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$[\mu\text{-}N^1, N^2\text{-Bis(pyridin-2-yl)hydrazine-1,2-dicarbothioamidato}]_2[\text{chlorido-copper(II)}]$

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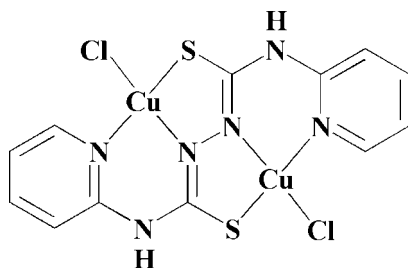
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 Key indicators: single-crystal X-ray study; $T = 293\text{ K}$; mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$; R factor = 0.024; wR factor = 0.068; data-to-parameter ratio = 14.2.

The binuclear title compound, $[\text{Cu}_2(\text{C}_{12}\text{H}_{10}\text{N}_6\text{S}_2)\text{Cl}_2]$, possesses twofold rotational symmetry. The Cu^{II} atom occupies a four-coordinate pseudo-tetrahedral environment bound to one S atom, one imine N atom and one pyridine N atom from the N^1, N^2 -bis(pyridin-2-yl)hydrazine-1,2-dicarbothioamidate ligand, and one Cl^- anion. The metal atoms are connected *via* the bis-tridentate ligand into a binuclear structure. The molecule is bow-shaped with the pyridine rings inclined to one another by $51.56(14)^\circ$. In the crystal, $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds lead to the formation of ribbons propagating along $[001]$. These ribbons are connected *via* $\text{C}-\text{H}\cdots\text{Cl}$, $\text{C}-\text{H}\cdots\text{S}$ and $\pi-\pi$ interactions [centroid-centroid distance = $3.6146(19)\text{ \AA}$], leading to the formation of a three-dimensional structure.

Related literature

For the biological activity of thiosemicarbazides and their metal complexes, see: West *et al.* (1993). For related structures, see: Wang *et al.* (2011); Yamin & Yusof (2003); Akinchan *et al.* (2002). For the synthesis of the ligand, see: Szecsenyi *et al.* (2006).



Experimental

Crystal data

 $[\text{Cu}_2(\text{C}_{12}\text{H}_{10}\text{N}_6\text{S}_2)\text{Cl}_2]$
 $M_r = 500.36$

 Monoclinic, $C2/c$
 $a = 15.825(3)\text{ \AA}$
 $b = 7.6190(13)\text{ \AA}$
 $c = 15.082(4)\text{ \AA}$
 $\beta = 118.179(2)^\circ$
 $V = 1602.9(6)\text{ \AA}^3$
 $Z = 4$

 Mo $K\alpha$ radiation
 $\mu = 3.26\text{ mm}^{-1}$
 $T = 293\text{ K}$
 $0.32 \times 0.28 \times 0.27\text{ mm}$

Data collection

 Bruker SMART APEX CCD
 diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2003)
 $T_{\text{min}} = 0.422$, $T_{\text{max}} = 0.474$

 4270 measured reflections
 1561 independent reflections
 1445 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.068$
 $S = 1.07$
 1561 reflections

 110 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.73\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.34\text{ e \AA}^{-3}$

Table 1

 Selected bond lengths (\AA).

Cu1—Cl1	2.2619 (10)	Cu1—N1	1.986 (2)
Cu1—S2	2.2295 (9)	Cu1—N3 ⁱ	1.961 (3)

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

Table 2

 Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2A}\cdots\text{Cl1}^{\text{ii}}$	0.86	2.70	3.507 (2)	156
$\text{C2}-\text{H2}\cdots\text{Cl1}^{\text{iii}}$	0.93	2.77	3.482 (3)	134
$\text{C5}-\text{H5}\cdots\text{S2}^{\text{iv}}$	0.93	2.82	3.425 (3)	124

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

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; 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: SU2393).

