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Tetrakis(*N*-methylthiourea-κS)copper(I) iodide

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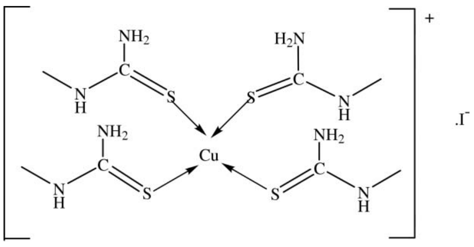
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(N–C) = 0.002 Å; R factor = 0.034; wR factor = 0.085; data-to-parameter ratio = 37.4.

In the title complex, $[Cu(C_2H_6N_2S)_4]I$, the Cu^I atom lies on a $\bar{4}$ axis. Each Cu^I centre binds to the S atoms of four *N*-methylthiourea ligands in a distorted tetrahedral environment. In the crystal structure, intermolecular N—H···S and N—H···I hydrogen bonds, together with weak C—H···N interactions, link the cations and anions into a three-dimensional network.

Related literature

For related literature on values of bond lengths, see: Allen *et al.* (1987). For related structures, see: Bombicz *et al.* (2004); Lobana *et al.* (2006). For related literature on the coordination chemistry of copper, see, for example: Dubler & Bensch (1986); Eller *et al.* (1977); Kaim & Schwederski (1994); Lobana *et al.* (2006).



Experimental

Crystal data

$[Cu(C_2H_6N_2S)_4]I$
M_r = 551.08
Tetragonal, $I4_1/a$
a = 12.5113 (6) Å
c = 13.4435 (9) Å
V = 2104.4 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.91 mm^{-1}
T = 100.0 (1) K
0.57 × 0.49 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{\min}$ = 0.205, $T_{\max}$ = 0.748
19549 measured reflections
2767 independent reflections
2149 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.104

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.085
S = 1.02
2767 reflections
74 parameters
All H-atom parameters refined
$\Delta\rho_{\max}$ = 1.41 e Å^{-3}
$\Delta\rho_{\min}$ = −0.97 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···S1^{i}	0.82 (3)	2.61 (2)	3.3908 (15)	159 (2)
N2—H1N2···I1^{ii}	0.90 (2)	2.73 (3)	3.5340 (14)	148 (2)
N1—H2N1···S1^{iii}	0.87 (2)	2.64 (2)	3.4407 (15)	154 (2)
C2—H2A···N2^{iii}	0.96 (3)	2.62 (3)	3.374 (2)	135.4 (19)

Symmetry codes: (i) $-x+1, -y+\frac{1}{2}, z$; (ii) $y-\frac{1}{4}, -x+\frac{3}{4}, z-\frac{1}{4}$; (iii) $y+\frac{1}{4}, -x+\frac{1}{4}, z+\frac{1}{4}$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2330).

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supplementary materials

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Tetrakis(*N*-methylthiourea-*κS*)copper(I) iodide

M. Mufakkar, S. Ahmad, I. U. Khan, H.-K. Fun and **S. Chantrapromma**

Comment

The study of coordination and structural chemistry of copper(I) complexes with sulfur containing ligands has been a matter of interest over the last decades due to their promising biological applications as well as due to their ability to adopt different geometries with variable nuclearities and structural diversity (Eller *et al.*, 1977; Kaim & Schwederski, 1994; Lobana *et al.*, 2006). Consequently, a number of attempts have been made to explore the structures of several copper(I) complexes with thiourea and its derivatives, and these structures have been reported (Bombicz *et al.*, 2004); Dubler & Bensch, 1986; Lobana *et al.*, 2006). Such studies provide models for naturally occurring copper–sulfur containing metalloproteins. As part of our continuing interest in the structural chemistry of metal–sulfur interactions, we report here the crystal structure of the title complex.

In the molecule of the title complex, Cu1 lies on a fourfold roto-inversion axis and the asymmetric unit therefore contain a quarter of the molecule (Fig. 1). The coordination of Cu1 is a distorted tetrahedron, being coordinated by the S atoms of the four *N*-methylthiourea ligands, with S—Cu—S angles of 107.19 (5) and 112.894 (18)° (Table 1). The Cu—S bond distances [2.3349 (4) and 2.3350 (4) Å] of the title complex lie within the range of those found in the Cu^I complexes with tetrahedral geometry (Bombicz *et al.*, 2004; Lobana *et al.*, 2006). The orientation of the ligand around Cu1 is indicated by the dihedral angle between the mean planes of Cu1/S1/C1/N1/N2 and C1/C2/N1/N2 [3.86 (9)°]. All other bond lengths and angles are in normal ranges (Allen *et al.*, 1987).

In the crystal packing (Fig. 2), the cations are linked by N1—H1N1···S1(1 − *x*, 1/2 − *y*, *z*) and N1—H2N1···S1(1/4 + *y*, 1/4 − *x*, 1/4 + *z*) hydrogen bonds, and these cations are linked to iodide anions by an N2—H1N2···I1(−1/4 + *y*, 3/4 − *x*, −1/4 + *z*) hydrogen bond to form molecular sheets parallel to the *ac* plane and these sheets are further connected by weak C2—H2A···N2(1/4 + *y*, 1/4 − *x*, 1/4 + *z*) interactions to form a three-dimensional network.

