# metal-organic compounds

# (Thiocyanato-κN)bis(thiosemicarbazide-κS)copper(I)

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In the title complex, $[Cu(CH_5N_3S)_2(NCS)]$, the non-H part of the molecule is strictly planar, lying on the mirror plane at $y = 0.25$. The Cu atom lies at the centre of a triangle formed by the coordination of three monodentate groups, *viz*. two thiosemicarbazide ligands and one $NCS^-$ anion. Weak intermolecular N—H···S interactions generate a two-dimensional network.

## Related literature

For related thiosemicarbazide metal complexes, see: Capacchi *et al.* (1968). For related literature, see: Chattopadhyay *et al.* (1991).
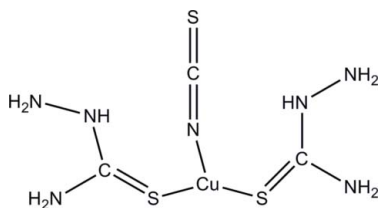


## Experimental

### Crystal data

| | |
|---|---|
| $[Cu(CH_5N_3S)_2(NCS)]$ | $a = 11.488$ (2) Å |
| $M_r = 303.90$ | $b = 6.6085$ (12) Å |
| Orthorhombic, $Pnma$ | $c = 14.650$ (3) Å |

| | |
|---|---|
| $V = 1112.2$ (4) Å$^3$ | $\mu = 2.50$ mm$^{-1}$ |
| $Z = 4$ | $T = 298$ (2) K |
| Mo $K\alpha$ radiation | $0.38 \times 0.27 \times 0.24$ mm |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 5593 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{min} = 0.44$, $T_{max} = 0.55$ | 1077 independent reflections 947 reflections with $I > 2\sigma(I)$ $R_{int} = 0.021$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.029$ | 86 parameters |
| $wR(F^2) = 0.080$ | H-atom parameters constrained |
| $S = 1.05$ | $\Delta\rho_{max} = 0.67$ e Å$^{-3}$ |
| 1077 reflections | $\Delta\rho_{min} = -0.54$ e Å$^{-3}$ |

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1$A$···S3$^i$ | 0.86 | 2.64 | 3.485 (3) | 167 |
| N1—H1$B$···N3$^i$ | 0.86 | 2.14 | 2.998 (4) | 177 |
| N2—H2···N7 | 0.86 | 2.24 | 3.093 (4) | 175 |
| N3—H3$A$···S2$^{ii}$ | 0.89 | 2.81 | 3.5481 (11) | 141 |
| N3—H3$B$···S2$^{iii}$ | 0.89 | 2.72 | 3.5481 (11) | 155 |
| N4—H4$A$···S2$^{iv}$ | 0.86 | 2.65 | 3.501 (3) | 170 |
| N4—H4$B$···N7 | 0.86 | 2.32 | 3.161 (4) | 167 |
| N5—H5···S3$^v$ | 0.86 | 2.64 | 3.342 (3) | 140 |
| N6—H6$A$···S1$^{vi}$ | 0.89 | 2.88 | 3.5144 (12) | 130 |
| N6—H6$B$···S1$^{vii}$ | 0.89 | 2.75 | 3.5144 (11) | 144 |

Symmetry codes: (i) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$; (iv) $x + \frac{1}{2}, y, -z + \frac{3}{2}$; (v) $x - \frac{1}{2}, y, -z + \frac{3}{2}$; (vi) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (vii) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); 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

Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Capacchi, L. C., Gasparri, G. F., Ferrari, M. & Nardelli, M. (1968). *Chem. Commun.* pp. 910–911.
Chattopadhyay, D., Majumdar, S. K., Lowe, P., Schwalbe, C. H., Chattopadhyay, S. K. & Ghosh, S. (1991). *Dalton Trans.* pp. 2121–2124.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supporting information

