

CRYSTAL AND MOLECULAR STRUCTURE OF COPPER CYCLOPENTAMETHYLENEDITHIOCARBAMATE

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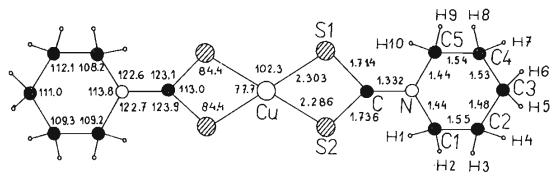
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Crystal and molecular structure of copper cyclopentamethylenedithiocarbamate, $\text{Cu} \cdot [\text{S}_2\text{CN}(\text{CH}_2)_5]_2$, was elucidated from X-ray diffraction measurements of single crystals. The structure was interpreted by means of the Patterson and Fourier methods. The complex crystallizes in the space symmetry group $P2_1/c$ with the lattice parameters $a = 6.170 \pm 0.006 \text{ \AA}$, $b = 8.600 \pm 0.006 \text{ \AA}$, $c = 15.220 \pm 0.011 \text{ \AA}$, and $\beta = 95.31 \pm 0.05^\circ$. The experimental density is $1.58 \text{ g} \cdot \text{cm}^{-3}$, the density calculated for $z = 2$ is $1.57 \text{ g} \cdot \text{cm}^{-3}$. The crystal structure is composed of monomeric units. The copper atom occupies a special position in the centre of symmetry; its coordination is planar, with approximately equal Cu—S distances, 2.303 (3) and 2.286 (3) \AA , angle S1—Cu—S2 $77.7 (1)^\circ$. The residue of the ligand fragment S_2CNC_2 is planar and the piperidine ring possesses the chair conformation.

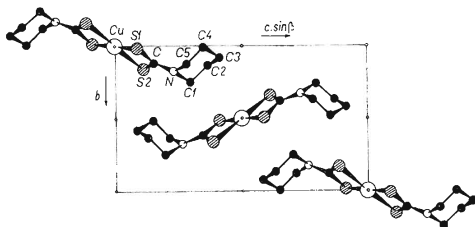
Complexes of bivalent copper with various substituted dialkyldithiocarbamates are rather well known; the Cu atom tends here to increase its coordination number on account of formation of dimers. The dimerization is enabled by the interaction of the d_{z^2} orbital of Cu in the fifth coordination position with the corresponding orbital of the sulfur atom of the neighbouring molecule, and seems to be conditioned by a planarity of the whole molecule such that the molecular pairs be able to parallel approach to a distance prerequisite for the interaction (about 2.9 \AA). This coordination geometry has been observed in the case of complexes* $\text{Cu}(\text{Et}_2\text{DTC})_2$ (ref.¹) and $\text{Cu}(\text{n-Pr}_2\text{DTC})_2$ (ref.²); in both complexes the intermolecular Cu—S distance is lower than 2.9 \AA . Cras and coworkers³ gave a structure description of the interesting complex $[\text{Cu}_3(\text{n-Bu}_2\text{DTC})_6]^{2+} \cdot [\text{Cd}_2\text{Br}_6]^{2-}$, where the cation is composed of three units $\text{Cu}(\text{n-Bu}_2\text{DTC})_2$ located in-plane in the B—A—B order. The Cu atoms in the B units possess the oxidation degree +3 and tetragonal-pyramidal coordination (the Cu—S distances are $\sim 2.22 \text{ \AA}$ in the base and 2.9 \AA in the apex of the pyramid), whereas in the A unit they possess the oxidation degree +2 and a tetragonally deformed octahedral coordination (Cu—S distances 2.30 and 2.35 \AA in the xy -plane and 3.2 \AA in the direction of the z -axis).

* Abbreviations used: DTC — dithiocarbamate ligand S_2CNR_2 , where R = Me (methyl), Et (ethyl), n-Pr (n-propyl), n-Bu (n-butyl), Ph (phenyl), Pip (piperidyl).



