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The Crystal and Molecular Structure of the Copper(I) Dipropylthiocarbamate Hexamer

ROLF HESSE and ULF AAVA

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

The crystal structure of copper(I) dipropylthiocarbamate, $(C_3H_7)_2NCOSCu$, has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/a$. Unit cell parameters are $a=13.425$ Å, $b=19.357$ Å, $c=11.630$ Å, $\beta=91.72°$. The structure consists of isolated $[(C_3H_7)_2NCOSCu]_6$ hexamers. There are two hexameric molecules in the unit cell. The copper atoms are situated in the central part of the $[(C_3H_7)_2NCOSCu]_6$ molecule forming an almost regular octahedron. The metal-metal distances are longer than those in the metallic phase of copper. Outside six of the faces of the octahedron a thiocarbamate ligand is situated, linked to the copper octahedron by metal-sulphur and metal-oxygen coordination. Each oxygen atom is linked to one, and each sulphur atom to two copper atoms. Each copper atom has three-fold coordination, which is not planar. The metal atoms are situated "inside" the plane of the coordinating sulphur and oxygen atoms. The mono- and the dithiocarbamate ligand molecules are compared.

Dithiocarbamates and monothiocarbamates of univalent metals usually occur as low polymers in solutions of organic solvents. Structure investigations at this Institute [1–3] have shown that several of these compounds also form low polymers in the solid state. The main polymers hitherto studied are dimers, tetramers, and hexamers. An extensive discussion of these compounds is presented in Ref. 3. Among the compounds which form hexamers are silver(I) dipropyldithiocarbamate,[3] silver(I) dipropylmonothiocarbamate,[4] and copper (I)dipropylmonothiocarbamate. In this paper the molecular and crystal structure of the copper(I) dipropylmonothiocarbamate hexamer, $[(C_3H_7)_2NCOSCu]_6$, is presented. It is the first example of a monothiocarbamate structure.

EXPERIMENTAL

A sample of copper(I) dipropylthiocarbamate was kindly supplied by Dr. S. Åkerström who had prepared the compound according to his published method.[5] The crystals were obtained from ligroin as yellowish red needles and did not contain any solvent of crystallisation. Their density was measured by the flotation method in an aqueous

solution of K_2HgI_4. Unit cell dimensions were determined from a Guinier-Hägg photograph using $CrK\alpha_1$ radiation ($\lambda = 2.2896$ Å)[6] with elementary silicon ($a = 5.4305$ Å)[7] as a calibrant.

The intensity data were obtained from a crystal with the dimensions $0.23 \times 0.050 \times 0.050$ mm, the needle axis corresponding to [001]. With the crystal rotating about this axis the X-ray reflexions were recorded on equiinclination Weissenberg photographs using CuK radiation. Ten layers, with $0 \leq l \leq 9$, were collected. The relative intensities were estimated visually with the use of multiple-film technique (five films), the intensities being compared with a calibrated intensity scale. The intensities of 1543 independent reflexions were measured and the data were corrected for the Lorentz and polarization effects. No corrections were made for absorption and extinction. Interlayer scale factors were obtained by exposing reflexions from all the layers on the same film set. These experimental scale factors were used in the first stages of the calculations. In the final refinement the individual scale factors were also refined but the changes were of no importance for the atomic coordinates.

Unit cell and symmetry

Formula unit:	$(C_3H_7)_2NCOSCu$.
Diffraction symmetry:	$2/m$.
Crystal system:	monoclinic.
Unit cell parameters:	$a = 13.425 \pm 0.003$ Å $b = 19.357 \pm 0.005$ Å, $c = 11.630 \pm 0.003$ Å, $\beta = 91.72 \pm 0.02°$.

Volume of unit cell: 3021 Å^3.
Density (measured): 1.476 g cm^{-3}.
Number of formula units per unit cell: 12.
Density (calculated): 1.476 g cm^{-3}.
Systematic absences: $h0l$ for $h = 2n+1$, $0k0$ for $k = 2n+1$.
Space group: $P2_1/a$.
Coordinates of equivalent positions:
x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $1/2-x, 1/2+y, \bar{z}$; $1/2+x, 1/2-y, z$.

DETERMINATION OF THE ATOMIC COORDINATES

The approximate positions of three copper and two sulphur atoms were derived from the three-dimensional Patterson function. The coordinates of these atoms were improved in a three-dimensional electron density calculation from which the positions of nine additional atoms (one sulphur, three oxygen, two nitrogen, and three carbon) also could be obtained. The remaining nineteen atoms to be determined (hydrogens excluded) were successively located in a series of three-dimensional F_o- and $(F_o - F_c)$-syntheses, interleaved by backshift corrections and least-squares calculations. Programs designated STRIX and PROFFS, written by Liminga and Olovsson [8] for the computer FACIT EDB, were employed for the structure factor and Fourier calculations.