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supporting information

Acta Cryst. (2013). E69, m45 [https://doi.org/10.1107/S1600536812048659]

**[μ - N^1, N^2 -Bis(pyridin-2-yl)hydrazine-1,2-dicarbothioamidato]bis-
[chloridocopper(II)]**

Yang Liu, Bingguang Zhang and Kejian Deng

S1. Comment

Thiosemicarbazide and their metal complexes have attracted considerable interest due to their biological activities, such as antiviral, antibacterial, antimalarial, antifungal, and antitumoral activities (West *et al.*, 1993). Thiosemicarbazide are versatile ligands that can coordinate as neutral ligands or in the deprotonated form. They can also be used as flexible spacers with potential multiple binding sites to construct coordination polymers with multiple dimensions and various topologies. In the present paper, the synthesis and crystal structure of the title thiosemicarbazide binuclear copper(II) compound is reported.

The title compound possesses twofold rotational symmetry (Fig.1). Each Cu^{II} center occupies a four-coordinated pseudotetrahedral environment bound to one sulfur atom, one imine nitrogen atom, and one pyridine nitrogen atom from one N, N' -di(pyridin-2-yl)hydrazine-1,2-bis(carbothioamide) ligand, and one chlorine anion. The metal centres are connected *via* the hexadentate ligand into a binuclear structure. The molecule is bow-shaped. The thiosemicarbazide moiety (S2/N2(N3/N6)) is twisted by 20.14 (13)° from the pyridine ring to which it is attached. The two thiosemicarbazide moieties, (S2/N2/N3/N6) and (S2A/N2A/N3A/N6A), are inclined to one another by 23.36 (13)°, while the pyridine rings make a dihedral angle of 51.56 (14)°.

The Cu—S distance is 2.2295 (9) Å, and the Cu—N distances vary between 1.961 (3)–1.986 (2) Å. The C—S bond distances of 1.711 (3) Å are within the normal range for a C—S single bond, indicating that the thiosemicarbazide moieties adopt the thiol tautomeric form, acting as a doubly charged negative ligand. The C6—N distances of 1.311 (3)–1.366 (3) Å and the N3—N3A distance of 1.399 (3) Å are intermediate between formal single and double bonds, pointing to extensive electron delocalization over the entire ligand skeleton. This agrees well with the same distances observed in related compounds (Wang *et al.*, 2011; Yamin & Yusof, 2003; Akinchan *et al.*, 2002).

In the crystal, there are N-H...Cl hydrogen bonds, leading to the formation of ribbons propagating along [001], and C-H...Cl and C-H...S interactions (Table 1). The latter link the ribbons and together with π - π interactions lead to the formation of a three-dimensional structure [Cg1...Cg1ⁱ 3.6146 (19) Å; perpendicular separation 3.5312 (11) Å; slippage 0.772 Å; Cg1 is the centroid of pyridine ring N1/C1-C5; symmetry code: (i) -x, -y+2, -z].

S2. Experimental

The ligand (**L**), N, N' -di(pyridin-2-yl)hydrazine-1,2-bis(carbothioamide), was prepared by the literature method (Szecsenyi *et al.*, 2006). **L** (0.05 mmol) was solved in DMF (5 ml) in a test tube, then an 8 ml solvent mixture of CH₃OH and DMF (v/v = 1:1) was added as a buffer layer. A solution of CuCl₂ (0.10 mmol) in CH₃OH (3 ml) was then carefully layered on top. The system was sealed and kept for a week, after which black block-like single crystals, suitable for X-ray analysis, were obtained. Anal. Calcd for C₁₂H₁₀Cl₂Cu₂N₆S₂: C 28.80, H 2.01, N16.80. Found: C 29.23; H, 2.40; N, 16.44.

S3. Refinement

The NH and C-bound H atoms were included in calculated positions and treated as riding atoms: N–H = 0.86 Å and C–H = 0.93 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N,C})$.