Experimental

To a solution of copper(I) iodide (0.19 g, 1.0 mmol) in acetonitrile (15 ml) was added 2 molar equivalents of *N*-methylthiourea in acetonitrile (10 ml). The mixture was stirred for half an hour. Then a clear solution was obtained. The solution was concentrated by slow evaporation at room temperature to yield colorless single crystals of the title compound suitable for X-ray stucture determination after a few days.

Refinement

All H atoms were located from the difference map and refined isotropically The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for methyl H atoms and $1.2U_{eq}$ for the remaining H atoms.

Figures

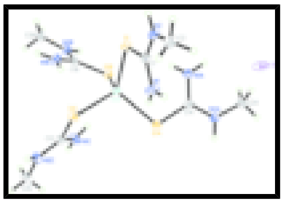

Fig. 1. The structure of the title compound, showing 50% probability displacement ellipsoids and the atomic numbering.

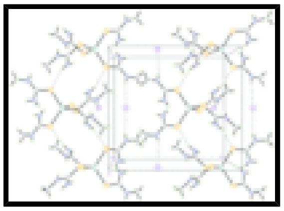

Fig. 2. The crystal packing of the title compound, viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

Tetrakis(*N*-methylthiourea-κ*S*)copper(I) iodide

Crystal data

$[Cu(C_2H_6N_2S_1)_4]I$

$M_r = 551.08$

Tetragonal, $I4_1/a$

Hall symbol: -I 4ad

$a = 12.5113$ (6) Å

$b = 12.5113$ (6) Å

$c = 13.4435$ (9) Å

$\alpha = 90°$

$\beta = 90°$

$\gamma = 90°$

$V = 2104.4$ (2) Å^3

$Z = 4$

$F_{000} = 1096$

$D_x = 1.739$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71073$ Å

Cell parameters from 2767 reflections

$\theta = 2.2–37.5°$

$\mu = 2.91$ mm^{-1}

$T = 100.0$ (1) K

Plate, colourless

0.57 × 0.49 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 8.33 pixels mm^{-1}

$T = 100.0(1)$ K

ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{min} = 0.205$, $T_{max} = 0.748$

19549 measured reflections

2767 independent reflections

2149 reflections with $I > 2\sigma(I)$

$R_{int} = 0.104$

$\theta_{max} = 37.5°$

$\theta_{min} = 2.2°$

$h = -21 \rightarrow 21$

$k = -19 \rightarrow 21$

$l = -22 \rightarrow 23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	All H-atom parameters refined
$wR(F^2) = 0.085$	$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 1.5035P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
2767 reflections	$\Delta\rho_{max} = 1.41$ e Å^{-3}
74 parameters	$\Delta\rho_{min} = -0.97$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. The low-temparture data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

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	0.2500	0.8750	0.02531 (7)
Cu1	0.5000	0.2500	0.3750	0.01643 (8)
S1	0.34596 (3)	0.27148 (3)	0.47100 (3)	0.01687 (8)
N1	0.43604 (11)	0.11480 (11)	0.57710 (11)	0.0221 (2)
N2	0.27169 (11)	0.17292 (12)	0.63020 (9)	0.0191 (2)
C1	0.35269 (11)	0.17989 (11)	0.56670 (11)	0.0166 (2)
C2	0.26350 (13)	0.09411 (15)	0.70884 (13)	0.0244 (3)
H2A	0.317 (2)	0.104 (2)	0.759 (2)	0.038 (7)*
H2B	0.274 (2)	0.027 (2)	0.688 (2)	0.036 (7)*
H2C	0.196 (2)	0.0992 (19)	0.7400 (18)	0.029 (6)*
H1N1	0.487 (2)	0.1281 (19)	0.541 (2)	0.030 (6)*
H2N1	0.441 (2)	0.071 (2)	0.6272 (16)	0.020 (6)*
H1N2	0.216 (2)	0.217 (2)	0.6193 (17)	0.032 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01276 (7)	0.01276 (7)	0.05041 (15)	0.000	0.000	0.000
Cu1	0.01618 (10)	0.01618 (10)	0.01692 (15)	0.000	0.000	0.000
S1	0.01308 (14)	0.01761 (15)	0.01992 (15)	0.00135 (10)	−0.00048 (11)	0.00227 (12)
N1	0.0165 (5)	0.0232 (6)	0.0267 (6)	0.0041 (4)	0.0037 (5)	0.0083 (5)
N2	0.0127 (5)	0.0240 (6)	0.0205 (5)	0.0013 (4)	0.0004 (4)	0.0030 (4)
C1	0.0133 (5)	0.0169 (5)	0.0195 (6)	−0.0002 (4)	−0.0020 (4)	−0.0002 (5)
C2	0.0187 (6)	0.0317 (8)	0.0229 (6)	−0.0009 (5)	0.0012 (5)	0.0080 (6)

Geometric parameters (Å, °)