## (Thiocyanato-*κN*)bis(thiosemicarbazide-*κS*)copper(I)

**Li Jia, Shouxin Ma and Dacheng Li**

### S1. Comment

Thiosemicarbazide can behave as a chelating agent(Chattopadhyay *et al.*,1991) or as a monodentate ligand(Capacchi *et al.*, 1968). Among the different N,*S* donors studies,thiosemicarbazides and thiosemicarbazines are of special interest as both of these free ligands and their copper complexes exhibit a variety of biological activities including antitumour activity(Chattopadhyay *et al.*,1991). In this paper, $Cu(CH_5N_3S)_2(NCS)$ was synthesized by the reaction of $CuCl_2.6H_2O$, thiosemicarbazide and NaSCN at room temperature and the structure of the resulting complex is presented herein. The non-H part of the molecule is strictly planar, lying on the mirror plane at y=0.25. The Cu atom lies at the centre of a planar triangle formed by coordination of three monodentate groups, two thiosemicarbazide ligands and one NCS anion (Fig. 1). The Cu—S bond length (2.2415 (13) Å) is comparable to those in $[Cu(SC(NH_2)NHNH_2)Cl_2]$ (2.266 (1) Å,Chattopadhyay *et al.*, 1991), while the Cu—N bond is shorter than the corresponding value therein (2.002 (4)Å).

In the crystal structure, weak intermolecular C—H···S interactions determine a two-dimensional network.

### S2. Experimental

Copper chloride dihydrate (0.3 mmol 51.2 mg) was dissolved in absolute methanol (10 ml), and was added dropwise to a solution of an equate ligand thiosemicarbazide in MeOH (10 ml). The solution was stirred for 10 minutes, then NaSCN was added. The solution became bottle-green. The mother liquid was placed at room temperature, and single crystals were obtained on standing. Elemental analysis for $C_3H_{10}Cu N_7S_3$ calculated: C 36.03, H 10.08, N %; found: C 36.12, H 10.26, N 98.05%.

### S3. Refinement

All H atoms were placed geometrically and treated as riding on their parent atoms with N—H 0.86 Å (thiosemicarbazide) $[U_{iso}(H) = 1.2U_{eq}(N)]$.

The copper atom presents an abnormally elongated displacement ellipsoid perpendicular to the mirror plane, suggeesting some kind of disorder around its (average) symmetric position.
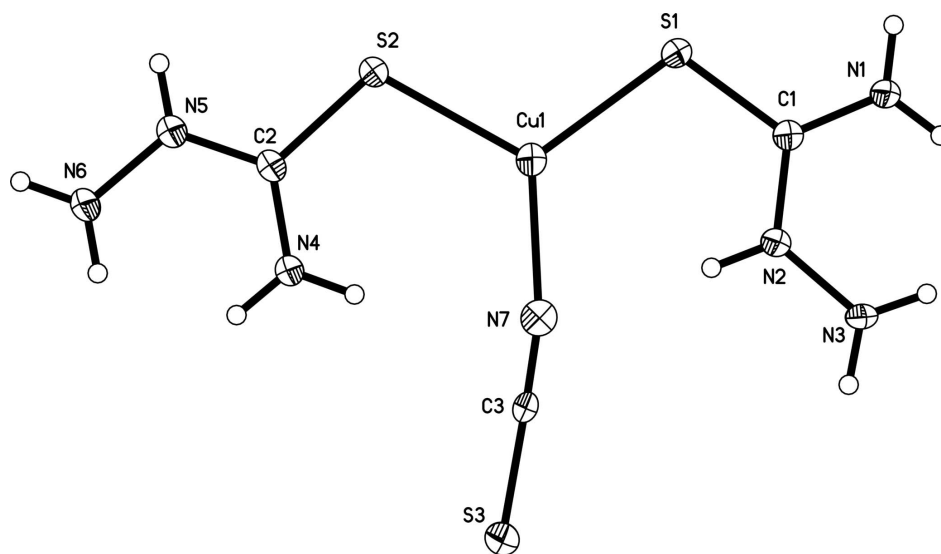
**Figure 1**

The crystal structure of the title compound showing the atomic numbering and 30% probability displacement ellipsoids. N-bound H atoms have been omitted for clarity.

