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## Copper(II) Bis-(*N,N*-dimethyldithiocarbamate)

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**Abstract.**  $[(\text{CH}_3)_2\text{NCS}_2]_2\text{Cu}$ , monoclinic,  $C2/c$ ,  $a = 15.243$  (3),  $b = 9.538$  (2),  $c = 8.086$  (2) Å,  $\beta = 101.31$  (1)°,  $Z = 4$ ,  $D_c = 1.75$ ,  $D_m = 1.76$  g cm<sup>-3</sup>, final  $R = 0.060$ . Magnetic gram susceptibility  $\chi = 2.66 \times 10^{-6}$  cgsu at 300 K. Crystals tend to grow as intimate twins, one individual of the twin being related to the other by reflexion across the  $bc$  plane; the  $b$  and  $c$  axes are common. The copper atom lies on a centre of symmetry and is octahedrally coordinated to six sulphur atoms [Cu–S(1) = 2.302 (2), Cu–S(2) = 2.319 (2), Cu–S(1') = 3.159 (2) Å]; the two longer bonds are to sulphur atoms in adjacent symmetry-related molecules.

**Introduction.** Black crystals were grown from a 1:1 methanol–ethanol mixed solvent system. Intensities and cell dimensions were measured on a computer-controlled Picker four-circle diffractometer with a crystal of dimensions  $0.18 \times 0.15 \times 0.11$  mm. Systematic absences are  $hkl$ ,  $h+k \neq 2n$  and  $h0l$ ,  $l \neq 2n$  confirming space group  $Cc$  or  $C2/c$ . Precession photographs of the  $h0l$  and  $h1l$  layers indicated that the crystal grew as a twin. One individual of the twin is the mirror image of the other; the  $b$  and  $c$  axes, which are common, define the mirror plane. Reflexions from the major twin (83% based on  $F^2$ ) are related to those from the minor twin by reflexion across the  $a^*b^*$  plane. Thus the  $hk0$  reflexions from each twin overlap in the  $a^*b^*$  plane while reflexions in the remainder of reciprocal space are in general well separated ( $\beta > 90^\circ$ ). Explicit calculation showed that for the  $hkl$ ,  $l \neq 0$  reflexions, partial overlap should only occur in the  $hk8$  layer. Data were collected by the  $\theta$ – $2\theta$  scan technique to a maximum  $2\theta$  value of  $55^\circ$  with Nb-filtered Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å, scan rate =  $2.0^\circ$  min<sup>-1</sup>, total scan width =  $0.6^\circ$  extended for spectral dispersion). 1333 reflexions were measured of which 733 ( $> 2.3\sigma$ ) were classed

as observed. The values for  $I$  and  $\sigma(I)$  were corrected for Lorentz and polarization effects. No absorption corrections were made; the maximum error that this would introduce in  $F$  is  $\pm 2\%$  ( $\mu = 26.1$  cm<sup>-1</sup>).

All non-hydrogen atom positions were located by routine Patterson and Fourier syntheses assuming space group  $C2/c$ . Refinement of the structure was carried out by full-matrix least-squares techniques; the function minimized was  $\sum w(|F_o| - |F_c|)^2$  and each reflexion was given weight  $[= 1/\sigma^2(F)]$  in terms of  $\sigma(F) = \sigma(I)/(Lp)2F_o$ . Separate scale factors for the  $hk0$  and  $hkl$  ( $l \neq 0$ ) reflexions were used; in this way contributions of the minor twin to the  $hk0$  reflexions were largely accounted for. Refinement of the non-hydrogen atom positions with anisotropic temperature factors for all atoms except the methyl carbon atoms converged at  $R = 0.076$ . A difference synthesis gave the positions of all the hydrogen atoms; during further refinement the hydrogen atom positions were allowed to vary but their isotropic temperature factors were fixed at a constant value of  $B = 5.00$  Å<sup>2</sup>.

