The Refined Crystal and Molecular Structure of
Copper(II) Bis-(*N,N'*-di-n-propyldithiocarbamate).

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The crystal structure of copper(II) bis-(*N,N'*-di-n-propyldithiocarbamate) was refined by least-squares methods, including anisotropic temperature factors from counter data (2534 reflexions) to a final $R = 0.07$. The crystals are monoclinic, space group $P2_1/a$, $Z = 4$, $a = 13.279$ (2), $b = 18.618$ (4), $c = 8.325$ (3) Å, $\beta = 100.01$ (5)°. The copper atom is located inside a tetragonal pyramid, because of a centrosymmetric dimerization of the complex, at 0.38 Å above the base plane of four sulphur atoms, coplanar within ± 0.006 Å, and at 2.74 Å below the fifth sulphur atom belonging to the second molecule of the dimer. The copper atom has, moreover, a short $Cu \cdots H$ intermolecular contact (2.93 Å) corresponding to the sixth position of a distorted octahedral coordination. The ligand molecule with one sulphur atom involved in the intermolecular Cu–S bond has bond distances [Cu–$S = 2.323$ (2), 2.332 (2); C–$S = 1.71$ (1), 1.73 (1); C–$N = 1.34$ (1); N–$C = 1.44$ (1), 1.50 (1) Å] which are less regular than those of the other ligand molecule [Cu–$S = 2.322$ (2), 2.324 (2); C–$S = 1.72$ (1), 1.72 (1); C–$N = 1.32$ (1); N–$C = 1.47$ (1), 1.48 (1) Å].

Introduction

The crystal structure of copper(II) bis-(*N,N'*-di-n-propyldithiocarbamate) was previously solved (Pignedoli & Peyronel, 1962) by two-dimensional $hk0$ and $0kl$ Fourier syntheses from photographic data. Two complex molecules form a centrosymmetric dimer which exists only in the solid state and not in benzene or cyclohexane solutions (Pignedoli, 1961). The copper atom is located inside a tetragonal pyramid with four short intramolecular and one longer intermolecular Cu–S bond. This structure has been refined from three-dimensional data and by least-squares methods in order to compare it with the refined structures of the analogous, but planar and centrosymmetric, nickel(II) bis-(*N,N'*-di-n-propyldithiocarbamate) (Peyronel & Pignedoli, 1967) and of the structurally similar copper-(II) bis-(*N,N'*-diethyldithiocarbamate) (Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965; later referred to as B.D.M.V.Z., 1965).

Experimental

The unit-cell parameters were redetermined, on two crystals oriented about the c and the b axes, by measuring, within 0.02°, the ω and 2θ positions of the $h00$, $0k0$, $00l$ and $hh0$ reflexions with a Weissenberg–Stoe counter diffractometer and Cu $K\alpha$ radiation. Plots of the $d(100)$, $d(010)$, $d(001)$ and $d(110)$ values, obtained from each series of measurements, *versus* the function $(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)/2$ gave straight lines which were calculated and extrapolated at 90° by the least-squares method. The angle β was evaluated from the expression $\beta = \cos^{-1}[d_{100} \cdot d_{001}/2hl(h^2/d_{100}^2 + l^2/d_{001}^2 - 1/d_{h0l}^2)]$. The following crystal data replace those reported in the previous publication (Pignedoli & Peyronel, 1962). Copper(II) bis-(*N,N'*-di-n-propyl-

dithiocarbamate): $CuS_4N_2C_{14}H_{28}$. F.W. 416.20. Monoclinic prismatic. Space group $P2_1/a(C_{2h}^5,$ No. 14) from systematic absences: $a = 13.279$ (2), $b = 18.618$ (4), $c = 8.325$ (3) Å, $\beta = 100.01$ (5)° at $t = 24$°C. $V = 2025.8$ Å³. $Z = 4$. $F(000) = 876$. $\mu(Cu) = 51.58$ cm⁻¹.

