Bis(μ-N,N-dimethyldithiocarbamato-κ³S,S′:S)bis[(N,N-dimethyldithio-carbamato-κ²S,S′)copper(II)]

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In the centrosymmetric dimeric title compound, $[Cu_2(C_3H_6NS_2)_4]$, 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 dialkyldithiocarbamates anions acting as mono-dentate, bidentate or bridging ligands, see: Engelhardt *et al.* (1988); Fernández *et al.* (2000); Koh *et al.* (2003).
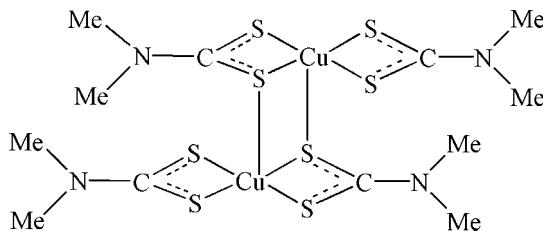
Experimental

Crystal data

$[Cu_2(C_3H_6NS_2)_4]$
$M_r = 607.91$
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)
$T_{min} = 0.807$, $T_{max} = 1.000$
(expected range = 0.552–0.683)

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

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
$\Delta\rho_{max} = 0.44$ e Å⁻³
$\Delta\rho_{min} = -0.58$ 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—S1ⁱ	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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supporting information

Bis(*μ-N,N*-dimethyldithiocarbamato-*κ*³*S,S′:S*)bis[(*N,N*-dimethyldithio-carbamato-*κ*²*S,S′*)copper(II)]

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S1. 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). Dialkyl-dithiocarbamates 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), containaing a dimethyl-dithiocarbamate 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 di-methyldithiocarbamate ligands. Each briding S atom simultaneously occupies an equatorial coordination site on one Cu^{II} ion and apical site on the other Cu^{II}. The axial Cu—S bond distance is longer than the equatorial Cu—S ones (Table 1).

S2. Experimental

A mixture of Cu(Ac)$_2$.H$_2$O (0.04 g, 0.2 mmol) and NaS$_2$CNMe$_2$.2H$_2$O (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).

S3. Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.96 Å, U_{iso}(H) = 1.5U_{eq}(C).
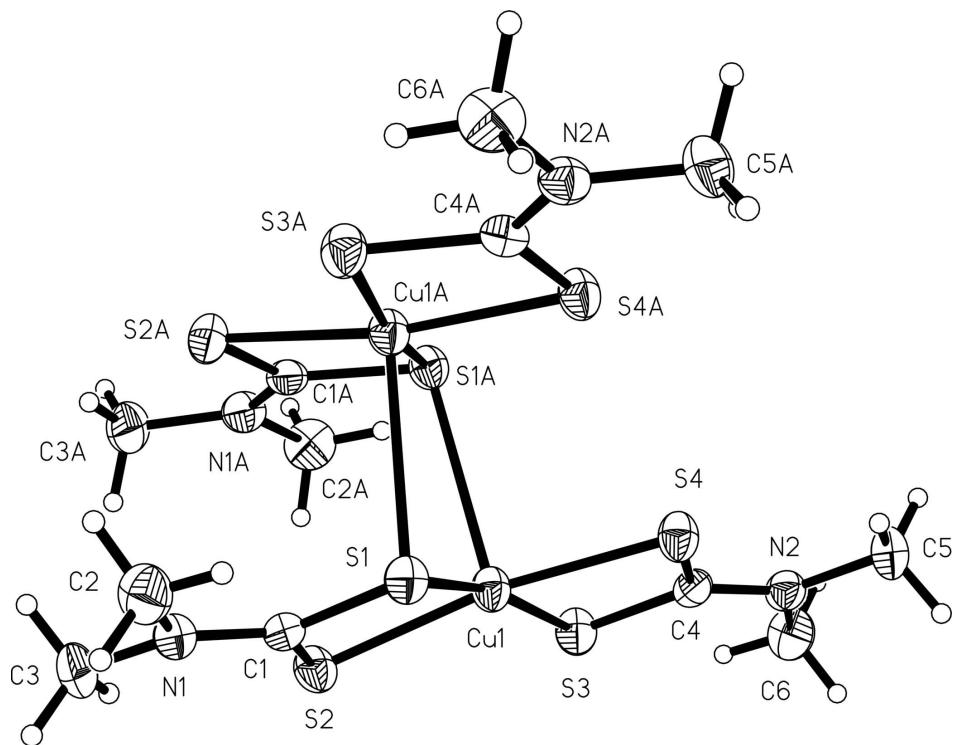
Figure 1

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

Bis(*µ-N,N*-dimethyldithiocarbamato- *κ³S,S′:S*)bis[(*N,N*- dimethyldithiocarbamato-*κ²S,S′*)copper(II)]

Crystal data

[Cu₂(C₃H₆NS₂)₄]	$F(000) = 1240$
$M_r = 607.91$	$D_x = 1.727$ Mg m⁻³
Monoclinic, *C*2/*c*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 3071 reflections
$a = 8.068$ (3) Å	$\theta = 2.5–27.5°$
$b = 19.446$ (7) Å	$\mu = 2.54$ mm⁻¹
$c = 15.108$ (6) Å	$T = 293$ K
$\beta = 99.354$ (6)°	Block, black
$V = 2338.7$ (15) Å³	$0.25 \times 0.20 \times 0.15$ mm
$Z = 4$	

Data collection

Rigaku Mercury CCD diffractometer	9796 measured reflections
Radiation source: Sealed Tube	2685 independent reflections
Graphite Monochromator monochromator	2423 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.048$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2007)	$\theta_{max} = 27.5°$, $\theta_{min} = 2.1°$
$T_{min} = 0.807$, $T_{max} = 1.000$	$h = -9\rightarrow10$
	$k = -25\rightarrow25$
	$l = -19\rightarrow18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.050$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.141$	
$S = 1.07$	H-atom parameters constrained
2685 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0741P)^2 + 4.6176P]$
118 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.44$ e Å^{-3}
	$\Delta\rho_{min} = -0.58$ e Å^{-3}

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*	$U_{iso}*/U_{eq}$
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 (Å²)

	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)

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 code: (i) −x+1, y, −z+1/2.