

Bis(μ -*N,N*-dimethyldithiocarbamato- κ^3 S, S' :S)bis[(*N,N*-dimethyldithiocarbamato- κ^2 S, S')copper(II)]

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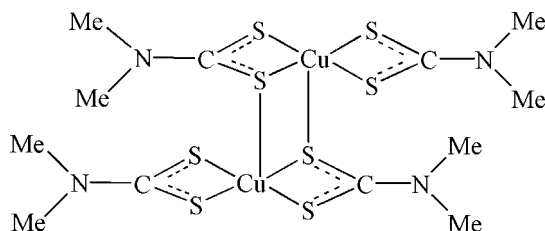
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{N}-\text{C}) = 0.005$ Å; R factor = 0.050; wR factor = 0.141; data-to-parameter ratio = 22.8.

In the centrosymmetric dimeric title compound, $[\text{Cu}_2(\text{C}_3\text{H}_6\text{NS}_2)_4]$, the Cu^{II} atom is five-coordinate in a square-pyramidal environment. The basal coordination positions are occupied by four S atoms from two dimethyldithiocarbamate ligands and the apical coordination position is occupied by an S atom also bonded to the other Cu atom.

Related literature

For the structural diversity and potential applications of transition metal complexes, see: Noro *et al.* (2000); Yaghi *et al.* (1998). For dialkyldithiocarbamate anions acting as monodentate, bidentate or bridging ligands, see: Engelhardt *et al.* (1988); Fernández *et al.* (2000); Koh *et al.* (2003).



Experimental

Crystal data

$[\text{Cu}_2(\text{C}_3\text{H}_6\text{NS}_2)_4]$
 $M_r = 607.91$
 Monoclinic, $C2/c$
 $a = 8.068$ (3) Å
 $b = 19.446$ (7) Å
 $c = 15.108$ (6) Å
 $\beta = 99.354$ (6)°

$V = 2338.7$ (15) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 2.54$ mm⁻¹
 $T = 293$ K
 $0.25 \times 0.20 \times 0.15$ mm

Data collection

Rigaku Mercury CCD diffractometer
 Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2007)
 $T_{\text{min}} = 0.807$, $T_{\text{max}} = 1.000$
 (expected range = 0.552–0.683)

9796 measured reflections
 2685 independent reflections
 2423 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.141$
 $S = 1.07$
 2685 reflections

118 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.44$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.58$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cu1—S3	2.3072 (13)	Cu1—S2	2.3278 (13)
Cu1—S4	2.3208 (13)	Cu1—S1 ⁱ	2.8258 (14)
Cu1—S1	2.3240 (13)		

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

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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: NG2548).

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supplementary materials

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Comment

Research into transition metal complexes has been rapidly expanding because of their fascinating structural diversity, as well as their potential applications as functional materials and enzymes (Noro *et al.*, 2000; Yaghi *et al.*, 1998). Dialkyldithiocarbamates anions, which are typical sulfur ligands, acting as monodentate, bidentate or bridging ligands, are often chosen for the preparation of a considerable structural variety of complexes (Engelhardt *et al.*, 1988; Fernández *et al.*, 2000; Koh, *et al.*, 2003). We report here the crystal structure of the title copper(II) complex, (I), containing a dimethyldithiocarbamate ligand.

The crystal structure of (I) is built up by dimeric entities of Cu^{II} complex (Fig. 1). The coordination geometry of Cu^{II} ion is described as a distorted square-pyramid. The basal coordination positions are occupied by four S atoms from two dimethyldithiocarbamate ligands. Each bridging S atom simultaneously occupies an equatorial coordination site on one Cu^{II} ion and apical site on the other Cu^{II} ion. The axial Cu—S bond distance is longer than the equatorial Cu—S ones (Table 1).

Experimental

A mixture of Cu(Ac)₂·H₂O (0.04 g, 0.2 mmol) and NaS₂CNMe₂·2H₂O (0.04 g, 0.2 mmol) was stirred in DMF (15 ml) at 313 K. 2-PrOH was diffused into the resulting solution, yielding single crystals of (I).

Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.96 Å, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

Figures

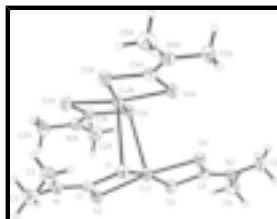


Fig. 1. The molecular structure of (I) with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). [Symmetry code: A 1 - *x*, *y*, 1/2 - *z*.]