While nonplanarity of the molecule does not allow interaction of the Cu atom in the direction of the z -axis, in complexes of Cu(II) dithiocarbamates a planar coordination with the formation of monomers is observed also in the crystal state⁴. Recently the structure of polymeric adducts of $(\text{Cu(II)(PipDTC)}_2)_n \cdot (\text{CuBr})_n$, where $n = 4$ and 6 , appeared in the literature⁵. The structures are composed of polymeric layers formed by individual molecules Cu(Pip DTC)_2 , which link the polymeric chains of CuBr through the Cu-S bonds.

As a part of the complex study of various substituted transition metal dithiocarbamates, we investigated in the present work the structure of the complex compound $\text{Cu(II)[cyclopentamethylenedithiocarbamate]}_2$.



EXPERIMENTAL AND RESULTS

Preparation of the Complex

The general technique of preparation of metal dithiocarbamates⁶ was modified for the preparation of the crystals as follows: 20 ml (0.2 mol) of piperidine, purified by distillation, was dissolved in 50 ml of water. 12 ml (0.2 mol) of carbon disulfide and 15 ml of 25% (0.2 mol) ammonia were added dropwise during constant stirring; colourless needles of ammonium cyclopentamethylenedithiocarbamate precipitated during the gradual cooling of the heated mixture. The crystals were dissolved by heating the mixture, and 24.9 g (0.4 mol) of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, dissolved in the lowest possible volume of water, was added gradually. The content of the flask was stirred at room temperature for 1 hour to yield a darkbrown paste, which was sucked off on a Buechner funnel and then dissolved in an appropriate amount of redistilled chloroform. The chloroform fraction obtained from a separation funnel was evaporated to a small volume,

which was then cooled rapidly to yield black-brown crystals of copper cyclopentamethylenedithiocarbamate. The crystals were sucked off and washed with ether; by triple crystallization from ether, the substance of sufficient purity (decomposition point in the temperature range of 200–270°C) was obtained, as indicated by the analysis (calculated/found, %): C 37.52/37.54, H 5.26/5.31, N 7.29/7.19, S 33.39/33.58, Cu 16.54/16.45.

Space Group and Unit Cell

The crystals of the composition $\text{Cu}(\text{PipDTC})_2$ have the form of needles and possess the monoclinic symmetry. Systematic extinction of reflections of the type $[h0l]$, $l = 2n + 1$, and $[0k0]$ $k = 2n + 1$, indicated the space symmetry group $P2_1/c$ (No 14) (ref.⁷).

The approximate dimensions of the unit cell determined from precession, rotation, and Weissenberg photographs were refined by using the least squares method⁸. From 23 reflections displayed by the powder diffraction patterns, the values $a = 6.170$ (6), $b = 8.600$ (6), $c = 15.220$ (11) Å, and $\beta = 95.31$ (5)° were obtained.

The density of the crystal at 25°C, $D_0 = 1.58 \text{ g cm}^{-3}$, was determined by the flotation method in a Clerici solution. The density calculated assuming the presence of two formula units in the unit cell ($z = 2$) is $D_c = 1.57 \text{ g cm}^{-3}$.

Elucidation of the Crystal Structure

The experimental crystallographic data were measured with a crystal (direction of growth — the z -axis) dimensions $0.3 \times 0.08 \times 0.1$ mm. The intensity values were determined from integrated photographs obtained by aplying the equi-inclination Weissenberg method with CuK_α radiation; the technique of multiple films and photometric measurement of the intensities were used. The layers $0kl - 5kl$ and $h0l - h2l$ respectively were recorded. After transformation to a common relative scale, all 1004 nonzero independent reflections were corrected for the Lorentz and polarization factors. The absorption was neglected ($\mu R = 0.6$).