The X-ray intensities ($hk0 \to hk5$) were recorded on an eight-faced, almost isodiametric ($\varnothing \simeq 0.27$ mm.) prismatic crystal elongated along the c axis by using a two-circle Weissenberg–Stoe automatic counter diffractometer, the equi-inclination ω-2θ method and filtered Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). The intensities were corrected for Lorentz and polarization factors and for absorption with the *CORIN* (1969) program taking into account the shape of the equatorial section of the crystal, according to the method described by Busing & Levy (1957), and evaluating the $\sigma(F_o)$'s by a statistical method. Both sets of $hk0$ and $\bar{h}k0$ reflexions were recorded and gave a 'reliability index' $\sum[F_o(hk0) - F_o(\bar{h}k0)]/\sum F_o(hk0) = 0.045$. Only the values of $F_o > 3\sigma(F_o)$ were used for the calculations.

Table 1. *Analytical confirmation of Renninger reflexions 050 and 0,11,0 from the hk0 layer*

Reflexion	θ	φ	ω	$10F_o$
$\bar{4},13,0$	$+36°00'$	$-23°39'$	$12°21'$	117
$\bar{4}, \bar{8},0$	$-24\ 00$	$+35\ 26$	$11\ 26$	191
$\overline{11},14,0$	$+60\ 26$	$-48\ 12$	$12\ 14$	116
$\overline{11}, \bar{9},0$	$-48\ 25$	$+60\ 06$	$11\ 41$	401
		mean	$11\ 56$	
$0, 5,0$	$+11\ 57$	$-$	$11\ 57$	83
$\bar{5},17,0$	$+49\ 44$	$-22\ 43$	$27\ 01$	48
$\bar{5}, \bar{6},0$	$-22\ 40$	$+49\ 54$	$27\ 14$	80
$\overline{10},17,0$	$+66\ 39$	$-39\ 57$	$26\ 42$	81
$\overline{10}, \bar{6},0$	$-39\ 46$	$+67\ 09$	$27\ 23$	274
		mean	$27\ 05$	
$0,11,0$	$+27\ 06$	$-$	$27\ 06$	62

Table 2. *Fractional coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^5$) *as defined by*

$$T = \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\right] \text{ for non-hydrogen atoms}$$

Standard deviations are given in brackets.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0556 (1)	0723 (1)	−0759 (1)	365 (5)	194 (3)	1351 (29)	− 26 (3)	24 (8)	− 44 (6)
S(1)	− 1025 (1)	0940 (1)	−2372 (3)	564 (11)	213 (5)	1996 (58)	72 (5)	−290 (19)	−135 (12)
S(3)	0133 (1)	−0373 (1)	−2059 (3)	378 (8)	200 (4)	1098 (47)	9 (4)	60 (14)	− 35 (10)
N(1)	− 1517 (5)	−0182 (3)	−4418 (9)	594 (39)	282 (20)	1437 (175)	17 (21)	−332 (63)	−121 (43)
C(1)	−0911 (5)	0092 (3)	−3108 (10)	462 (37)	205 (18)	1210 (191)	35 (20)	− 36 (64)	− 30 (43)
C(3)	− 2306 (7)	0282 (5)	−5435 (11)	901 (65)	515 (36)	376 (204)	−159 (39)	99 (84)	0 (63)
C(5)	− 3270 (9)	0223 (6)	−4856 (19)	1007 (87)	530 (47)	4533 (414)	26 (53)	347 (153)	−137 (112)
C(7)	−4053 (8)	0732 (6)	−5962 (17)	850 (71)	666 (53)	2964 (361)	224 (49)	−465 (122)	170 (96)
C(9)	− 1356 (7)	−0889 (5)	−5032 (13)	831 (62)	329 (28)	1767 (267)	− 40 (32)	− 99 (97)	− 32 (61)
C(11)	− 1977 (8)	− 1472 (5)	−4512 (14)	1168 (87)	361 (31)	2136 (285)	− 12 (41)	595 (121)	129 (70)
C(13)	− 1832 (9)	− 2179 (5)	−5295 (14)	1292 (91)	307 (28)	2161 (266)	− 66 (40)	281 (121)	38 (67)
S(2)	1161 (1)	1886 (1)	−0243 (3)	392 (8)	187 (4)	1779 (53)	− 14 (5)	108 (15)	− 17 (11)
S(4)	2307 (1)	0566 (1)	0026 (3)	398 (8)	201 (4)	1282 (50)	− 4 (5)	44 (15)	− 26 (10)
N(2)	3203 (4)	1862 (3)	0163 (8)	441 (30)	251 (16)	775 (142)	− 43 (18)	222 (49)	9 (36)
C(2)	2346 (5)	1492 (3)	0025 (9)	433 (34)	224 (17)	274 (169)	− 25 (19)	37 (54)	− 37 (38)
C(4)	3208 (5)	2652 (4)	0179 (11)	579 (42)	234 (20)	1280 (206)	−117 (23)	231 (69)	74 (49)
C(6)	3127 (6)	2989 (4)	1789 (14)	695 (53)	281 (24)	2722 (267)	−113 (29)	− 17 (95)	−354 (65)
C(8)	3990 (8)	2779 (5)	3116 (13)	1006 (76)	441 (35)	1890 (269)	−182 (41)	295 (109)	−278 (72)
C(10)	4204 (5)	1499 (4)	0310 (11)	389 (34)	344 (23)	678 (199)	0 (22)	124 (61)	− 94 (49)
C(12)	4481 (7)	1378 (5)	−1330 (14)	617 (53)	567 (41)	2192 (280)	− 57 (37)	417 (99)	−328 (81)
C(14)	5521 (8)	1024 (8)	−1227 (22)	884 (82)	706 (58)	7378 (574)	107 (56)	1339 (180)	−834 (149)