**(Thiocyanato-$\kappa$N)bis(thiosemicarbazide-$\kappa$S)copper(I)**

*Crystal data*

| | |
|---|---|
| [Cu(CH$_5$N$_3$S)$_2$(NCS)] | $F(000) = 616$ |
| $M_r = 303.90$ | $D_x = 1.815$ Mg m$^{-3}$ |
| Orthorhombic, *Pnma* | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ac 2n | Cell parameters from 3130 reflections |
| $a = 11.488$ (2) Å | $\theta = 2.3$–28.2° |
| $b = 6.6085$ (12) Å | $\mu = 2.50$ mm$^{-1}$ |
| $c = 14.650$ (3) Å | $T = 298$ K |
| $V = 1112.2$ (4) Å$^3$ | Block, black |
| $Z = 4$ | $0.38 \times 0.27 \times 0.24$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 5593 measured reflections |
| Radiation source: fine-focus sealed tube | 1077 independent reflections |
| Graphite monochromator | 947 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{\text{int}} = 0.021$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $\theta_{\text{max}} = 25.0°$, $\theta_{\text{min}} = 2.3°$ |
| $T_{\text{min}} = 0.44$, $T_{\text{max}} = 0.55$ | $h = -13 \rightarrow 13$ |
| | $k = -7 \rightarrow 7$ |
| | $l = -17 \rightarrow 10$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.029$ | |
| $wR(F^2) = 0.080$ | |
| $S = 1.05$ | Hydrogen site location: inferred from neighbouring sites |
| 1077 reflections | H-atom parameters constrained |
| 86 parameters | |
| 0 restraints | |

$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.712P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.67$ e Å$^{-3}$

$\Delta\rho_{min} = -0.54$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick,
    2008), Fc*=kFc[1+0.001xFc²$\lambda$³/sin(2$\theta$)]$^{-1/4}$
Extinction coefficient: 0.0072 (9)

*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* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Cu1 | 0.28439 (4) | 0.2500 | 0.53244 (3) | 0.0689 (3) | |
| N1 | 0.1200 (2) | 0.2500 | 0.25507 (19) | 0.0338 (6) | |
| H1A | 0.1489 | 0.2500 | 0.2009 | 0.041* | |
| H1B | 0.0458 | 0.2500 | 0.2625 | 0.041* | |
| N2 | 0.3047 (2) | 0.2500 | 0.31376 (19) | 0.0361 (7) | |
| H2 | 0.3483 | 0.2500 | 0.3615 | 0.043* | |
| N3 | 0.3600 (2) | 0.2500 | 0.22780 (18) | 0.0348 (6) | |
| H3A | 0.3244 | 0.1616 | 0.1914 | 0.052* | 0.50 |
| H3B | 0.3555 | 0.3732 | 0.2035 | 0.052* | 0.50 |
| N4 | 0.4655 (2) | 0.2500 | 0.7081 (2) | 0.0457 (8) | |
| H4A | 0.5262 | 0.2500 | 0.7423 | 0.055* | |
| H4B | 0.4729 | 0.2500 | 0.6496 | 0.055* | |
| N5 | 0.3516 (2) | 0.2500 | 0.83438 (18) | 0.0349 (7) | |
| H5 | 0.2839 | 0.2500 | 0.8594 | 0.042* | |
| N6 | 0.4526 (2) | 0.2500 | 0.88959 (19) | 0.0414 (7) | |
| H6A | 0.4426 | 0.1645 | 0.9359 | 0.062* | 0.50 |
| H6B | 0.4647 | 0.3741 | 0.9112 | 0.062* | 0.50 |
| N7 | 0.4475 (3) | 0.2500 | 0.4928 (2) | 0.0415 (7) | |
| S1 | 0.13368 (7) | 0.2500 | 0.43541 (6) | 0.0335 (2) | |
| S2 | 0.23512 (7) | 0.2500 | 0.68064 (5) | 0.0318 (2) | |
| S3 | 0.68866 (8) | 0.2500 | 0.47665 (7) | 0.0528 (3) | |
| C1 | 0.1893 (3) | 0.2500 | 0.3264 (2) | 0.0283 (7) | |
| C2 | 0.3611 (3) | 0.2500 | 0.7450 (2) | 0.0286 (7) | |
| C3 | 0.5450 (3) | 0.2500 | 0.4851 (2) | 0.0278 (7) | |