Table 1. *Atomic parameters*

(a) Fractional coordinates with e.s.d.'s

	$x/a$	$y/b$	$z/c$
Cu	0.0	0.0	0.5
S(1)	0.1184 (1)	-0.0311 (2)	0.3654 (3)
S(2)	0.0256 (1)	-0.2395 (2)	0.5227 (3)
N	0.1497 (5)	-0.3048 (7)	0.3415 (9)
C(1)	0.1041 (5)	-0.2063 (9)	0.4003 (10)
C(2)	0.2122 (7)	-0.2718 (13)	0.2338 (16)
C(3)	0.1351 (8)	-0.4531 (13)	0.3650 (19)
H(21)	0.251 (6)	-0.359 (8)	0.231 (10)
H(22)	0.193 (7)	-0.224 (10)	0.159 (12)
H(23)	0.252 (6)	-0.209 (10)	0.280 (12)
H(31)	0.097 (7)	-0.479 (10)	0.294 (12)
H(32)	0.195 (6)	-0.500 (10)	0.381 (11)
H(33)	0.092 (6)	-0.455 (10)	0.434 (12)

Table 1 (cont.)

(b) Mean square atomic vibrations ( $\times 10^3 \text{ \AA}^2$ ,  $\times 10^4 \text{ \AA}^2$  for Cu and S)

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cu	406 (8)	319 (8)	614 (13)	13 (8)	278 (8)	24 (9)
S(1)	358 (12)	304 (13)	495 (17)	-29 (9)	178 (12)	-31 (12)
S(2)	386 (12)	369 (12)	474 (15)	0 (9)	190 (11)	32 (12)
N	42 (4)	39 (4)	38 (5)	11 (3)	12 (4)	-3 (4)
C(1)	30 (4)	48 (5)	32 (6)	-1 (4)	-6 (4)	-8 (5)
C(2)	48 (6)	67 (8)	76 (10)	14 (6)	24 (7)	2 (7)
C(3)	65 (8)	59 (8)	93 (12)	12 (6)	23 (7)	-8 (8)

Hydrogen atoms:  $B=5.00 \text{ \AA}^2$ 

$R$  at this stage was 0.065. Inspection of the observed and calculated structure factors confirmed our expectation that the  $hk8$  reflexions partially overlap reflexions from the minor twin. The  $hk8$  reflexions showed somewhat worse agreement than other reflexions with

either the same  $|\bar{F}_o|$  or similar  $\sin \theta/\lambda$ ; in addition the data collection output showed a small number of unusually asymmetric background counts for the  $hk8$  data. Of the 40 observed  $hk8$  reflexions only eight could be predicted as being unaffected by the twinning, *i.e.* where  $F_o$  for the minor twin would be unobserved while  $F_o$  for the major twin would be observed. In view of the small number involved it appeared prudent (and simpler!) not to include any  $hk8$  reflexion in the final refinement.

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Cu—S(1)	2.302 (2)	N—C(3)	1.45 (2)
Cu—S(2)	2.319 (2)	C(2)—H(21)	1.03 (8)
Cu—S(1')	3.159 (3)*	C(2)—H(22)	0.78 (9)
S(1)—C(1)	1.716 (8)	C(2)—H(23)	0.89 (9)
S(2)—C(1)	1.726 (9)	C(3)—H(31)	0.77 (10)
C(1)—N	1.31 (1)	C(3)—H(32)	1.00 (9)
N—C(2)	1.45 (2)	C(3)—H(33)	0.94 (9)
S(1)—Cu—S(2)	77.0 (1)	S(1)—C(1)—S(2)	113.4 (5)
S(1)—Cu—S(1')	84.4 (1)	S(1)—C(1)—N	123.1 (6)
S(2)—Cu—S(1')	92.2 (1)	S(2)—C(1)—N	123.5 (6)
Cu—S(1)—Cu'	94.2 (1)	C(1)—N—C(2)	121.3 (8)
Cu—S(1)—C(1)	84.9 (3)	C(1)—N—C(3)	123.1 (8)
Cu'—S(1)—C(1)	100.2 (3)	C(2)—N—C(3)	115.3 (9)
Cu—S(2)—C(1)	84.2 (3)		

\* Intermolecular distance (see Fig. 1 for labelling of atoms).