The coordinates and isotropic temperature factors of all but the hydrogen atoms were refined by least-squares methods. The calculations were carried out on a CD 3600 computer with the full-matrix program LALS.[9] In the expression $\sum\omega(|F_o| - |F_c|)^2$, which wasminimized , the weights, ω, were calculated according to the equation, suggested by Cruickshank *et al.*,[10] $\omega = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$. The constants used in the final cycles were $a = 10.4$, $c = 0.0092$, and $d = 0$. Atomic scattering factors for the elements were obtained from the following sources: copper, Thomas and Umeda,[11] sulphur, Dawson,[12] oxygen, nitrogen, and carbon, Hoerni and Ibers.[13] Dispersion corrections for copper were introduced into the calculations.

The least squares calculations were continued until the shifts of the parameters were less than one tenth of the estimated standard deviations. At this stage of the

Table 1. Atomic parameters. The parameters of all atoms, with the exception of those marked with an asterisk, are taken from the final least squares refinement. The coordinates of the atoms marked with an asterisk are determined from geometrical considerations and the electron density distribution. The least squares parameters of these atoms are given in parentheses.

Atom	x	σx	y	σy	z	σz	B	σB
Metal atoms:								
Cu_I	0.1410	0.0003	−0.0100	0.0002	−0.0581	0.0003	7.13	0.10
Cu_{II}	0.0443	0.0003	0.0655	0.0002	0.1272	0.0003	7.25	0.11
Cu_{III}	−0.0329	0.0003	0.0738	0.0002	−0.1224	0.0003	7.40	0.11
Thiocarbamate molecule I:								
S_I	0.0283	0.0005	−0.1494	0.0003	−0.0211	0.0006	6.71	0.16
O_I	0.2052	0.0012	−0.1054	0.0009	−0.0946	0.0014	7.7	0.4
C_I	0.1540	0.0020	−0.1575	0.0015	−0.0723	0.0023	8.4	0.6
N_I	0.1927	0.0015	−0.2224	0.0011	−0.0728	0.0018	7.8	0.5
C_{IA_1}	0.2954	0.0020	−0.2281	0.0013	−0.1184	0.0024	8.3	0.6
C_{IA_2}	0.2842	0.0029	−0.2565	0.0020	−0.2476	0.0035	13.6	1.1
C_{IA_3}	0.3950	0.0035	−0.2615	0.0024	−0.2949	0.0042	17.3	1.5
C_{IB_1}	0.1389	0.0020	−0.2869	0.0015	−0.0417	0.0025	9.1	0.7
C_{IB_2}*	0.183		−0.306		0.082		16	
	(0.186)	(0.003)	(−0.301)	(0.002)	(0.091)	(0.004)	(15.7)	(1.4)
C_{IB_3}*	0.133		−0.373		0.125		21	
	(0.148)	(0.004)	(−0.362)	(0.003)	(0.115)	(0.005)	(21.5)	(2.1)
Thiocarbamate molecule II:								
S_{II}	−0.1038	0.0005	−0.0485	0.0003	0.2157	0.0005	6.13	0.15
O_{II}	−0.0065	0.0013	0.0623	0.0009	0.2928	0.0015	8.3	0.4
C_{II}	−0.0715	0.0019	0.0199	0.0013	0.3084	0.0022	7.4	0.6
N_{II}	−0.1173	0.0016	0.0226	0.0011	0.4141	0.0020	8.4	0.6
C_{IIA_1}	−0.0872	0.0019	0.0766	0.0014	0.5022	0.0022	8.2	0.7
C_{IIA_2}	−0.1447	0.0023	0.1428	0.0016	0.4583	0.0028	10.5	0.8
C_{IIA_3}	−0.1103	0.0026	0.1991	0.0019	0.5460	0.0032	12.6	1.0
C_{IIB_1}*	−0.167		−0.039		0.461		13	
	(−0.186)	(0.003)	(−0.051)	(0.002)	(0.469)	(0.003)	(13.2)	(1.1)
C_{IIB_2}*	−0.280		−0.032		0.445		18	
	(−0.265)	(0.004)	(−0.015)	(0.003)	(0.432)	(0.005)	(17.8)	(1.6)
C_{IIB_3}	−0.3289	0.0036	−0.0942	0.0025	0.4929	0.0042	17.7	1.5
Thiocarbamate molecule III:								
S_{III}	−0.2048	0.0005	−0.0380	0.0003	−0.1015	0.0005	6.28	0.14
O_{III}	−0.1702	0.0013	0.0771	0.0009	−0.2091	0.0014	8.0	0.4
C_{III}	−0.2310	0.0019	0.0360	0.0013	−0.1877	0.0020	6.7	0.5
N_{III}	−0.3282	0.0019	0.0440	0.0013	−0.2215	0.0022	10.3	0.6
C_{IIIA_1}	−0.3545	0.0025	0.1088	0.0019	−0.2956	0.0030	12.1	1.0
C_{IIIA_2}*	−0.361		0.172		−0.216		15	
	(−0.357)	(0.003)	(0.166)	(0.002)	(−0.198)	(0.004)	(15.3)	(1.3)
C_{IIIA_3}	−0.3925	0.0036	0.2337	0.0028	−0.2935	0.0047	19.2	1.7
C_{IIIB_1}*	−0.413		0.017		−0.158		16	
	(−0.422)	(0.004)	(0.005)	(0.002)	(−0.150)	(0.005)	(15.6)	(1.4)
C_{IIIB_2}*	−0.474		−0.032		−0.236		21	
	(−0.438)	(0.005)	(−0.027)	(0.003)	(−0.244)	(0.006)	(21.0)	(2.1)
C_{IIIB_3}	−0.5594	0.0042	−0.0594	0.0027	−0.1704	0.0049	19.6	1.8