*Atomic displacement parameters (Å$^2$)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0292 (3) | 0.1520 (7) | 0.0256 (3) | 0.000 | −0.00124 (17) | 0.000 |
| N1 | 0.0205 (13) | 0.0557 (17) | 0.0252 (13) | 0.000 | −0.0003 (10) | 0.000 |
| N2 | 0.0214 (13) | 0.0632 (18) | 0.0237 (14) | 0.000 | −0.0002 (11) | 0.000 |

| N3 | 0.0254 (13) | 0.0517 (17) | 0.0274 (15) | 0.000 | 0.0048 (11) | 0.000 |
|---|---|---|---|---|---|---|
| N4 | 0.0261 (15) | 0.088 (2) | 0.0236 (14) | 0.000 | −0.0024 (11) | 0.000 |
| N5 | 0.0260 (13) | 0.0529 (17) | 0.0259 (15) | 0.000 | −0.0030 (11) | 0.000 |
| N6 | 0.0339 (15) | 0.0617 (19) | 0.0285 (15) | 0.000 | −0.0088 (12) | 0.000 |
| N7 | 0.0338 (18) | 0.0549 (19) | 0.0357 (16) | 0.000 | 0.0011 (13) | 0.000 |
| S1 | 0.0242 (4) | 0.0521 (5) | 0.0242 (4) | 0.000 | 0.0021 (3) | 0.000 |
| S2 | 0.0232 (4) | 0.0477 (5) | 0.0243 (4) | 0.000 | −0.0017 (3) | 0.000 |
| S3 | 0.0279 (5) | 0.0971 (8) | 0.0333 (5) | 0.000 | −0.0009 (4) | 0.000 |
| C1 | 0.0242 (15) | 0.0345 (16) | 0.0263 (16) | 0.000 | −0.0003 (12) | 0.000 |
| C2 | 0.0256 (15) | 0.0335 (16) | 0.0265 (16) | 0.000 | −0.0038 (12) | 0.000 |
| C3 | 0.0286 (18) | 0.0395 (18) | 0.0152 (14) | 0.000 | 0.0017 (12) | 0.000 |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu1—N7 | 1.962 (3) | N4—H4A | 0.8600 |
| Cu1—S1 | 2.2401 (10) | N4—H4B | 0.8600 |
| Cu1—S2 | 2.2437 (10) | N5—C2 | 1.314 (4) |
| N1—C1 | 1.313 (4) | N5—N6 | 1.414 (4) |
| N1—H1A | 0.8600 | N5—H5 | 0.8600 |
| N1—H1B | 0.8600 | N6—H6A | 0.8900 |
| N2—C1 | 1.339 (4) | N6—H6B | 0.8900 |
| N2—N3 | 1.410 (4) | N7—C3 | 1.126 (4) |
| N2—H2 | 0.8600 | S1—C1 | 1.721 (3) |
| N3—H3A | 0.8900 | S2—C2 | 1.727 (3) |
| N3—H3B | 0.8900 | S3—C3 | 1.655 (3) |
| N4—C2 | 1.315 (4) | | |
| | | | |
| N7—Cu1—S1 | 123.38 (10) | C2—N5—H5 | 119.9 |
| N7—Cu1—S2 | 121.85 (10) | N6—N5—H5 | 119.9 |
| S1—Cu1—S2 | 114.77 (4) | N5—N6—H6A | 109.3 |
| C1—N1—H1A | 120.0 | N5—N6—H6B | 109.4 |
| C1—N1—H1B | 120.0 | H6A—N6—H6B | 109.5 |
| H1A—N1—H1B | 120.0 | C3—N7—Cu1 | 168.5 (3) |
| C1—N2—N3 | 124.7 (3) | C1—S1—Cu1 | 107.58 (11) |
| C1—N2—H2 | 117.7 | C2—S2—Cu1 | 108.46 (11) |
| N3—N2—H2 | 117.7 | N1—C1—N2 | 119.4 (3) |
| N2—N3—H3A | 109.2 | N1—C1—S1 | 120.9 (2) |
| N2—N3—H3B | 109.4 | N2—C1—S1 | 119.7 (2) |
| H3A—N3—H3B | 109.5 | N5—C2—N4 | 119.0 (3) |
| C2—N4—H4A | 120.0 | N5—C2—S2 | 118.3 (2) |
| C2—N4—H4B | 120.0 | N4—C2—S2 | 122.7 (3) |
| H4A—N4—H4B | 120.0 | N7—C3—S3 | 178.6 (3) |
| C2—N5—N6 | 120.1 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N1—H1A···S3ⁱ | 0.86 | 2.64 | 3.485 (3) | 167 |

| | | | | |
|---|---|---|---|---|
| N1—H1*B*···N3<sup>i</sup> | 0.86 | 2.14 | 2.998 (4) | 177 |
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