From the number of the formula units and the space group it follows that the Cu atom occupies a special position in the centre of symmetry. The threedimensional Patterson synthesis using all the data available is in accordance with that position and enabled the localization of the sulfur atoms. The copper atoms were located to (0, 0, 0) and (0, 1/2, 1/2) and the other atoms to the general positions (x, y, z) , $(\bar{x}, \bar{y}, \bar{z})$, $(x, 1/2 - y, 1/2 + z)$, and $(\bar{x}, 1/2 + y, 1/2 - z)$. The successive threedimensional Fourier synthesis gave the positions of all non-hydrogen atoms, the isotropic thermal coefficient being assumed to be 2.0 Å. The structure parameters were refined by least squares method using the full matrix, the minimization function $\sum w(|F_0| - |F_c|)^2$, and the weighting scheme according Cruickshank⁹, $w = (a + |F_0| + b|F_0|^2)^{-1/2}$, where $a = 4.5$ and $b = 0.014$. The values of the atomic factors were taken from the tables¹⁰. After three iteration cycles the factor R , defined as $\sum ||F_0| - |F_c|| / \sum |F_0|$, converged to the value of 0.14. Further two cycles of anisotropic refinement decreased R to 0.096. During the last cycle, all the shifts of the position parameters were lower than 0.2σ , and those of the thermal parameters were lower than 0.3σ . The differential Fourier synthesis calculated at this stage contained the highest maximum at the origin (1.4 e Å^{-3}), and additional maxima with the electron density values of $\sim 1 \text{ e Å}^{-3}$ mostly lying near the positions of the hydrogen atoms, which were calculated assuming the sp^3 hybridization of the carbon atoms of the piperidine ring and the bond distances 1.09 Å. The positions of the hydrogen atoms were not refined, but their introduction into the structure (their thermal parameters were taken equal to those of the carbon atoms to which they are bound) gave the final value of $R = 0.090$. The refined coordinates are given in Table I, the

TABLE I
Coordinates of Atoms in the Crystal Structure of $\text{Cu}(\text{Pip DTC})_2$
The standard deviations are given in parentheses.

Atom	x/a	y/b	z/c
Cu	0	0	0
S1	0.3249 (5)	0.0162 (4)	0.0872 (2)
S2	-0.0865 (5)	0.1596 (3)	0.1115 (2)
C	0.1765 (17)	0.1221 (11)	0.1562 (6)
N	0.2559 (14)	0.1723 (9)	0.2360 (5)
C1	0.1231 (20)	0.2486 (14)	0.2954 (6)
C2	0.0907 (20)	0.1368 (15)	0.3725 (7)
C3	0.3008 (20)	0.0830 (16)	0.4169 (7)
C4	0.4441 (20)	0.0117 (13)	0.3500 (7)
C5	0.4696 (17)	0.1293 (13)	0.2758 (6)
H1	0.201	0.354	0.320
H2	-0.032	0.277	0.261
H3	0.001	0.197	0.420
H4	0.000	0.036	0.347
H5	0.384	0.181	0.449
H6	0.270	-0.004	0.446
H7	0.601	-0.016	0.382
H8	0.370	-0.094	0.323
H9	0.552	0.232	0.302
H10	0.562	0.077	0.227

TABLE II
Anisotropic Thermal Coefficients ($\times 10^4$) of the Expression $\{\exp[-(B11 \cdot h^2 + B12 \cdot hk + \dots)]\}$
The standard deviations are given in parentheses.

Atom	$B11$	$B22$	$B33$	$B12$	$B13$	$B23$
Cu	159 (2)	113 (3)	26 (1)	32 (7)	11 (4)	4 (2)
S1	50 (3)	144 (5)	22 (1)	53 (9)	10 (5)	-22 (3)
S2	100 (3)	112 (4)	28 (1)	93 (9)	-1 (5)	-15 (4)
C	99 (3)	80 (14)	23 (4)	-43 (35)	37 (17)	23 (13)
N	103 (5)	100 (13)	23 (3)	28 (28)	41 (14)	-2 (10)
C1	249 (6)	124 (18)	26 (5)	45 (47)	18 (23)	-50 (15)
C2	195 (7)	163 (20)	25 (4)	-15 (48)	47 (21)	-33 (16)
C3	156 (2)	178 (14)	24 (4)	-3 (46)	14 (22)	-1 (16)
C4	151 (3)	117 (8)	30 (5)	33 (39)	-12 (22)	14 (14)
C5	106 (5)	139 (18)	22 (4)	-71 (40)	-23 (19)	-12 (14)

anisotropic coefficients of thermal vibrations of the refined atoms in Table II, the bond distances and angles in Table III and the nonbonding interatomic distances in Table III. The designation of the atoms in the molecule and the molecular geometry can be seen in Fig. 1, the projection of the structure into the (100) plane in Fig. 2. The values of the observed and calculated structure factors are available from the authors. The calculations were performed on a computer Siemens 4004/150.