Cu1—S1^{i}	2.3349 (4)	N1—H2N1	0.87 (2)
Cu1—S1^{ii}	2.3350 (4)	N2—C1	1.3279 (19)
Cu1—S1^{iii}	2.3350 (4)	N2—C2	1.449 (2)
Cu1—S1	2.3350 (4)	N2—H1N2	0.90 (3)
S1—C1	1.7249 (15)	C2—H2A	0.96 (3)
N1—C1	1.3305 (19)	C2—H2B	0.90 (3)
N1—H1N1	0.82 (3)	C2—H2C	0.94 (2)
S1^{i}—Cu1—S1^{ii}	107.789 (9)	C1—N2—H1N2	116.7 (16)
S1^{i}—Cu1—S1^{iii}	107.789 (9)	C2—N2—H1N2	118.5 (17)
S1^{ii}—Cu1—S1^{iii}	112.894 (18)	N2—C1—N1	119.36 (14)
S1^{i}—Cu1—S1	112.894 (18)	N2—C1—S1	119.07 (11)
S1^{ii}—Cu1—S1	107.786 (9)	N1—C1—S1	121.55 (12)
S1^{iii}—Cu1—S1	107.786 (9)	N2—C2—H2A	112.0 (16)
C1—S1—Cu1	107.19 (5)	N2—C2—H2B	113.5 (18)
C1—N1—H1N1	115.2 (17)	H2A—C2—H2B	104 (2)
C1—N1—H2N1	121.5 (16)	N2—C2—H2C	110.0 (15)
H1N1—N1—H2N1	122 (2)	H2A—C2—H2C	108 (2)
C1—N2—C2	124.59 (14)	H2B—C2—H2C	109 (2)
S1^{i}—Cu1—S1—C1	−42.97 (5)	C2—N2—C1—S1	174.96 (12)
S1^{ii}—Cu1—S1—C1	75.96 (5)	Cu1—S1—C1—N2	−177.32 (10)
S1^{iii}—Cu1—S1—C1	−161.90 (5)	Cu1—S1—C1—N1	1.32 (14)
C2—N2—C1—N1	−3.7 (2)		

Symmetry codes: (i) −*x*+1, −*y*+1/2, *z*; (ii) −*y*+3/4, *x*−1/4, −*z*+3/4; (iii) *y*+1/4, −*x*+3/4, −*z*+3/4.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N1···S1^{i}	0.82 (3)	2.61 (2)	3.3908 (15)	159 (2)
N2—H1N2···I1^{iv}	0.90 (2)	2.73 (3)	3.5340 (14)	148 (2)
N1—H2N1···S1^{v}	0.87 (2)	2.64 (2)	3.4407 (15)	154 (2)
C2—H2A···N2^{v}	0.96 (3)	2.62 (3)	3.374 (2)	135.4 (19)

Symmetry codes: (i) −*x*+1, −*y*+1/2, *z*; (iv) *y*−1/4, −*x*+3/4, *z*−1/4; (v) *y*+1/4, −*x*+1/4, *z*+1/4.

Fig. 1

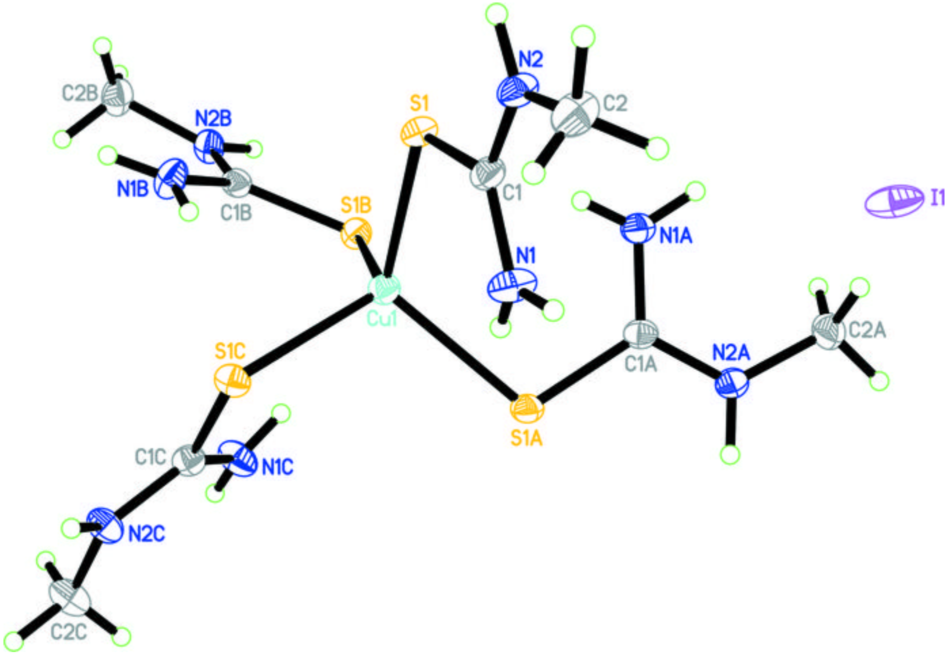

Fig. 2