refinement the discrepancy index, R, was 0.113. The atomic coordinates and isotropic temperature factors obtained from the last cycle can all be found in Table 1. For the atoms marked by an asterisk in this table the least squares values are, however, given in parentheses. The coordinates of these atoms presented without parentheses are obtained from geometrical calculations combined with considerations of the electron density distribution. The least squares values were regarded as less accurate because they gave interatomic distances and angles in the propyl chains, which were considered to deviate too much from expected values (see Table 4). The discrepancy index, R, corresponding to the corrected positions was 0.118.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Notations. The copper atoms and ligands for which the atomic coordinates are given in Table 1 are denoted by I, II, and III. The metal atoms and ligands which are related to these by a centre of symmetry in the origin are designated $\bar{\text{I}}$, $\bar{\text{II}}$, and $\bar{\text{III}}$. The individual atoms of the thiocarbamate ligands are given additional notations according to Fig. 1. The propyl chains A and B correspond

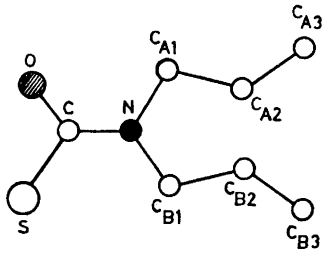


Fig. 1. The thiocarbamate ligand with notation of the atoms.

to the oxygen and sulphur atoms, respectively, as is shown in the figure. As an example $C_{\bar{\text{III}}A1}$ means the carbon atom C_{A1} of the thiocarbamate ligand $\bar{\text{III}}$. For further notations, see Table 5.

Molecular arrangement. The crystal structure of copper(I) dipropylthiocarbamate is built from discrete $[(C_3H_7)_2NCOSCu]_6$ molecules. The molecular packing is illustrated in Fig. 2. There are two hexamers per elementary cell, with their molecular centres at 0, 0, 0 and 1/2, 1/2, 0. The molecules in the structure are related to each other by screw axes and glide planes. In each of the hexameric molecules the metal atoms and the ligands are linked together by Cu–S and Cu–O bonds as will be described in more detail later. There are no bonds of this kind between different hexamers. The central active part of a molecule, comprising copper, sulphur, and oxygen atoms, is accordingly shielded by the surrounding inert alkyl groups and the forces acting between different hexamers are of van der Waals type. Intermolecular distances shorter than 4.0 Å are given in Table 5.

The hexamer. The $[(C_3H_7)_2NCOSCu]_6$ molecule is centrosymmetric. The molecule comprises atoms with the general notations I, II, III and atoms which are related to these by a centre of symmetry with the notations $\bar{\text{I}}$, $\bar{\text{II}}$, $\bar{\text{III}}$. A diagram of the central part of a hexamer is given in Fig. 3, which