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Crystal data

[Cu₂(C₃H₆NS₂)₄]

$F_{000} = 1240$

supplementary materials

$M_r = 607.91$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 8.068\ (3)\ \text{\AA}$

$b = 19.446\ (7)\ \text{\AA}$

$c = 15.108\ (6)\ \text{\AA}$

$\beta = 99.354\ (6)^\circ$

$V = 2338.7\ (15)\ \text{\AA}^3$

$Z = 4$

$D_x = 1.727\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3071 reflections

$\theta = 2.5\text{--}27.5^\circ$

$\mu = 2.54\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, black

$0.25 \times 0.20 \times 0.15\ \text{mm}$

Data collection

Rigaku Mercury CCD
diffractometer

Radiation source: Sealed Tube

Monochromator: Graphite Monochromator

$T = 293\ \text{K}$

ω scans

Absorption correction: Multi-scan
(CrystalClear; Rigaku, 2007)

$T_{\min} = 0.807$, $T_{\max} = 1.000$

9796 measured reflections

2685 independent reflections

2423 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

$\theta_{\max} = 27.5^\circ$

$\theta_{\min} = 2.1^\circ$

$h = -9 \rightarrow 10$

$k = -25 \rightarrow 25$

$l = -19 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.141$

$S = 1.07$

2685 reflections

118 parameters

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0741P)^2 + 4.6176P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.44\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.58\ \text{e \AA}^{-3}$

Extinction correction: none

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.58962 (6)	0.37634 (2)	0.36682 (3)	0.04294 (19)
S1	0.72601 (13)	0.39120 (5)	0.24400 (7)	0.0438 (3)
S2	0.66137 (15)	0.49238 (5)	0.37410 (7)	0.0493 (3)
S3	0.50794 (15)	0.35823 (5)	0.50440 (7)	0.0497 (3)
S4	0.56076 (14)	0.25771 (5)	0.37160 (7)	0.0478 (3)
N1	0.7709 (4)	0.52631 (17)	0.2215 (2)	0.0482 (8)
N2	0.4789 (4)	0.22341 (17)	0.5308 (2)	0.0451 (7)
C1	0.7268 (5)	0.47699 (19)	0.2734 (3)	0.0410 (8)
C2	0.8173 (7)	0.5106 (3)	0.1342 (3)	0.0660 (13)
H2A	0.8225	0.4616	0.1269	0.099*
H2B	0.9251	0.5303	0.1307	0.099*
H2C	0.7348	0.5295	0.0876	0.099*
C3	0.7562 (7)	0.5986 (2)	0.2445 (4)	0.0642 (13)
H3A	0.7251	0.6022	0.3030	0.096*
H3B	0.6717	0.6201	0.2011	0.096*
H3C	0.8620	0.6211	0.2444	0.096*
C4	0.5123 (5)	0.27279 (19)	0.4761 (2)	0.0396 (8)
C5	0.4841 (6)	0.1509 (2)	0.5072 (3)	0.0616 (12)
H5A	0.5085	0.1466	0.4473	0.092*
H5B	0.3773	0.1301	0.5103	0.092*
H5C	0.5699	0.1281	0.5483	0.092*
C6	0.4417 (6)	0.2385 (3)	0.6202 (3)	0.0631 (13)
H6A	0.4415	0.2874	0.6291	0.095*
H6B	0.5257	0.2178	0.6645	0.095*
H6C	0.3333	0.2202	0.6258	0.095*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0524 (3)	0.0380 (3)	0.0398 (3)	0.00016 (19)	0.0115 (2)	0.00059 (18)
S1	0.0478 (6)	0.0412 (5)	0.0442 (5)	0.0025 (4)	0.0125 (4)	-0.0010 (4)
S2	0.0613 (7)	0.0414 (5)	0.0462 (6)	-0.0044 (4)	0.0114 (5)	-0.0078 (4)
S3	0.0667 (7)	0.0447 (5)	0.0397 (5)	0.0014 (5)	0.0144 (5)	-0.0027 (4)
S4	0.0643 (7)	0.0385 (5)	0.0430 (6)	0.0041 (4)	0.0158 (5)	-0.0005 (4)
N1	0.0478 (19)	0.0466 (18)	0.0489 (19)	-0.0053 (15)	0.0041 (15)	0.0071 (15)
N2	0.0445 (18)	0.0467 (17)	0.0438 (18)	-0.0017 (14)	0.0063 (14)	0.0063 (14)
C1	0.0365 (18)	0.0425 (18)	0.041 (2)	-0.0001 (15)	-0.0015 (15)	0.0027 (15)
C2	0.069 (3)	0.072 (3)	0.059 (3)	-0.008 (2)	0.018 (2)	0.013 (2)
C3	0.076 (3)	0.042 (2)	0.071 (3)	-0.012 (2)	0.002 (2)	0.008 (2)
C4	0.0359 (18)	0.0454 (19)	0.0367 (18)	0.0026 (15)	0.0034 (14)	0.0051 (15)
C5	0.071 (3)	0.043 (2)	0.070 (3)	-0.002 (2)	0.009 (2)	0.013 (2)
C6	0.071 (3)	0.072 (3)	0.050 (3)	-0.005 (2)	0.021 (2)	0.016 (2)

