 0.2875 (2) | 0.9112 (3) | 0.4274 (2) | 0.0309 (6) |
| Cu1 | 0.26574 (3) | 1.19634 (5) | 0.57370 (3) | 0.04022 (12) |
| N1 | 0.20322 (18) | 0.8710 (3) | 0.45837 (19) | 0.0397 (6) |
| H1 | 0.1810 | 0.9377 | 0.4952 | 0.048* |
| N2 | 0.31731 (18) | 0.8164 (3) | 0.36364 (17) | 0.0317 (6) |
| H2 | 0.2765 | 0.7407 | 0.3393 | 0.038* |
| N3 | 0.33636 (18) | 1.0893 (3) | 0.11266 (18) | 0.0328 (6) |
| N4 | −0.11373 (19) | 0.7591 (3) | 0.4956 (2) | 0.0396 (6) |
| S3 | 0.35264 (6) | 1.07993 (10) | 0.46956 (6) | 0.0397 (2) |
| I1 | 0.24731 (2) | 1.03780 (3) | 0.728706 (18) | 0.05208 (10) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0309 (16) | 0.0383 (16) | 0.0344 (17) | 0.0077 (12) | 0.0101 (13) | −0.0001 (13) |
| C2 | 0.0242 (14) | 0.0350 (16) | 0.0285 (16) | −0.0015 (12) | 0.0072 (12) | −0.0040 (13) |
| C3 | 0.0323 (16) | 0.0333 (16) | 0.0322 (17) | −0.0006 (12) | 0.0140 (13) | −0.0037 (13) |
| C4 | 0.0379 (17) | 0.0451 (17) | 0.0268 (16) | −0.0068 (14) | 0.0102 (14) | −0.0002 (14) |
| C5 | 0.0462 (19) | 0.0439 (18) | 0.0348 (18) | 0.0034 (15) | 0.0184 (15) | −0.0077 (15) |
| C6 | 0.0418 (18) | 0.0334 (16) | 0.0396 (19) | 0.0072 (13) | 0.0134 (14) | −0.0025 (14) |
| C7 | 0.0335 (17) | 0.0461 (18) | 0.0370 (18) | −0.0018 (14) | 0.0139 (14) | −0.0007 (15) |
| C8 | 0.0338 (17) | 0.0328 (16) | 0.047 (2) | −0.0057 (13) | 0.0128 (15) | −0.0044 (15) |
| C9 | 0.0371 (19) | 0.065 (2) | 0.052 (2) | 0.0022 (16) | 0.0035 (16) | 0.0058 (19) |
| C10 | 0.055 (2) | 0.076 (3) | 0.040 (2) | −0.0008 (19) | 0.0097 (17) | 0.0101 (19) |
| C11 | 0.0411 (19) | 0.056 (2) | 0.040 (2) | −0.0058 (16) | 0.0171 (15) | 0.0028 (17) |
| C12 | 0.0329 (17) | 0.0378 (17) | 0.056 (2) | −0.0043 (14) | 0.0151 (15) | −0.0110 (16) |
| C13 | 0.0311 (16) | 0.0309 (15) | 0.0312 (16) | 0.0012 (12) | 0.0079 (13) | −0.0013 (13) |
| Cu1 | 0.0403 (2) | 0.0416 (2) | 0.0416 (2) | −0.00434 (17) | 0.01496 (18) | −0.00960 (18) |
| N1 | 0.0378 (14) | 0.0374 (14) | 0.0495 (17) | −0.0068 (12) | 0.0223 (13) | −0.0140 (13) |
| N2 | 0.0346 (14) | 0.0321 (13) | 0.0297 (13) | −0.0022 (10) | 0.0097 (11) | −0.0049 (11) |
| N3 | 0.0324 (13) | 0.0361 (13) | 0.0311 (14) | −0.0004 (11) | 0.0099 (11) | 0.0023 (11) |
| N4 | 0.0324 (14) | 0.0475 (16) | 0.0412 (16) | −0.0010 (12) | 0.0129 (12) | 0.0011 (13) |
| S3 | 0.0369 (4) | 0.0383 (4) | 0.0488 (5) | −0.0085 (3) | 0.0203 (4) | −0.0128 (4) |
| I1 | 0.07354 (19) | 0.04215 (15) | 0.04564 (16) | 0.00823 (11) | 0.02411 (12) | 0.01044 (10) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—N2 | 1.457 (4) | C9—H9 | 0.9300 |
| C1—C2 | 1.506 (4) | C10—C11 | 1.370 (5) |
| C1—H1A | 0.9700 | C10—H10 | 0.9300 |