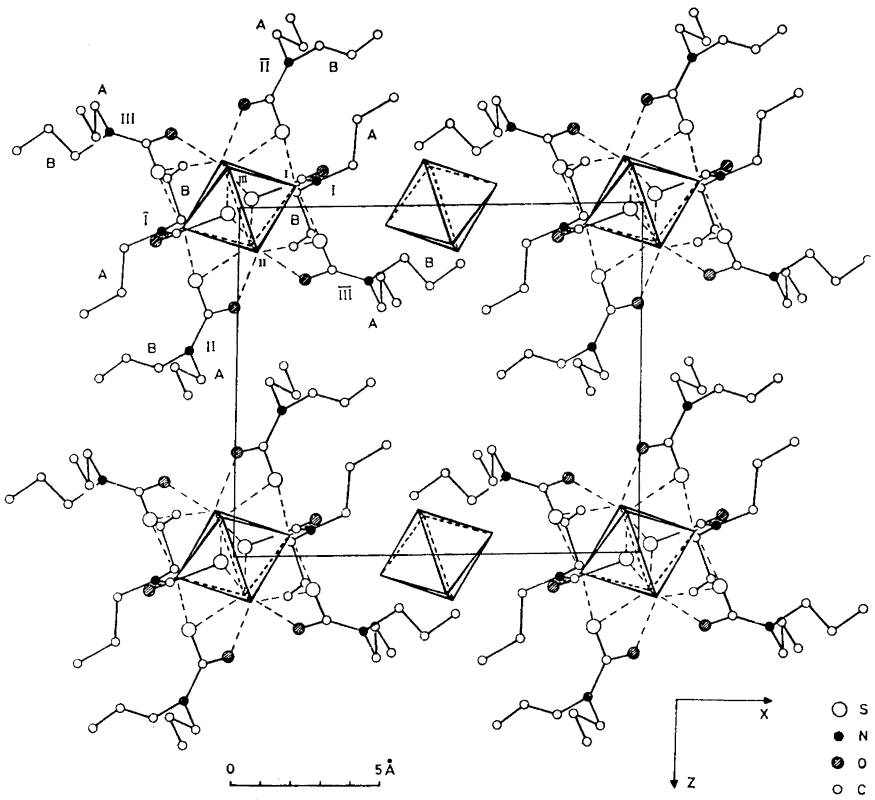


Fig. 2. [010]-Projection of the crystal structure of copper(I) dipropylthiocarbamate showing the packing of the hexameric molecules. Molecular centres at 0,0,0 and 1/2, 1/2, 0. For the sake of clarity only the metal arrangement is outlined for the molecules having their centres at 1/2, 1/2, 0.

is an orthogonal projection in a direction perpendicular to the plane of the atoms Cu_I, Cu_{II} and Cu_{III}. Table 6 is a good complement to Fig. 3 for the description of the structure. In this table the atomic coordinates are given in Ångström units in an orthonormalized coordinate system, X, Y, Z. The Y- and Z-axes are parallel to the plane of the projection. The X-axis is perpendicular to this plane. The origin of the coordinate system is situated at the centre of the molecule.

As is seen form Table 6 the copper, sulphur, and oxygen atoms in a hexamer are situated close to six levels parallel to the YZ-plane. The X-coordinates of these levels are: ± 0.25 Å (O); ± 1.10 Å (Cu); ± 2.01 Å (S). The ligands I, II, and III are inclined downwards and the ligands $\bar{I}$, $\bar{II}$, and $\bar{III}$ upwards in Fig. 3. As is seen from the figure the structure of the hexamer can be regarded as a deformation of an arrangement with the symmetry $\bar{3}$. It is reasonable

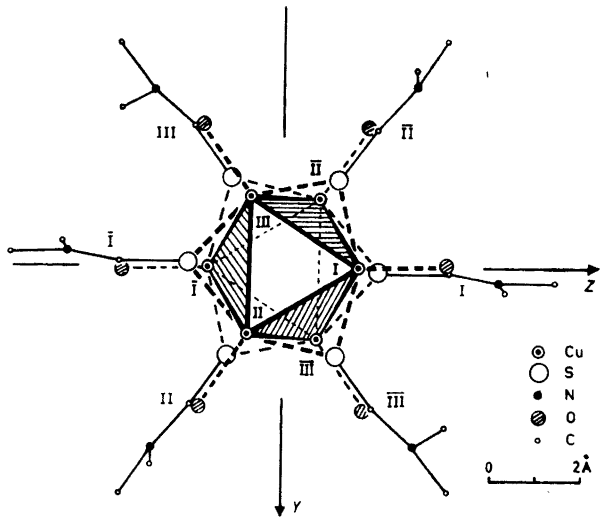


Fig. 3. The central part of the $[(C_3H_7)_2NCOSCu]_6$ molecule. The coordination is indicated by broken lines. Orthogonal projection in a direction perpendicular to the $Cu_ICu_{II}Cu_{III}$ plane. The ligands are situated outside six of the faces of the copper octahedron. The coordinate system XYZ has its origin at the centre of the molecule. The Y- and Z-axes are parallel to the plane of the projection and the X-axis is perpendicular to it. The coordinates of the atoms in this system are given in Table 6 in Ångström units, and the deviation of the atoms from the YZ-plane can accordingly be obtained from the X-coordinates in this table.

to assume that in solution the molecule, or at least the central part of it, has this symmetry, and that the slight deformation observed in the crystal structure is due to packing effects.