Table 2 (*cont.*)

Calculated fractional coordinates ($\times 10^3$) *and assumed thermal paramaters B as defined by* $\exp[-B(\sin \theta/\lambda)^2]$ *for hydrogen atoms.*

	x	y	z	B
H(31)	− 205	083	− 535	5·0
H(32)	− 241	011	− 669	5·0
H(51)	− 354	−033	−496	8·3
H(52)	− 318	039	− 360	8·3
H(71)	− 479	070	− 557	7·5
H(72)	− 413	056	− 722	7·5
H(73)	− 377	128	− 585	7·5
H(91)	−056	− 102	−464	5·0
H(92)	− 152	−086	− 635	5·0
H(111)	− 277	− 132	− 482	5·7
H(112)	− 177	− 153	− 320	5·7
H(131)	− 231	− 258	− 486	6·3
H(132)	− 104	− 234	− 499	6·3
H(133)	− 204	− 213	− 660	6·3
H(41)	391	283	−017	3·3
H(42)	257	284	−071	3·3
H(61)	313	357	165	4·4
H(62)	241	282	213	4·4
H(81)	389	304	424	5·9
H(82)	471	295	279	5·9
H(83)	399	220	327	5·9
H(101)	417	099	091	3·0
H(102)	478	183	103	3·0
H(121)	449	189	− 194	5·5
H(122)	391	104	− 203	5·5
H(141)	568	095	− 244	9·1
H(142)	552	051	−063	9·1
H(143)	610	136	−054	9·1

The refinement of the structure was carried out by the full-matrix least-squares method using the *ORFLS* program of Busing, Martin & Levy (1962) on a CDC 6600 computer, starting from the atomic parameters found in the previous work (Pignedoli & Peyronel, 1962) for non-hydrogen atoms. The atomic scattering factors (Hanson, Herman, Lea & Skillman, 1964) of non-hydrogen atoms were corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1962).

Firstly, the positional parameters and the isotropic temperature factors of the non-hydrogen atoms were refined; then hydrogen atoms were introduced in their calculated positions at each cycle and with the last isotropic temperature factors of the carbon atoms to which they are bonded. After a number of cycles of anisotropic refinement 54 reflexions with low indexes and unrefinable $F_o \ll F_c$ were excluded; they may be affected by extinction or double reflexion.