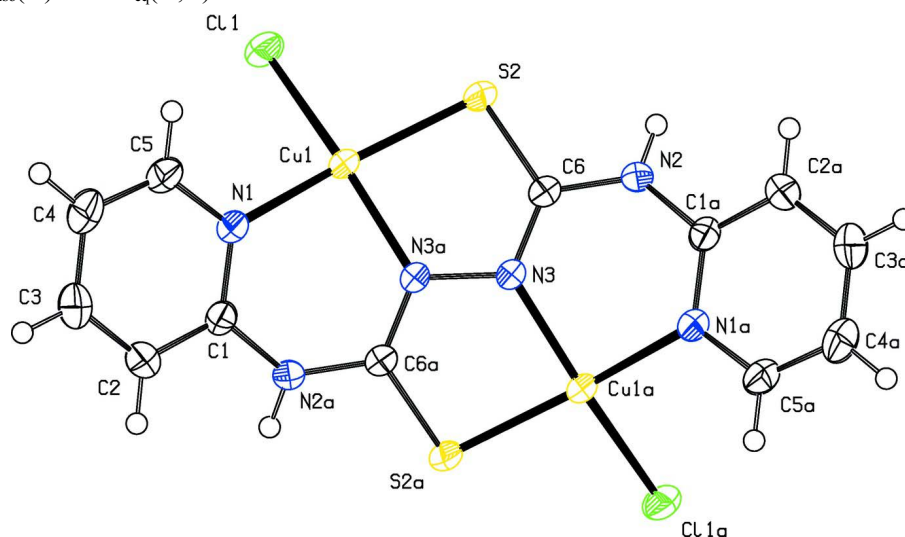


Figure 1

The molecular structure of title compound, with the atom numbering. The displacement ellipsoids are drawn at the 50% probability level [symmetry code: (a) $-x, y, -z + 1/2$].

[μ - N^1, N^2 -Bis(pyridin-2-yl)hydrazine-1,2-dicarbothioamidato]bis[chloridocopper(II)]

Crystal data

$[\text{Cu}_2(\text{C}_{12}\text{H}_{10}\text{N}_6\text{S}_2)\text{Cl}_2]$

$M_r = 500.36$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 15.825\ (3)\ \text{\AA}$

$b = 7.6190\ (13)\ \text{\AA}$

$c = 15.082\ (4)\ \text{\AA}$

$\beta = 118.179\ (2)^\circ$

$V = 1602.9\ (6)\ \text{\AA}^3$

$Z = 4$

$F(000) = 992$

$D_x = 2.073\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 253 reflections

$\theta = 2.9\text{--}29.5^\circ$

$\mu = 3.26\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, black

$0.32 \times 0.28 \times 0.27\ \text{mm}$

Data collection

Bruker SMART APEX CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2003)

$T_{\text{min}} = 0.422, T_{\text{max}} = 0.474$

4270 measured reflections

1561 independent reflections

1445 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\text{max}} = 26.0^\circ, \theta_{\text{min}} = 2.9^\circ$

$h = -19 \rightarrow 18$

$k = -9 \rightarrow 7$

$l = -18 \rightarrow 17$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.024$ $wR(F^2) = 0.068$ $S = 1.07$

1561 reflections

110 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 2.3083P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.73 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$ Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0018 (3)