The metal atoms in the central part of the molecule form an almost regular octahedron. The metal-metal distances are given in Table 2. The distances

Table 2. Metal-metal distances.

Atoms	Distance	Atoms	Distance
Cu_I-Cu_{II}	2.938 ± 0.005 Å	$Cu_I-Cu_{\overline{III}}$	2.867 ± 0.005 Å
$-Cu_{\overline{II}}$	2.805 ± 0.005	$Cu_{II}-Cu_{III}$	3.057 ± 0.005
$-Cu_{III}$	2.922 ± 0.005	$-Cu_{\overline{III}}$	2.701 ± 0.005

Atoms	Distance
$Cu_I-Cu_{\overline{I}}$	4.077 ± 0.007 Å
$Cu_{II}-Cu_{\overline{II}}$	4.048 ± 0.007
$Cu_{III}-Cu_{\overline{III}}$	4.111 ± 0.007

between adjacent metal atoms in the octahedron have values ranging from 2.70 Å to 3.06 Å. The deviation from the average distance, 2.88 Å, is not more than 6 %. None of the distances seem to be short enough to indicate

bonding interactions between the metal atoms. It is thus probable that the formation of the metal "cluster" in the present compound is due to the metal-ligand linkage. The ligands are situated outside six of the eight faces of the octahedron. The linkage will be described in more detail later.

The structure of the copper(I) dipropylthiocarbamate hexamer is closely related to that of the silver(I) dipropyldithiocarbamate hexamer.[3] The molecule $[(C_3H_7)_2NCOSCu]_6$ is, however, more regular than $[(C_3H_7NCS_2Ag]_6$. The packing of the molecules in the two compounds is also different. Copper(I) dipropylthiocarbamate is monoclinic, whereas silver(I) dipropyldithiocarbamate is triclinic. The principle of the metal-ligand linkage is, however, the same in these two compounds (Fig. 4a). In contrast to this copper(I) diethyldithio-

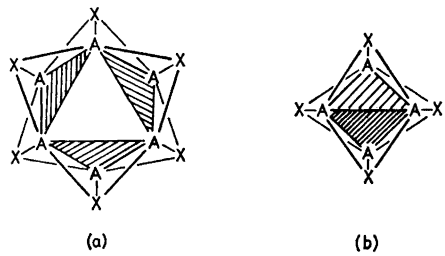


Fig. 4. The principle of the linkage in a) $[(C_3H_7)_2NCOSCu]_6$; b) $[(C_2H_5)_2NCS_2Cu]_4$.

carbamate [2] forms tetrameric molecules. The principle of the linkage between the ligands and the metal atoms in $[(C_2H_5)_2NCS_2Cu]_4$ is given in Fig. 4b. It is probable that the type of linkage formed in these related compounds is determined by geometrical factors such as the radii of the metal atoms and the separation between the two coordinating atoms of the ligands. Even if the metal atoms and ligands are linked together in different ways in the tetramers and the hexamers they have certain features of linkage in common. Thus each of the metal atoms is linked to three ligands and each ligand to three metal atoms.

Coordination. As mentioned earlier the ligands are situated outside six of the faces of the central metal octahedron and are attached to the metal atoms in the manner shown in Fig. 3. The sulphur atom of each ligand coordinates two copper atoms and the oxygen atom coordinates one copper atom. The metal coordination is accordingly threefold, each metal atom coordinating two sulphur atoms and one oxygen atom. Threefold metal coordination is also found in copper(I) diethyldithiocarbamate,[2] silver(I) dipropyldithiocarbamate,[3] and silver(I) dipropylmonothiocarbamate.[4]

The copper-sulphur distances in the present compound (Table 3) have values rangning from 2.20 Å to 2.25 Å and are thus somewhat shorter than those occurring in copper(I) diethyldithiocarbamate (2.25 – 2.29 Å). They are, however, appreciably longer than the Cu – S distance (2.15 Å) in ammonium copper(I) sulphite, NH_4CuSO_3.[14] The Cu – O bond distances in copper(I) dipropylthiocarbamate have the values 2.06, 2.08, and 2.09 Å, which are comparable to the value 2.12 Å reported in NH_4CuSO_3.[14] The Cu – O distances in $CuCrO_2$[15] where copper has twofold coordination, is 1.85 Å.