Double reflexions had already been observed on the 0*kl* Weissenberg photographs (Pignedoli & Peyronel, 1962). Two forbidden reflexions 050 and 0,11,0 were also observed on the *hk*0 layer. Their analytical confirmation was obtained by the method of Speakman (1965) (Table 1) with the following attributions: 050 to the pairs $\bar{4}$,13,0/4$\bar{8}$0 and $\overline{11}$,14,0/11,$\bar{9}$,0 and 0,11,0 to the pairs $\bar{5}$,17,0/5$\bar{6}$0 and $\overline{10}$,17,0/10,$\bar{6}$,0 with a sufficiently good vertical collinearity.

With the last positional and thermal parameters (Table 2) the 2534 reflexions used, about 85% of the reflexions explored, gave a final reliability index $R = 0\cdot07$. Residual ($\varrho_o - \varrho_c$) densities of about 1 e.Å^{-3} were observed in the vicinity of the heavier atoms. All hydrogen atoms could be observed in the difference Fourier syntheses, at the calculated positions. Interatomic distances and angles with their e.s.d's (Table 3, Fig. 1) were calculated with the *ORFFE* program of Busing, Martin & Levy (1964). The more relevant least-squares planes and the atomic distances from them are given in Table 4. An orthographic projection, along the *c* axis on the plane *a* sin β *b* of the dimer

centrosymmetric in (000) is shown in Fig. 2. The structure factor tables have been deposited at the National Lending Library.*

Results and discussion

The intramolecular Cu–S bonds with S(1), S(2) and S(4) are very nearly equal (2·322, 2·323, 2·324 Å), within their standard deviation (0·002 Å), while in the ethyl derivative (B.D.M.V.Z., 1965) (2·297, 2·301, 2·317 Å) they differ by about 0·02 Å, ten times their standard deviation; the fourth intramolecular Cu–S(3) bond, with the sulphur atom involved in the inter-

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* This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30015. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

molecular S(3)–Cu' bond [asymmetric unit (') = $-x, -y, -z$], is longer (2·332 Å), as in the ethyl derivative (2.339 Å). The Cu–S(3') bond (2·741 Å) is about 0·1 Å shorter than the corresponding bond in the ethyl derivative (2·851 Å), indicating a stronger intermolecular bond in the propyl derivative. Correspondingly, (a) the distance of the copper atom from the mean plane S(1)S(2) S(3)S(4) in the propyl (0·38 Å) is about 0·1 Å longer than the analogous distance in the ethyl derivative (0·259 Å), (b) the coplanarity of the S(1) to S(4) atoms is better in the propyl (±0·006 Å) than in the ethyl derivative (±0·1 Å), and (c) the angles S(1)CuS(4) (160·9°) and S(2)CuS(3) (161·6°) differ by less than 1° while the corresponding angles in the ethyl derivative differ by about 10°.

While the CuS₄(S) group is more regular in the propyl than in the ethyl derivative, the opposite occurs for the dithiocarbamic groups of the ligand molecules

Table 3. *Interatomic distances* (Å) *and angles* (°) *and their e.s.d.'s*

Bond lengths

Cu—S(1)	2·323 (2)	N(1)—C(3)	1·50 (1)
Cu—S(2)	2·324 (2)	N(1)—C(9)	1·44 (1)
Cu—S(3)	2·332 (2)	N(2)—C(4)	1·47 (1)
Cu—S(4)	2·322 (2)	N(2)—C(10)	1·48 (1)
Cu—S(3')	2·741 (3)	C(3)—C(5)	1·45 (2)
S(1)–C(1)	1·711 (7)	C(5)—C(7)	1·58 (2)
S(3)–C(1)	1·735 (6)	C(9)—C(11)	1·47 (2)
S(2)–C(2)	1·715 (6)	C(11)–C(13)	1·50 (2)
S(4)–C(2)	1·724 (6)	C(4)—C(6)	1·50 (2)
C(1)–N(1)	1·339 (9)	C(6)—C(8)	1·50 (2)
C(2)–N(2)	1·318 (7)	C(10)–C(12)	1·50 (2)
		C(12)–C(14)	1·52 (2)