*Special details***Geometry.** Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles**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	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.12780 (2)	0.63445 (4)	0.20890 (2)	0.0266 (1)
Cl1	0.25399 (4)	0.50248 (9)	0.20491 (5)	0.0355 (2)
S2	0.18501 (4)	0.59737 (10)	0.37400 (5)	0.0336 (2)
N1	0.07304 (14)	0.7259 (3)	0.06931 (14)	0.0267 (6)
N2	0.08612 (15)	0.6577 (3)	0.46876 (15)	0.0297 (6)
N3	-0.00303 (14)	0.6631 (3)	0.29480 (15)	0.0258 (6)
C1	-0.02056 (17)	0.7259 (3)	0.00390 (18)	0.0265 (7)
C2	-0.05668 (19)	0.7912 (4)	-0.09283 (19)	0.0356 (8)
C3	0.0058 (2)	0.8611 (4)	-0.1223 (2)	0.0452 (10)
C4	0.1031 (2)	0.8622 (4)	-0.0559 (2)	0.0434 (10)
C5	0.13323 (19)	0.7951 (4)	0.03822 (19)	0.0340 (8)
C6	0.07986 (17)	0.6433 (3)	0.37555 (18)	0.0248 (7)
H2	-0.12210	0.78770	-0.13690	0.0430*
H2A	0.13840	0.61870	0.51760	0.0360*
H3	-0.01690	0.90740	-0.18660	0.0540*
H4	0.14670	0.90750	-0.07490	0.0520*
H5	0.19850	0.79710	0.08320	0.0410*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0178 (2)	0.0406 (2)	0.0238 (2)	0.0017 (1)	0.0118 (1)	0.0002 (1)
Cl1	0.0250 (3)	0.0472 (4)	0.0381 (3)	0.0039 (3)	0.0181 (3)	-0.0055 (3)
S2	0.0188 (3)	0.0567 (4)	0.0270 (3)	0.0091 (3)	0.0123 (3)	0.0067 (3)

N1	0.0221 (10)	0.0354 (12)	0.0249 (10)	-0.0031 (8)	0.0131 (8)	-0.0023 (9)
N2	0.0190 (10)	0.0477 (13)	0.0217 (10)	0.0072 (9)	0.0090 (9)	0.0026 (9)
N3	0.0191 (10)	0.0392 (12)	0.0213 (9)	-0.0001 (8)	0.0113 (8)	0.0005 (8)
C1	0.0251 (12)	0.0323 (13)	0.0260 (11)	-0.0019 (10)	0.0152 (10)	-0.0031 (10)
C2	0.0294 (13)	0.0508 (17)	0.0245 (12)	-0.0022 (12)	0.0109 (11)	0.0020 (11)
C3	0.0462 (18)	0.064 (2)	0.0302 (14)	-0.0015 (14)	0.0221 (14)	0.0078 (13)
C4	0.0428 (17)	0.0564 (19)	0.0422 (16)	-0.0074 (13)	0.0294 (15)	0.0031 (13)
C5	0.0268 (13)	0.0445 (15)	0.0354 (13)	-0.0062 (11)	0.0186 (12)	-0.0029 (12)
C6	0.0204 (12)	0.0304 (13)	0.0252 (11)	0.0001 (9)	0.0121 (10)	0.0007 (9)

Geometric parameters (Å, °)