Table 3. Distances and angles of coordination.

a. *Distances*

Atoms	Distance	Atoms	Distance	Atoms	Distance
$Cu_I-S_{\bar{II}}$	2.20±0.01 Å	$Cu_{II}-S_{\bar{I}}$	2.25±0.01 Å	$Cu_{III}-S_{\bar{I}}$	2.22±0.01
$-S_{\bar{III}}$	2.22±0.01	$-S_{\bar{III}}$	2.25±0.01	$-S_{\bar{II}}$	2.22±0.01
$-O_I$	2.09±0.02	$-O_{II}$	2.06±0.02	$-O_{III}$	2.08±0.02

b. *Angles*

Atoms	Angle	Atoms	Angle
$S_{\bar{II}}-Cu_I-S_{\bar{III}}$	123.5±0.3°	$Cu_I-S_{\bar{III}}-Cu_{II}$	82.1±0.3°
$S_{\bar{II}}-Cu_I-O_I$	111.8±0.5	$Cu_I-S_{\bar{II}}-Cu_{III}$	82.9±0.2
$S_{\bar{III}}-Cu_I-O_I$	112.9±0.5	$Cu_{II}-S_{\bar{I}}-Cu_{III}$	86.5±0.3
$S_{\bar{I}}-Cu_{II}-S_{\bar{III}}$	120.0±0.3	$Cu_I-O_I-C_{\bar{I}}$	116.0±1.6
$S_{\bar{I}}-Cu_{II}-O_{II}$	112.6±0.5	$Cu_{II}-O_{II}-C_{II}$	114.7±1.6
$S_{\bar{III}}-Cu_{II}-O_{II}$	117.5±0.5	$Cu_{III}-O_{III}-C_{III}$	119.4±1.6
$S_{\bar{I}}-Cu_{III}-S_{\bar{II}}$	120.6±0.3	$Cu_I-S_{\bar{II}}-C_{\bar{II}}$	99.8±0.9
$S_{\bar{I}}-Cu_{III}-O_{III}$	110.5±0.5	$Cu_I-S_{\bar{III}}-C_{\bar{III}}$	101.5±0.8
$S_{\bar{II}}-Cu_{III}-O_{III}$	120.4±0.5	$Cu_{II}-S_{\bar{I}}-C_{\bar{I}}$	106.0±0.9
		$Cu_{II}-S_{\bar{III}}-C_{\bar{III}}$	106.9±0.9
		$Cu_{III}-S_{\bar{I}}-C_{\bar{I}}$	107.4±0.9
		$Cu_{III}-S_{\bar{II}}-C_{\bar{II}}$	106.0±0.9

The angles of coordination are given in Table 3. They vary from 111° to 124° and the coordination is accordingly not quite regular, nor is it planar. The distance from each copper atom to the plane of the coordinating oxygen and sulphur atoms is 0.44 Å (Cu_I), 0.40 Å (Cu_{II}), and 0.37 Å (Cu_{III}). As in copper diethyldithiocarbamate [2] and silver(I) dipropyldithiocarbamate [3] the metal atoms are situated "inside" the plane of the coordinating atoms, *i.e.* on the same side of the plane as the centre of the molecule.

Table 4. Distances and angles in the thiocarbamate ligands. The values given in parentheses represent distances or angles based on coordinates given in parentheses in Table 1.

a. *Distances.*

Atoms	Ligand I	Ligand II	Ligand III	Average
S···O	2.69±0.02 Å	2.65±0.02 Å	2.60±0.02 Å	2.65 Å
S–C	1.81±0.03	1.75±0.03	1.78±0.03	1.78
O–C	1.25±0.03	1.22±0.03	1.17±0.03	1.21
C–N	1.36±0.04	1.39±0.03	1.36±0.04	1.37
$N-C_{A1}$	1.50±0.03	1.51±0.03	1.56±0.04	1.52
$N-C_{B1}$	1.49±0.04	1.48	1.47	1.49
		(1.82±0.04)	(1.71±0.05)	
$C_{A1}-C_{A2}$	1.60±0.05	1.57±0.04	1.53	1.59
			(1.59±0.06)	
$C_{A2}-C_{A3}$	1.61±0.06	1.55±0.05	1.55	1.58
			(1.77±0.07)	
$C_{B1}-C_{B2}$	1.59	1.53	1.54	
	(1.67±0.06)	(1.34±0.06)	(1.27±0.08)	
$C_{B2}-C_{B3}$	1.55	1.49	1.49	
	(1.32±0.08)	(1.91±0.07)	(1.97±0.09)	