DISCUSSION

The crystal structure of the complex $\text{Cu}(\text{PipDTC})_2$ is composed of discrete monomeric units, which are centrosymmetric, so that the cyclopentamethylene rings lie in the *trans* position. The copper atom is chelated by two pairs of sulfur atoms of two ligands; the geometry of the CuS_4 fragment is thus necessarily planar and the two pairs of Cu—S distances approximately equal.

In order to find the degree of coplanarity of the S_2CNC_2 ligand fragment, we constructed planes of the form $AX + BY + CZ = D$ (l) through some of the atoms, using the least squares method. The values of the coefficients of the equation, the angles between some of the planes are given in Table IV, and the deviations of some selected atoms from the planes in Table V. Here X, Y, Z are the cartesian coordinates, which are associated with the fractional coordinates through the relations $X = ax + cz \cdot \cos \beta$, $Y = by$, $Z = cz \cdot \sin \beta$.

With regard to the very high degree of conjugation in the S_2CNC_2 ligand fragment, its lower coplanarity is rather surprising; it can be probably explained in terms of the closest-packing principle for molecules in the molecular crystal and a considerable overlap of the van der Waals spheres of some of the hydrogen atoms of the piperidine ring with those of the Cu and S2 atoms (Table III). In this respect the complex under study resembles the dimer complex $\text{Cu}(\text{n-Pr}_2\text{DTC})_2$ (ref.²) rather than its own monomer analogue $\text{Cu}(\text{MePhDTC})_2$ (ref.⁴). The fact that the complex does not form dimers is obviously a consequence of the nonplanarity of the piperidine rings, which are present in the chair conformation and in mutual *trans* configuration, and their $\sim 50^\circ$ departure from the plane 1 (Table IV). As a result, the molecules cannot approach each other to the distance requisite for the Cu—S interaction. The shortest Cu—Cu distance is 6.17 Å (a axis). A similar planar geometry of the CuS_4 grouping and the formation of monomers have been observed⁴ for the complex $\text{Cu}(\text{MePhDTC})_2$, where the benzene ring plane is 82° tilted from the plane formed by the remaining atoms of the ligand and where the benzene rings are in mutual *trans* configuration too.

From Table IV, which shows the geometry of the CuS_2CNC_2 fragment of complexes of differently substituted Cu(II) dithiocarbamates as described in the literature, some conclusions can be drawn. Firstly, the Cu—S and S—C bond lengths in the chelate ring are approximately equal (in the complex studied the average values are 2.295 and 1.725 Å, respectively) and are in accordance with analogous

TABLE III

Interatomic Bond Distances (Å) and Bond Angles (deg) in the Asymmetric Unit
The standard deviations are given in parentheses.

Bond	Bond length	Bond	Bond length
Cu—S1	2.303 (3)	C1—C2	1.548 (16)
Cu—S2	2.286 (3)	C2—C3	1.476 (17)
S1—C	1.724 (10)	C3—C4	1.529 (17)
S2—C	1.736 (11)	C4—C5	1.541 (15)
N—C	1.332 (12)		
N—C1	1.439 (14)		
N—C5	1.442 (14)		
Atoms	angle	Atoms	angle
S1—Cu—S2	77.7 (1)	C1—N—C5	113.8 (8)
Cu—S1—C	84.4 (4)	N—C1—C2	108.2 (9)
Cu—S2—C	84.4 (3)	C1—C2—C3	112.1 (10)
S1—C—S2	113.0 (5)	C2—C3—C4	111.0 (9)
S1—C—N	123.9 (8)	C3—C4—C5	109.3 (9)
S2—C—N	123.1 (8)	C4—C5—N	109.2 (9)
C—N—C1	122.6 (9)		
C—N—C5	122.7 (9)		