Cu1—C11	2.2619 (10)	N3—N3 ⁱ	1.399 (3)
Cu1—S2	2.2295 (9)	N2—H2A	0.8600
Cu1—N1	1.986 (2)	C1—C2	1.384 (4)
Cu1—N3 ⁱ	1.961 (3)	C2—C3	1.369 (5)
S2—C6	1.711 (3)	C3—C4	1.385 (4)
N1—C1	1.337 (4)	C4—C5	1.366 (4)
N1—C5	1.352 (4)	C2—H2	0.9300
N2—C6	1.366 (3)	C3—H3	0.9300
N2—C1 ⁱ	1.386 (4)	C4—H4	0.9300
N3—C6	1.311 (3)	C5—H5	0.9300
C11—Cu1—S2	94.32 (3)	N1—C1—C2	122.7 (3)
C11—Cu1—N1	94.39 (7)	N1—C1—N2 ⁱ	120.3 (2)
C11—Cu1—N3 ⁱ	159.80 (7)	C1—C2—C3	118.7 (3)
S2—Cu1—N1	166.41 (7)	C2—C3—C4	119.6 (3)
S2—Cu1—N3 ⁱ	85.31 (6)	C3—C4—C5	118.2 (3)
N1—Cu1—N3 ⁱ	90.08 (9)	N1—C5—C4	123.3 (3)
Cu1—S2—C6	96.01 (9)	N2—C6—N3	120.1 (3)
Cu1—N1—C1	123.98 (19)	S2—C6—N2	115.6 (2)
Cu1—N1—C5	118.58 (18)	S2—C6—N3	124.3 (2)
C1—N1—C5	117.4 (2)	C1—C2—H2	121.00
C1 ⁱ —N2—C6	129.5 (2)	C3—C2—H2	121.00
Cu1 ⁱ —N3—C6	124.48 (19)	C2—C3—H3	120.00
N3 ⁱ —N3—C6	113.7 (2)	C4—C3—H3	120.00
Cu1 ⁱ —N3—N3 ⁱ	119.99 (16)	C3—C4—H4	121.00
C6—N2—H2A	115.00	C5—C4—H4	121.00
C1 ⁱ —N2—H2A	115.00	N1—C5—H5	118.00
N2 ⁱ —C1—C2	117.0 (3)	C4—C5—H5	118.00
C11—Cu1—S2—C6	-165.43 (8)	C5—N1—C1—N2 ⁱ	-179.7 (2)
N3 ⁱ —Cu1—S2—C6	-5.68 (11)	Cu1—N1—C5—C4	-179.7 (2)
C11—Cu1—N1—C1	138.8 (2)	C1 ⁱ —N2—C6—S2	166.0 (2)
C11—Cu1—N1—C5	-42.3 (2)	C6 ⁱ —N2 ⁱ —C1—N1	26.4 (4)
N3 ⁱ —Cu1—N1—C1	-21.5 (2)	C6 ⁱ —N2 ⁱ —C1—C2	-154.0 (3)
N3 ⁱ —Cu1—N1—C5	157.5 (2)	C1 ⁱ —N2—C6—N3	-14.5 (4)
C11—Cu1—N3 ⁱ —N3	94.0 (2)	N3 ⁱ —N3—C6—N2	173.7 (2)

Cu1—Cu1—N3 ⁱ —C6 ⁱ	-69.8 (3)	Cu1 ⁱ —N3—C6—S2	157.76 (14)
S2—Cu1—N3 ⁱ —N3	4.18 (18)	Cu1 ⁱ —N3—C6—N2	-21.7 (3)
S2—Cu1—N3 ⁱ —C6 ⁱ	-159.6 (2)	C6—N3—N3 ⁱ —Cu1	0.2 (3)
N1—Cu1—N3 ⁱ —N3	-163.03 (19)	C6—N3—N3 ⁱ —C6 ⁱ	165.6 (2)
N1—Cu1—N3 ⁱ —C6 ⁱ	33.2 (2)	Cu1 ⁱ —N3—N3 ⁱ —Cu1	-165.23 (11)
Cu1—S2—C6—N2	-171.77 (17)	N3 ⁱ —N3—C6—S2	-6.9 (3)
Cu1—S2—C6—N3	8.8 (2)	N1—C1—C2—C3	-1.0 (4)
C1—N1—C5—C4	-0.7 (4)	N2 ⁱ —C1—C2—C3	179.4 (3)
Cu1—N1—C1—C2	179.7 (2)	C1—C2—C3—C4	1.1 (4)
C5—N1—C1—C2	0.8 (4)	C2—C3—C4—C5	-1.0 (5)
Cu1—N1—C1—N2 ⁱ	-0.7 (3)	C3—C4—C5—N1	0.8 (5)

Symmetry code: (i) $-x, y, -z+1/2$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2A \cdots C11 ⁱⁱ	0.86	2.70	3.507 (2)	156
C2—H2 \cdots C11 ⁱⁱⁱ	0.93	2.77	3.482 (3)	134
C5—H5 \cdots S2 ^{iv}	0.93	2.82	3.425 (3)	124

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