supplementary materials

Geometric parameters (Å, °)

Cu1—S3	2.3072 (13)	N2—C5	1.457 (5)
Cu1—S4	2.3208 (13)	C2—H2A	0.9600
Cu1—S1	2.3240 (13)	C2—H2B	0.9600
Cu1—S2	2.3278 (13)	C2—H2C	0.9600
Cu1—S1 ⁱ	2.8258 (14)	C3—H3A	0.9600
S1—C1	1.726 (4)	C3—H3B	0.9600
S2—C1	1.715 (4)	C3—H3C	0.9600
S3—C4	1.717 (4)	C5—H5A	0.9600
S4—C4	1.713 (4)	C5—H5B	0.9600
N1—C1	1.324 (5)	C5—H5C	0.9600
N1—C2	1.461 (6)	C6—H6A	0.9600
N1—C3	1.457 (6)	C6—H6B	0.9600
N2—C4	1.323 (5)	C6—H6C	0.9600
N2—C6	1.460 (5)		
S3—Cu1—S4	77.03 (4)	H2A—C2—H2B	109.5
S3—Cu1—S1	168.48 (5)	N1—C2—H2C	109.5
S4—Cu1—S1	102.20 (4)	H2A—C2—H2C	109.5
S3—Cu1—S2	102.16 (4)	H2B—C2—H2C	109.5
S4—Cu1—S2	170.94 (5)	N1—C3—H3A	109.5
S1—Cu1—S2	76.75 (4)	N1—C3—H3B	109.5
S3—Cu1—S1 ⁱ	100.81 (5)	H3A—C3—H3B	109.5
S4—Cu1—S1 ⁱ	91.99 (4)	N1—C3—H3C	109.5
S1—Cu1—S1 ⁱ	90.70 (4)	H3A—C3—H3C	109.5
S2—Cu1—S1 ⁱ	97.01 (4)	H3B—C3—H3C	109.5
C1—S1—Cu1	84.09 (14)	N2—C4—S3	122.2 (3)
C1—S2—Cu1	84.21 (13)	N2—C4—S4	123.5 (3)
C4—S3—Cu1	84.45 (13)	S3—C4—S4	114.3 (2)
C4—S4—Cu1	84.12 (13)	N2—C5—H5A	109.5
C1—N1—C2	121.1 (4)	N2—C5—H5B	109.5
C1—N1—C3	121.2 (4)	H5A—C5—H5B	109.5
C2—N1—C3	117.3 (4)	N2—C5—H5C	109.5
C4—N2—C6	121.7 (4)	H5A—C5—H5C	109.5
C4—N2—C5	122.2 (4)	H5B—C5—H5C	109.5
C6—N2—C5	116.1 (4)	N2—C6—H6A	109.5
N1—C1—S2	123.4 (3)	N2—C6—H6B	109.5
N1—C1—S1	122.5 (3)	H6A—C6—H6B	109.5
S2—C1—S1	114.1 (2)	N2—C6—H6C	109.5
N1—C2—H2A	109.5	H6A—C6—H6C	109.5
N1—C2—H2B	109.5	H6B—C6—H6C	109.5

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

Fig. 1