Table 4. Continued.

b. *Angles*

S–C–O	121.4±2.0°	125.7±2.0°	122.7±2.0	123.3°
S–C–N	116.2±1.9	117.6±1.9	115.3±1.9	116.4
O–C–N	122.1±2.3	116.4±2.3	122.0±2.4	120.2
C–N–C_{A1}	115.2±2.1	120.6±2.3	116.8±2.4	117.5
C–N–C_{B1}	125.8±2.1	120.8	124.3	125.8
		(121.5±2.1)	(121.6±2.5)	
C_{A1}–N–C_{B1}	118.8±2.0	114.9	113.5	118.8
		(115.4±2.1)	(118.0±2.5)	
N–C_{A1}–C_{A2}	107.2±2.3	103.0±2.1	108.7	105.1
			(100.2±2.7)	
C_{A1}–C_{A2}–C_{A3}	106.3±3.0	103.0±2.4	106.5	104.7
			(94.6±3.1)	
N–C_{B1}–C_{B2}	104.3	109.0	109.5	
	(100.7±2.4)	(83.6±2.9)	(84.7±4.1)	
C_{B1}–C_{B2}–C_{B3}	109.5	109.0	109.2	
	(101.5±3.9)	(79.8±3.2)	(84.2±4.3)	

The thiocarbamate ligand. The interatomic distances and angles in the thiocarbamate ligands are presented in Table 4. The average values are given in the last column in the table. The notations of the atoms can be seen in Fig. 1. As is seen from the standard deviations of the distances and angles the accuracy of the values is not high enough to permit any far reaching

Table 5. Interligand distances shorter than 4.00 Å. The coordinates of the atoms with the additional notations (a)–(i) are related to those given in Table 1 (coordinates x, y, z) as follows:

(a)	x,	y,	$1+z$
(b)	$1+x$,	y,	z
(c)	$1/2+x$,	$1\ 1/2-y$,	z
(d)	$1/2-x$,	$1\ 1/2+y$,	$2-z$
(e)	$1/2+x$,	$-(1/2+y)$,	z
(f)	$-(1/2+x)$,	$-(1/2-y)$,	$-z$
(g)	$2-x$,	$-y$,	$1-z$
(h)	$1/2+x$,	$1/2-y$,	$1+z$
(i)	$1-x$,	$-y$,	$2-z$

Atoms	Distance	Atoms	Distance	Atoms	Distance
S_I–$S_{\overline{II}}$	3.82 Å	S_I–$S_{\overline{III}}$	3.89 Å	S_{II}–$S_{\overline{III}}$	3.90 Å
S_I–$O_{\overline{II}}$	3.59	S_I–$O_{\overline{III}}$	3.53	S_{II}–$O_{\overline{I}}$	3.55
S_{II}–$O_{\overline{III}}$	3.72	S_{III}–$O_{\overline{I}}$	3.59	S_{III}–$O_{\overline{II}}$	3.69
O_I–$O_{\overline{II}}$	3.57	O_I–$O_{\overline{III}}$	3.62	O_{II}–$O_{\overline{III}}$	3.74
O_I–$C_{\overline{II}}$	3.45	O_I–$C_{\overline{III}}$	3.56	O_{II}–$C_{\overline{I}}$	3.69
O_{II}–$C_{\overline{III}}$	3.94	O_{III}–$C_{\overline{I}}$	3.63	O_{III}–$C_{\overline{II}}$	3.95
C_I–$C_{\overline{II}}$	3.96	C_I–$C_{\overline{III}}$	3.94	N_{II}–N_{II}(g)	3.78
C_{IA3}–S_I(c)	4.00	C_{IB2}–$C_{\overline{IIIA2}}$	3.83	C_{IIA3}–O_{III}(a)	3.80
C_{IA3}–O_{II}(d)	3.73	C_{IB2}–$C_{\overline{IIIA3}}$	3.94	C_{IIA3}–C_{IIIA3}(h)	3.66
C_{IB3}–S_{II}(e)	3.96	C_{IIA1}–O_{II}(g)	3.78	C_{IIB1}–O_{II}(g)	3.66
C_{IB3}–S_{III}(e)	3.87	C_{IIA1}–C_{II}(g)	3.55	C_{IIB3}–C_{IIIB2}(a)	3.95
C_{IB3}–C_{IIIA2}(f)	3.93	C_{IIA1}–N_{II}(g)	3.47	C_{IIIB3}–O_I(b)	3.42
C_{IB3}–C_{IIIB1}(f)	3.67	C_{IIA1}–C_{IIA1}(g)	3.78	C_{IIIB3}–C_{IA1}(a)	3.86
C_{IB3}–C_{IIIB2}(f)	3.99	C_{IIA1}–C_{IIB1}	3.50	C_{IIIB3}–C_{IIIB1}(i)	3.94
C_{IB3}–C_{IIIB3}(f)	3.78	C_{IIA1}–O_{III}(a)	3.57		