Other distances

S(1)–S(2)	3·589 (3)	S(3')–S(1)	3·822 (4)
S(3)–S(4)	3·558 (3)	S(3')–S(2)	3·964 (3)
S(1)–S(3)	2·876 (2)	S(3')–S(3)	3·771 (4)
S(2)–S(4)	2·879 (2)	S(3')–S(4)	3·924 (3)
Cu—Cu'	3·417 (2)		

Bond angles

S(1)–Cu—S(2)	101·1 (1)	N(1)—C(1)—S(1)	124·4 (5)
S(4)–Cu—S(3)	99·7 (1)	N(1)—C(1)—S(3)	122·3 (5)
S(2)–Cu—S(4)	76·6 (1)	N(2)—C(2)—S(2)	123·1 (5)
S(3)–Cu—S(1)	76·3 (1)	N(2)—C(2)—S(4)	123·2 (5)
S(1)–Cu—S(3')	97·7 (1)	C(1)—N(1)—C(3)	120·1 (6)
S(3)–Cu—S(3')	95·7 (1)	C(1)—N(1)—C(9)	122·1 (6)
S(2)–Cu—S(3')	102·7 (1)	C(3)—N(1)—C(9)	117·2 (7)
S(4)–Cu—S(3')	101·3 (1)	C(2)—N(2)—C(4)	121·8 (5)
S(1)–Cu—S(4)	160·9 (1)	C(2)—N(2)—C(10)	121·2 (5)
S(2)–Cu—S(3)	161·6 (1)	C(4)—N(2)—C(10)	117·0 (5)
Cu—S(3)–Cu'	84·3 (1)	N(1)—C(3)—C(5)	109·8 (9)
Cu—S(1)–C(1)	85·3 (2)	N(1)—C(9)—C(11)	116·3 (9)
Cu—S(3)–C(1)	84·5 (2)	N(2)—C(4)—C(6)	115·2 (7)
Cu—S(2)–C(2)	84·5 (2)	N(2)—C(10)—C(12)	110·8 (7)
Cu—S(4)–C(2)	84·4 (2)	C(3)—C(5)—C(7)	106·9 (12)
S(1)–C(1)–S(3)	113·1 (4)	C(9)—C(11)—C(13)	113·5 (9)
S(2)–C(2)–S(4)	113·7 (3)	C(4)—C(6)—C(8)	112·6 (8)
		C(10)–C(12)–C(14)	112·4 (10)

Other angles

S(1)–S(3)–S(4)	90·1 (1)	Cu–S(3')–S(1)	37·0 (1)
S(3)–S(4)–S(2)	90·5 (1)	Cu–S(3')–S(2)	34·9 (1)
S(4)–S(2)–S(1)	89·5 (1)	Cu–S(3')–S(3)	38·0 (1)
S(2)–S(1)–S(3)	89·9 (1)	Cu–S(3')–S(4)	35·5 (1)

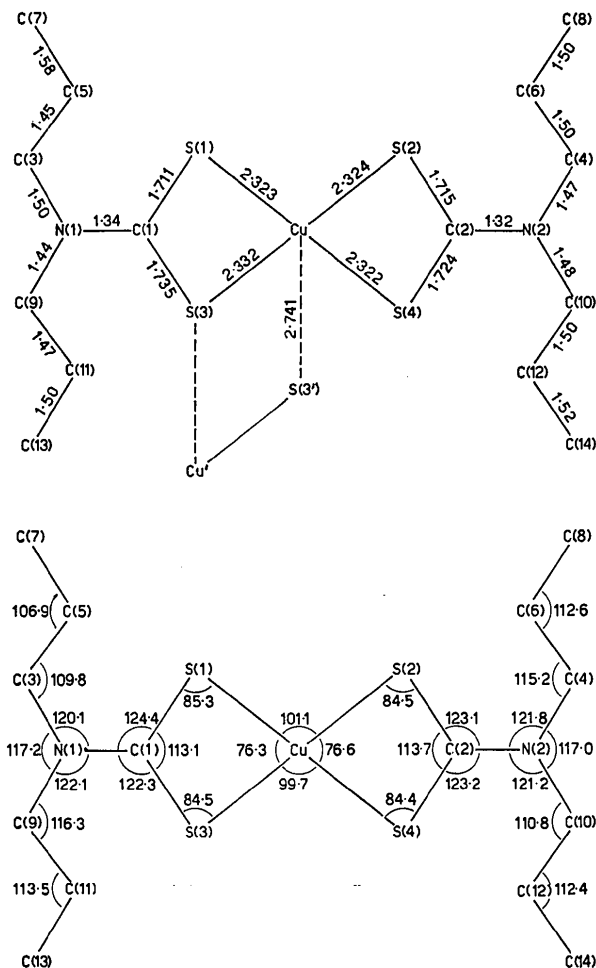(') asymmetric unit $-x, -y, -z$.

