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(Thiocyanato- κN)bis(thiosemicarbazide- κS)copper(I)Li Jia,^a Shouxin Ma^b and Dacheng Li^{c*}

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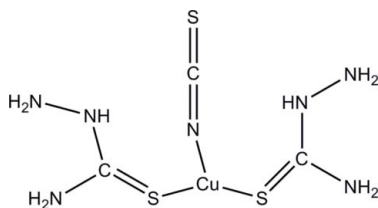
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{N}-\text{C}) = 0.005$ Å; R factor = 0.029; wR factor = 0.080; data-to-parameter ratio = 12.5.

In the title complex, $[\text{Cu}(\text{CH}_5\text{N}_3\text{S})_2(\text{NCS})]$, 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 $\text{N}-\text{H}\cdots\text{S}$ 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*

$[\text{Cu}(\text{CH}_5\text{N}_3\text{S})_2(\text{NCS})]$
 $M_r = 303.90$
 Orthorhombic, $Pnma$

$a = 11.488$ (2) Å
 $b = 6.6085$ (12) Å
 $c = 14.650$ (3) Å

$V = 1112.2$ (4) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 2.50$ mm⁻¹
 $T = 298$ (2) K
 $0.38 \times 0.27 \times 0.24$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.44$, $T_{\max} = 0.55$

5593 measured reflections
 1077 independent reflections
 947 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.080$
 $S = 1.05$
 1077 reflections

86 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.67$ e Å⁻³
 $\Delta\rho_{\min} = -0.54$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1A}\cdots\text{S3}^i$	0.86	2.64	3.485 (3)	167
$\text{N1}-\text{H1B}\cdots\text{N3}^i$	0.86	2.14	2.998 (4)	177
$\text{N2}-\text{H2}\cdots\text{N7}$	0.86	2.24	3.093 (4)	175
$\text{N3}-\text{H3A}\cdots\text{S2}^{ii}$	0.89	2.81	3.5481 (11)	141
$\text{N3}-\text{H3B}\cdots\text{S2}^{iii}$	0.89	2.72	3.5481 (11)	155
$\text{N4}-\text{H4A}\cdots\text{S2}^{iv}$	0.86	2.65	3.501 (3)	170
$\text{N4}-\text{H4B}\cdots\text{N7}$	0.86	2.32	3.161 (4)	167
$\text{N5}-\text{H5}\cdots\text{S3}^v$	0.86	2.64	3.342 (3)	140
$\text{N6}-\text{H6A}\cdots\text{S1}^{vi}$	0.89	2.88	3.5144 (12)	130
$\text{N6}-\text{H6B}\cdots\text{S1}^{vii}$	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) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (v) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2183).

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supplementary materials

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

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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, $\text{Cu}(\text{CH}_5\text{N}_3\text{S})_2(\text{NCS})$ was synthesized by the reaction of $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$, 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 $[\text{Cu}(\text{SC}(\text{NH}_2)\text{NHNH}_2)\text{Cl}_2]$ (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 \cdots S interactions determine a two-dimensional network.

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 $\text{C}_3\text{H}_{10}\text{Cu N}_7\text{S}_3$ calculated: C 36.03, H 10.08, N %; found: C 36.12, H 10.26, N 98.05%.

Refinement

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

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

Figures

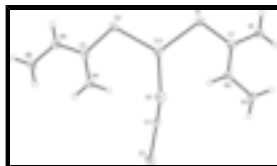


Fig. 1. The crystal structure of the title compound showing the atomic numbering and 30% probability displacement ellipsoids. N-bound H atoms have been omitted for clarity.

(Thiocyanato- κ N)bis(thiosemicarbazide- κ S)copper(I)

Crystal data

[Cu(CH ₅ N ₃ S) ₂ (NCS)]	$F(000) = 616$
$M_r = 303.90$	$D_x = 1.815 \text{ Mg m}^{-3}$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: -P 2ac 2n	Cell parameters from 3130 reflections
$a = 11.488 (2) \text{ \AA}$	$\theta = 2.3\text{--}28.2^\circ$
$b = 6.6085 (12) \text{ \AA}$	$\mu = 2.50 \text{ mm}^{-1}$
$c = 14.650 (3) \text{ \AA}$	$T = 298 \text{ K}$
$V = 1112.2 (4) \text{ \AA}^3$	Block, black
$Z = 4$	$0.38 \times 0.27 \times 0.24 \text{ mm}$

Data collection

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

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.029$	H-atom parameters constrained
$wR(F^2) = 0.080$	$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.712P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
1077 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
86 parameters	$\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.54 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
	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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	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 (\AA^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

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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 (\AA , $^\circ$)

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 (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots S3 ⁱ	0.86	2.64	3.485 (3)	167.
N1—H1B \cdots N3 ⁱ	0.86	2.14	2.998 (4)	177.
N2—H2 \cdots N7	0.86	2.24	3.093 (4)	175.
N3—H3A \cdots S2 ⁱⁱ	0.89	2.81	3.5481 (11)	141.
N3—H3B \cdots S2 ⁱⁱⁱ	0.89	2.72	3.5481 (11)	155.
N4—H4A \cdots S2 ^{iv}	0.86	2.65	3.501 (3)	170.
N4—H4B \cdots N7	0.86	2.32	3.161 (4)	167.
N5—H5 \cdots S3 ^v	0.86	2.64	3.342 (3)	140.

N6—H6A···S1 ^{vi}	0.89	2.88	3.5144 (12)	130.
N6—H6B···S1 ^{vii}	0.89	2.75	3.5144 (11)	144.

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