Interatomic Intermolecular Distances Below 4 Å and Nonbonding Hydrogen Interactions (Å) of the van der Waals Type with the Cu and S atoms^a

Cu...C2 ^b	3.75 (1)	H3...Cu ^c	2.87
Cu...C1 ^b	3.92 (1)	H1...S2 ^c	2.94
C1...S2 ^c	3.82 (1)	H8...S2 ^d	2.95
C3...S2 ^d	3.88 (1)	H10...S2 ^e	2.99
C4...S2 ^d	3.82 (1)		
C5...S2 ^e	3.88 (1)		
C3...C3 ^f	3.65 (2)		
C3...C4 ^f	3.83 (2)		
C4...N ^g	3.76 (1)		
C4...C5 ^g	3.87 (2)		
C5...C2 ^e	3.98 (2)		

^a Transformations of the coordinates of atoms of different asymmetric units with respect to the symmetrically equivalent atoms of the basic unit (with coordinates x, y, z) as follows: ^b $x, 1/2-y, 1/2+z=1$; ^c $\bar{x}, 1/2+y, 1/2-z$; ^d $\bar{x}, 1/2+y-1, 1/2-z$; ^e $1+x, y, z$; ^f $1-x, \bar{y}, 1-z$; ^g $1-x, 1/2+y-1, 1/2-z$.

data of Table VI. This confirms the idea that the π -electron pair of the dithiocarbamate C=S bond delocalizes completely over the four-membered ring during the chelate formation. The average value of the C—S bond length from Table VI (except for the complexes $\text{Cu}(\text{PipDTC})_2(\text{CuBr})_{4,6}$, 1.71 Å, can be compared with that in thiourea, some of its derivatives, and coordinated thiourea¹¹, and seems to correspond to the single S—C (sp^2) bond. Similar results have been observed also in other dithiocarbamates irrespective of the metal nature and the number of ligands¹²⁻¹⁷ and even of whether the two sulfur atoms of the ligand are bound to the same metal or whether they act in a polynuclear complex as a bridge¹⁸. In this respect it is interesting to examine¹⁹ the structure of $\text{Na}(\text{Et}_2\text{DTC}) \cdot 3 \text{H}_2\text{O}$, where only one of the two sulfur atoms is bound to the metal atom. In this salt, too, the two C—S distances are approximately equal, in average 1.72 (1) Å. A lowered-delocalization of the electrons and consequent nonequivalence of the chelate ring bonds has been observed only in nontransition metal dithiocarbamates²⁰⁻²², where the metal ions contain free $(n + 1) s^2$ electron pairs.

From Table VI it follows further that the C—N bond length (1.33 Å) is lower than the N—C (1) or N—C (2) bond length, which indicates its considerable double bond character, similarly as in other dithiocarbamates — possibly except for $\text{Fe} \cdot (\text{n-BuDTC})_3$, where Hoskins and Kelly¹⁹ report the C—N bond distance 1.42 Å.

TABLE IV

Values of the Coefficients of Equation (1) and Atoms Through Which the Plane is Constructed

Plane	Atoms	A	B	C	D
1	Cu, S1, S2, C, N, C1, C5	0.3444	0.8422	-0.4149	0.1378
2	Cu, S1, S2, C, N	0.3317	0.8264	-0.4549	0.0739
3	Cu, S1, S2	0.3076	0.7957	-0.5217	0.0000
4	S1, S2, C, N, C1, C5	0.3570	0.8559	-0.3741	0.3103
5	N, C1, C2, C3, C4, C5	-0.4422	-0.7938	-0.4175	-0.5056

Angles (deg) Formed by the Normals of Some Planes

Planes ^a	Angle	Planes ^a	Angle
1-2	2.56	1-5	130.35
1-3	7.00	2-5	127.79

^a In accordance with the designation in part a of this table.