Fig. 1. Interatomic distances and angles.

as shown by the maximum deviation from planarity of the following groups of atoms:

Mean plane of atoms (propyl derivative)	Propyl deriv. (this work)	Maximum deviation (+ or −) Ethyl deriv. (B.D.M.V.Z., 1965)
CuS(1)S(3)C(1)	0·066 Å	0·019 Å
CuS(2)S(4)C(2)	0·070	0·016
N(1)C(1)S(1)S(3)	0·023	0·003
N(2)C(2)S(2)S(4)	0·013	0·003

Bond distances in the ligand molecule with the sulphur atom S(3) involved in the intermolecular Cu–S bond are less regular than in the other ligand molecule (Table 3, Fig. 1), and than in the same ligand molecules of the analogous, but planar, Ni(II) bis-(N,N'-di-n-propyldithiocarbamate) (Peyronel & Pignedoli, 1967).

A 'short' intermolecular contact, Cu···H(92″)= 2·93 Å [asymmetric unit ($''$)= $-x, -y, -z-1$], makes an angle H(92″)CuS(3′)=170°. A similar Cu···H contact (2·86 Å) was observed in the ethyl derivative (B.D.M. V.Z., 1966). In both complexes this hydrogen atom occupies approximately the sixth octahedral position around the copper atom (Fig. 2), as in other structures reported by B.D.M.V.Z. (1966).

Table 4. *Least-squares planes*

Equation in the form $Ax+By+Cz-D=0$ referred to the crystallographic axes a b and c. Atom deviations from the plane, in Å.

Coefficients ($\times 10^4$)

	Plane	A	B	C	D
(1)	S(1)S(2)S(3)S(4)	−4524	−1898	9367	−15599
(2)	CuS(1)S(3)C(1)	−6222	−3039	8186	−13516
(3)	CuS(2)S(4)C(2)	−2492	−0635	9950	−8620
(4)	N(1)C(1)S(3)S(1)	−7044	−3665	7210	−10993
(5)	N(2)C(2)S(4)S(2)	−1248	0137	9987	−3428
(6)	C(1)N(1)C(3)C(9)	−7664	−3405	6697	−8480
(7)	C(2)N(2)C(4)C(10)	−0957	−0085	9969	−3008
(8)	CuS(1)S(3)C(1)N(1)C(3)C(9)	−7037	−3321	7409	−12373
(9)	CuS(2)S(4)C(2)N(2)C(4)C(10)	−1592	−0249	9996	−6193
(10)	N(1)C(1)CuC(2)N(2)	5115	−8535	0092	−7797
(11)	CuCu′S(3)S(2)S(3′)S(2′)	8497	−3593	2323	0000

Atom deviations from the plane (Å × 10³).