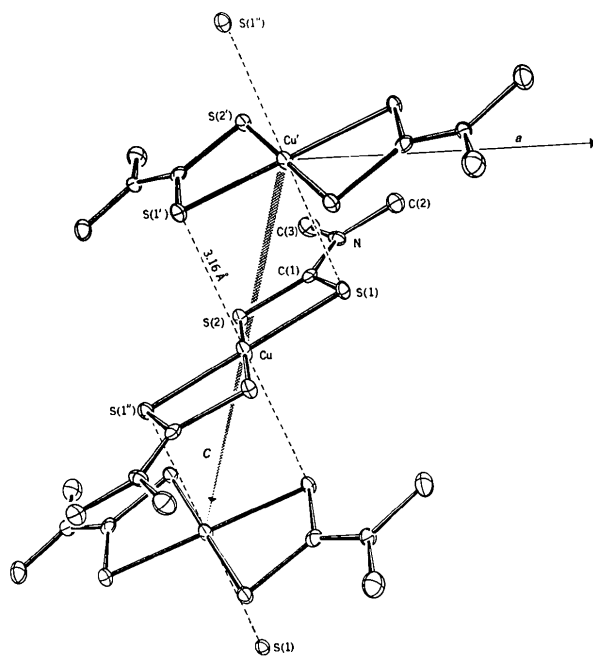


Fig. 1. Projection of the partial structure down a line which makes an angle of  $15^\circ$  with the  $b$  axis and  $90^\circ$  with the  $a$  axis. 12% thermal probability ellipsoids are shown.

The final discrepancy indices (693 reflexions) are  $R=0.060$  and  $R_w=0.057$ . A final difference map showed no peaks greater than  $0.6 (2) e \text{ \AA}^{-3}$ . The atomic scattering factors used were those of Cromer & Waber (1965) except for hydrogen where those of Stewart, Davidson & Simpson (1965) were used. Anomalous dispersion corrections were applied to the copper and sulphur atoms with values listed in *International Tables for X-ray Crystallography* (1962). The programs used were those described by Einstein & Jones (1972).

Atomic coordinates and temperature factors are listed in Table 1 and bond lengths and angles in Table 2.\* The labelling of the atoms is shown in Fig. 1.

**Discussion.** There are four  $[(\text{CH}_3)_2\text{NCS}_2]_2\text{Cu}$  molecules in the unit cell; each copper atom is situated on a centre of symmetry and thus the asymmetric unit consists of

\* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30641 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Intermolecular contacts  $\leq 3.5 \text{ \AA}$  ( $\text{H} \cdots \text{H}$  contacts  $< 3.0 \text{ \AA}$ )

Roman superscripts refer to the following transformation of the coordinates of the second atom:

I	$-x, y, \frac{1}{2}-z$	II	$x, -y, \frac{1}{2}+z$
III	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	IV	$\frac{1}{2}-x, \frac{1}{2}-y, 1-z$
V	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$	VI	$x, -1-y, -0.5+z$

Cu $\cdots$ S(1) <sup>III</sup>	3.159*	C(1) $\cdots$ H(23) <sup>IV</sup>	3.15
S(1) $\cdots$ H(21) <sup>III</sup>	2.80	C(2) $\cdots$ H(32) <sup>III</sup>	3.18
S(1) $\cdots$ H(32) <sup>IV</sup>	3.18	C(3) $\cdots$ H(23) <sup>IV</sup>	3.41
S(2) $\cdots$ H(22) <sup>I</sup>	3.37	C(3) $\cdots$ H(23) <sup>V</sup>	3.33
N $\cdots$ H(23) <sup>IV</sup>	3.13	H(23) $\cdots$ H(32) <sup>III</sup>	2.60
C(1) $\cdots$ H(21) <sup>IV</sup>	3.40	H(31) $\cdots$ H(33) <sup>VI</sup>	2.96

\* Bonded contact.