| | | | |
|---|---|---|---|
| C1—H1B | 0.9700 | C11—N4 | 1.337 (4) |
| C2—C6 | 1.384 (4) | C11—H11 | 0.9300 |
| C2—C3 | 1.388 (4) | C12—N1 | 1.464 (4) |
| C3—N3 | 1.332 (4) | C12—H12A | 0.9700 |
| C3—H3 | 0.9300 | C12—H12B | 0.9700 |
| C4—N3 | 1.348 (4) | C13—N2 | 1.330 (4) |
| C4—C5 | 1.363 (4) | C13—N1 | 1.335 (4) |
| C4—H4 | 0.9300 | C13—S3 | 1.701 (3) |
| C5—C6 | 1.371 (5) | Cu1—N3$^i$ | 2.049 (2) |
| C5—H5 | 0.9300 | Cu1—N4$^{ii}$ | 2.099 (3) |
| C6—H6 | 0.9300 | Cu1—S3 | 2.2852 (8) |
| C7—N4 | 1.335 (4) | Cu1—I1 | 2.6341 (5) |
| C7—C8 | 1.372 (4) | N1—H1 | 0.8600 |
| C7—H7 | 0.9300 | N2—H2 | 0.8600 |
| C8—C9 | 1.374 (5) | N3—Cu1$^{iii}$ | 2.049 (2) |
| C8—C12 | 1.512 (4) | N4—Cu1$^{ii}$ | 2.099 (3) |
| C9—C10 | 1.376 (5) | | |
| | | | |
| N2—C1—C2 | 113.3 (2) | C9—C10—H10 | 120.3 |
| N2—C1—H1A | 108.9 | N4—C11—C10 | 122.4 (3) |
| C2—C1—H1A | 108.9 | N4—C11—H11 | 118.8 |
| N2—C1—H1B | 108.9 | C10—C11—H11 | 118.8 |
| C2—C1—H1B | 108.9 | N1—C12—C8 | 108.8 (2) |
| H1A—C1—H1B | 107.7 | N1—C12—H12A | 109.9 |
| C6—C2—C3 | 117.6 (3) | C8—C12—H12A | 109.9 |
| C6—C2—C1 | 121.3 (3) | N1—C12—H12B | 109.9 |
| C3—C2—C1 | 121.1 (2) | C8—C12—H12B | 109.9 |
| N3—C3—C2 | 123.6 (3) | H12A—C12—H12B | 108.3 |
| N3—C3—H3 | 118.2 | N2—C13—N1 | 118.0 (3) |
| C2—C3—H3 | 118.2 | N2—C13—S3 | 122.2 (2) |
| N3—C4—C5 | 122.7 (3) | N1—C13—S3 | 119.8 (2) |
| N3—C4—H4 | 118.6 | N3$^i$—Cu1—N4$^{ii}$ | 108.54 (10) |
| C5—C4—H4 | 118.6 | N3$^i$—Cu1—S3 | 106.38 (7) |
| C4—C5—C6 | 119.6 (3) | N4$^{ii}$—Cu1—S3 | 110.01 (8) |
| C4—C5—H5 | 120.2 | N3$^i$—Cu1—I1 | 109.34 (7) |
| C6—C5—H5 | 120.2 | N4$^{ii}$—Cu1—I1 | 103.57 (7) |
| C5—C6—C2 | 119.1 (3) | S3—Cu1—I1 | 118.69 (3) |
| C5—C6—H6 | 120.4 | C13—N1—C12 | 125.3 (2) |
| C2—C6—H6 | 120.4 | C13—N1—H1 | 117.4 |
| N4—C7—C8 | 123.9 (3) | C12—N1—H1 | 117.4 |
| N4—C7—H7 | 118.0 | C13—N2—C1 | 125.2 (3) |
| C8—C7—H7 | 118.0 | C13—N2—H2 | 117.4 |
| C7—C8—C9 | 118.0 (3) | C1—N2—H2 | 117.4 |
| C7—C8—C12 | 120.1 (3) | C3—N3—C4 | 117.3 (3) |
| C9—C8—C12 | 121.9 (3) | C3—N3—Cu1$^{iii}$ | 122.7 (2) |
| C8—C9—C10 | 118.8 (3) | C4—N3—Cu1$^{iii}$ | 119.9 (2) |
| C8—C9—H9 | 120.6 | C7—N4—C11 | 117.2 (3) |
| C10—C9—H9 | 120.6 | C7—N4—Cu1$^{ii}$ | 123.0 (2) |

| C11—C10—C9 | 119.5 (3) | C11—N4—Cu1ⁱⁱ | 119.4 (2) |
| C11—C10—H10 | 120.3 | C13—S3—Cu1 | 106.95 (10) |

Symmetry codes: (i) $x$, $-y+5/2$, $z+1/2$; (ii) $-x$, $-y+2$, $-z+1$; (iii) $x$, $-y+5/2$, $z-1/2$.