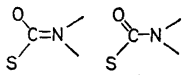
conclusions regarding the bonding conditions. Some comments concerning the shape of the ligand and some of the average distances will, however, be made. The NCOS part of each of the ligands is planar within experimental errors. The group of atoms formed by the nitrogen atom and its carbon neighbours exhibits small but significant deviations from planarity. This contrasts

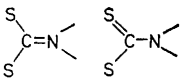
Table 6. Atomic coordinates in Ångström units in the orthonormalized coordinate system, X, Y, Z (*cf.* Fig. 3). The coordinates of atoms with the notations $\bar{\text{I}}$, $\bar{\text{II}}$, and $\bar{\text{III}}$ can be obtained from those in the table by reversing the signs of the coordinates.

Metal atoms:	X	Y	Z
Cu_{I}	1.10	0.00	1.72
Cu_{II}	1.10	1.49	−0.82
Cu_{III}	1.10	−1.57	−0.75
Thiocarbamate molecule I:			
S_{I}	−2.00	0.09	2.14
O_{I}	0.24	0.01	3.62
C_{I}	−1.01	0.09	3.66
N_{I}	−1.68	0.34	4.81
C_{IA1}	−0.85	0.30	6.05
C_{IA2}	−1.11	−1.11	6.76
C_{IA3}	−0.20	−1.13	8.08
C_{IB1}	−3.16	0.52	4.94
C_{IB2}	−3.34	2.09	5.14
C_{IB3}	−4.84	2.41	5.29
Thiocarbamate molecule II:			
S_{II}	−2.00	1.95	−1.23
O_{II}	0.32	3.07	−1.89
C_{II}	−0.89	3.01	−2.08
N_{II}	−1.42	3.95	−2.95
C_{IIA1}	−0.54	4.97	−3.62
C_{IIA2}	0.09	4.15	−4.81
C_{IIA3}	1.05	5.18	−5.47
C_{IIB1}	−2.86	4.33	−2.87
C_{IIB2}	−3.63	3.64	−4.00
C_{IIB3}	−5.06	4.03	−3.92
Thiocarbamate molecule III:			
S_{III}	−2.03	−1.95	−1.18
O_{III}	0.21	−3.11	−1.82
C_{III}	−0.94	−3.09	−2.00
N_{III}	−1.54	−3.90	−2.92
C_{IIIA1}	−0.62	−4.90	−3.68
C_{IIIA2}	0.13	−4.15	−4.78
C_{IIIA3}	0.97	−5.20	−5.55
C_{IIIB1}	−2.75	−3.54	−3.66
C_{IIIB2}	−3.84	−4.59	−3.39
C_{IIIB3}	−5.07	−4.22	−4.14

to the practically complete planarity of the nitrogen-carbon arrangement in dithiocarbamates.[2,3,16–19] The deviation from planarity of the entire central part, CCNCOS, is, however, not very pronounced.

The average value of the S–C distances is 1.78 Å and these distances are accordingly somewhat longer than the S–C distances in dithiocarbamates (1.70–1.74 Å).[2,3,16–19] The average C–O distance is 1.21 Å which is comparable with the shorter C–O distance in carboxylic acids and esters (av. 1.23 Å).[20] The features described seem to indicate that of the canonical forms given below


(monothiocarbamate)


(dithiocarbamate)

the one with single bond character of the C–N bond is more important in the monothiocarbamate than in the dithiocarbamates. In accordance with this the average length of this bond (1.37 Å) is somewhat greater than that in the dithiocarbamates. The uncertainty of the distances in the present investigation must, however, be kept in mind.

The difficulties encountered in fixing the positions of some of the atoms in the propyl chains are probably due to disorder phenomena which are also encountered in some dithiocarbamates studied at this Institute. These disturbances are reflected in the temperature factors which have the highest values for the outermost carbon atoms. These are the ones which would be most easily affected by disorder effects. Even if the coordinates of the carbon atoms are somewhat uncertain, there is no doubt as to the shape and orientation of the propyl chains. The exact positions of these atoms are of little chemical interest.

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