Table 4. Mean planes and deviations from plane I

## (a) Mean planes

Equations are in the form  $lX + mY + nZ + p = 0$  and refer to an orthogonal system of axes ( $X, Y, Z$ ) with  $X$  along the  $a$  axis,  $Y$  in the  $ab$  plane and  $Z$  along the  $c^*$  axis.

	$l$	$m$	$n$	$p$	$\chi^2$
Plane I					
S(1), S(2), N, C(1)–C(3)	–0.570	–0.038	–0.821	3.070	36.7
Plane II					
Cu, S(1), S(2)	–0.479	–0.143	–0.866	3.054	0.0
Plane III					
Cu', S(1'), S(2')	–0.479	0.143	–0.866	0.0	0.0

Dihedral angles ( $^\circ$ ): I and III, 11.9; II and III, 16.4

(b) Selected distances ( $\text{\AA}$ ) of atoms from the ligand plane (I)

Cu	0.270	N	–0.035
S(1)	0.006	C(1)	–0.003
S(2)	0.006	C(2)	0.013
		C(3)	0.013

a copper atom and a single dimethyldithiocarbamate ligand. The sulphur atoms of the chelate ligands form an approximately square planar array [ $S(1)–Cu–S(2) = 77.0^\circ$ ] around copper; in addition there are two long axial bonds (3.159  $\text{\AA}$ ) from copper to a sulphur atom, S(1), in an adjacent  $c$  glide related molecule. In this way molecules located along the  $c$  axis are linked by intermolecular Cu–S bonds to give an infinite polymeric chain (see Fig. 1). Apart from a short  $S(1) \cdots H(21)$  intermolecular contact of 2.80  $\text{\AA}$  the  $C$ -centred related molecules are well separated; Table 3 gives significant intermolecular contacts of various types.

The intermolecular Cu–S(1') bonds are clearly weak interactions; such a distortion from ideal octahedral geometry around the copper atom ( $d^9$  configuration) can be attributed to the static Jahn–Teller effect. Similar weak intermolecular interactions exist in the closely related Cu(II) bis- $(N,N)$ -diethyldithiocarbamate structure (Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965). In that structure a methylene hydrogen atom occupies the sixth octahedral site around copper (Cu–H' = 2.859  $\text{\AA}$ ). Of particular interest is the unusually low effective magnetic moment of 1.53 B.M. (corrected for diamagnetism) observed for the present compound;  $\mu_{\text{eff}}$  for Cu(II) compounds is normally 1.8–1.9 B.M. at 300 K (Cotton & Wilkinson, 1972). Any coupling of electron spin presumably takes place via the Cu–S(1) bridge bonds; the shortest Cu $\cdots$ Cu distance (4.043  $\text{\AA}$ ) appears too great for any direct spin coupling mechanism. It is thus noteworthy that the Cu–S(1) distance [2.302 (2)  $\text{\AA}$ ] is shorter than the Cu–S(2) distance [2.319 (2)  $\text{\AA}$ ] at the  $5\sigma$  significance level. Also pertinent is the value of the Cu–S(1)–Cu' bridging angle ( $94.2^\circ$ ); other workers have shown that there is an inverse correlation between the Cu–O–Cu bridging angle and the exchange integral,  $J$ , for several dihydroxo-bridged copper(II) complexes (Lewis, McGregor, Hatfield & Hodgson, 1974).

The geometry of the dimethyldithiocarbamate ligand is similar to that in related metal dialkyldithiocarbamates (Bonamico, Mazzone, Vaciago & Zambonelli, 1965). Table 4 gives the equation of the least-squares plane through the ligand atoms together with distances of atoms from this plane. Both the near planarity of the dimethyldithiocarbamate ligand and the short C(1)–N bond (1.31  $\text{\AA}$ ), confirm the original suggestion based

on infrared evidence that  $\cdots \bar{S}_2 = \overset{+}{N}R_2$  is an important canonical form in the structure of dialkyldithiocarbamates (Chatt, Duncanson & Venanzi, 1956).

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