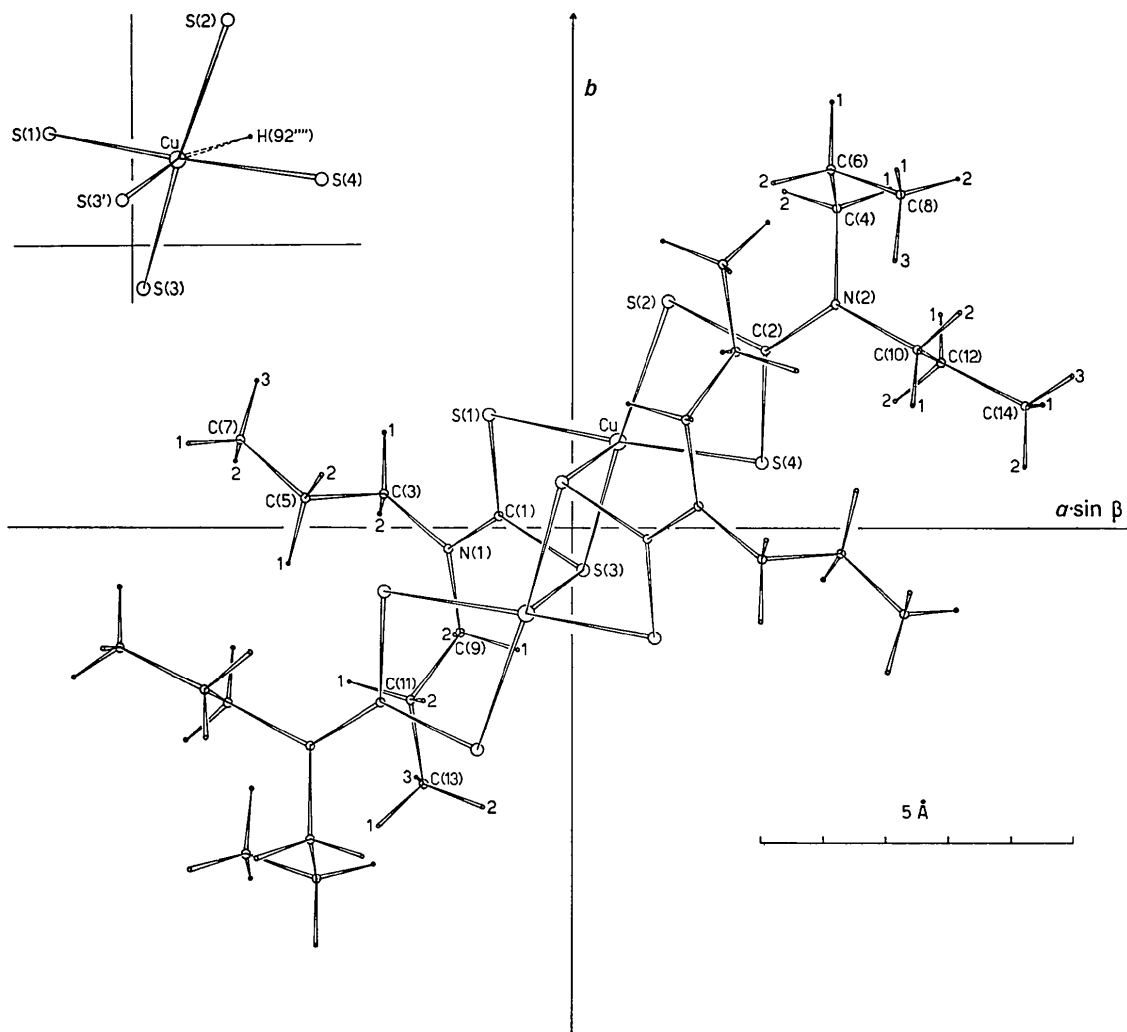|	Cu	S(1)	S(2)	S(3)	S(4)	C(1)	N(1)	C(2)	N(2)	C(3)	C(9)	C(4)	C(10)
(1)		−6	6	6	−6								
(2)	− 34	50		50		−66							
(3)	− 36		53		53			−70					
(4)		−7		− 7		23	−10						
(5)			− 4		−4			13	−5				
(6)						−16	44			− 14	−14		
(7)							0	0				0	0
(8)	−197	151		74		115	42			−134	−50		
(9)	−163		84		127			75	−9			−33	−81
(10)	3					− 8	5	3	−2				
(11)	−3		1	1		Cu′= 3		S(2′) = −1		S(3′) = −1			

Fig. 2. Orthographic projection on the plane $a \sin \beta\ b$ of the dimer centrosymmetric in (000) position. Molecule with labelled atoms used as asymmetric unit (x, y, z). Coordination geometry of the copper atom.

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