The experimental value is 0.07 Å shorter than the sum of the C (sp^2) and N covalent radii²³, which leads to the conclusion that the nitrogen lone electron pair is to a considerable extent conjugated with the chelate ring. Comparing the C—N and C—S bond lengths in the complex $\text{Cu}(\text{PipDTC})_2$ with the corresponding values in the polymeric adduct of this complex with $(\text{CuBr})_n$ (Table VI) we find the π -electron transfer from the nitrogen atom to the sulfur atom more pronounced in the latter case, where the sulfur atoms are allowed to extend their valency; this is in a full accordance with the IR spectra⁵.

TABLE V

Deviations ($\text{Å} \times 10^3$) of Atoms from the Planes Defined in Table IV
Designation of the atoms and planes agrees with Table IV and Fig. 1.

Plane	Cu	S1	S2	C	N	C1	C2	C3	C4	C5
1	-138	79	81	63	58	-72				-71
2	-74	64	65	5	-60	-225				-223
3	0	0	0	-132	-300					
4	-310	-14	-12	13	67	-28				-26
5					287	-215	197	-257	216	-228

TABLE VI

Comparison of Bond Distances and Bond Angles in $\text{Cu}(\text{S}_2\text{C.piperidine})_2$ With Those in Other Cu-Dithiocarbamates

Compound ^a	Cu—S	S1—Cu—S2	C—S (1, 2)	C—N	S1—C—S2	N—C (1, 2)
1	2.301, 2.339	76.4	1.71, 1.74	1.33	112.9	1.46, 1.48
	2.297, 2.317	77.6	1.71, 1.71	1.35	114.6	1.47, 1.43
2	2.32, 2.32	74.6	1.67, 1.70	1.33	116	1.47, 1.46
	2.33, 2.33	76.3	1.68, 1.73	1.33	115	1.46, 1.45
3	2.274, 2.329	77.2	1.72, 1.73	1.31	113.9	1.45, 1.49
4	2.316	77.1	1.740	1.32	112.1	1.470
5	2.306	77.3	1.753	1.32	110.6	1.470
6	2.303, 2.286	77.7	1.71, 1.74	1.33	113.0	1.44, 1.44

^a Numbering of the compounds: 1 $\text{Cu}(\text{Et}_2\text{DTC})_2^3$, 2 $\text{Cu}(\text{Pr}_2\text{DTC})_2^2$, 3 $\text{Cu}(\text{MePhDTC})_2^4$, 4 $\text{Cu}(\text{PipDTC})_2 \cdot (\text{CuBr})_4^5$, 5 $\text{Cu}(\text{PipDTC})_2 \cdot (\text{CuBr})_6^5$, 6 $\text{Cu}(\text{PipDTC})_2$ (this work).

The considerably distorted S—C—S bond angles (with respect to the value of 90°) in the complex studied result from the strain in the four-membered ring. Distortions are found also in other metal dithiocarbamates, and similarly also in the related xanthates²⁴⁻²⁷ and dithiobenzoates²⁸. In most of the bis-dithiocarbamates so far studied, the average value of the S—C—S bond angle is approximately 110° , irrespective of the nature of the central metal ion, its charge, number of ligands bound, and the monomer or dimer nature of the complex¹¹⁻¹⁷.

In $\text{Cu}(\text{PipDTC})_2$, the piperidine ring possesses the chair conformation, similarly as in other investigated dithiocarbamates with that substituent^{16,29}. The bond lengths correspond to single bonds with the average value of 1.44 \AA for the distance N-alkyl (the corresponding bond lengths in the complex under study emerge 0.03 \AA lower than the average value in other dithiocarbamates) and 1.52 \AA for the C—C bond, which agrees well with the corresponding bond lengths in the piperidine ring of a pseudotropine³⁰ molecule (1.45 and 1.52 \AA , respectively). The average value of the bond angle at the carbon atom is $110(1)^\circ$, which represents the sp^3 tetrahedral angle within the limits of one standard deviation.

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