THE CRYSTAL AND MOLECULAR STRUCTURE OF THE COPPER(II) BIS(DIALYLDITHIOCARBAMATE) COMPLEX

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The crystal structure of $\{Cu[S_2CN(C_3H_5)_2]_2\}_2$ was solved by the single crystal method of X-ray structural analysis. The substance crystallized as a dimer in the triclinic system with space group of $P\bar{1}$ and lattice parameters $a = 1{\cdot}0161\,(4)$, $b = 0{\cdot}9294(4)$, $c = 1{\cdot}0518(3)$ nm, $\alpha = 77{\cdot}46(3)$, $\beta = 77{\cdot}10(3)$, $\gamma = 89{\cdot}02(3)°$. The structure was refined by the least squares method to a final value of $R = 4{\cdot}9\%$ using all the 1 713 observed reflections. The crystal structure consists of dimeric molecules, where each pair of centrosymmetrically dependent Cu atoms lies at a distance of 0·3742 nm. The coordination polyhedron of the Cu atom is a tetragonal pyramid, where the four sulphur atoms lie at distances of Cu—S1 0·2314, Cu—S2 0·2309, Cu—S3 0·2324, Cu—S4 0·2328 and are approximately in a plane from which the Cu atom lies at a distance of 0·026 nm. The fifth, longer bond, Cu—S′4 0·2888 nm forms the apex of the tetragonal pyramid. In the stereochemistry of the dithiocarbamate ligands of the studied substances there are no marked differences in the bond lengths and corresponding angles compared with the values for the solved structures of the other dialkyl-dtc complexes. The lengths of the sulphur-carbon bonds lie in the range from 0·170 to 0·173 nm and both lengths of the $C(sp)^2-N(sp^2)$ bonds equal to 0·134 and 0·133 nm indicate marked double bond character of the C—N bond. The S_2CN ligand fragment is planar. In the alyl part of the ligand, the N—C bond lengths lie in the range 0·147—0·149 nm, the average C—C bond length is 0·149 nm and C=C bond length is 0·132 nm.

The studied $[Cu(alyl_2dtc)_2]_2$ complex belongs among compounds in which the nitrogen atom with a lone electron pair participates in the conjugation with the C=S group, leading to the formation of a conjugated system formed as a result of delocalization of the π-electrons originally localized on the C=S bond and on the nitrogen atom. The delocalization of the π-electrons is demonstrated not only by the results of X-ray structural analysis (length of the C—N bond) but also by the results of measurements of the IR spectra of a large number of dithiocarbamates[1-4] through the presence of the absorption band of ν(C—N) in the region around 1 500 cm^{-1}.

It follows from the literature data[5-14] for the Cu(II)–dtc (where dtc designates dithiocarbamate) complexes that considerable variability has been observed in the coordination polyhedra of the copper atom, in contrast to the dtc compounds

of Ni(II) (ref.[15–24]) or Zn(II) (ref.[25–31]); all Ni(II)–dtc complexes are characterized by square-planar coordination of the central atom and dimeric Zn(II)–dtc compounds contain trigonal bipyramid or tetragonal pyramidal coordination. It has been found that the type of coordination polyhedron and interatomic distances are affected by the nature of radical bonded to the nitrogen atom of the dtc group[15]. There are only a few dtc complexes in which the carbon chain contains multiple bonds. Consequently, we carried out an X-ray structural study of the above complex.

EXPERIMENTAL

Preparation of the Complex

The copper(II) salt of dialyldithiocarbamidic acid was prepared in the usual manner by precipitating $Cu(alyl_2dtc)_2$ from an aqueous solution of the sodium salt of N,N-dialyldithiocarbamidic acid and $CuSO_4.5\,H_2O$. A black-brown precipitate is formed, which was dried and dissolved in CH_2Cl_2. Shiny, rhombohedral crystals formed in the solution. The purity of the substance was confirmed by analysis. For $[CuS_2CN(C_3H_5)_2]_2$ (408·1) was calculated 41·20% C, 4·94% H, 6·89% N, 15·57% Cu and found 41·18% C, 5·05% H, 6·85% N, 15·35% Cu. A crystal density of $1{\cdot}43(2)\,.\,10^3$ kg m^{-3} was measured by the flotation method in a saturated $ZnSO_4$ solution. The measured density is in good agreement with the calculated value of $1{\cdot}44\,.\,10^3$ kg m^{-3} assuming the presence of 2 formula units per unit cell ($Z = 2$).

The compound $[CuS_2CN(C_3H_5)_2]_2$ crystallizes in the triclinic system (Table I). A crystal

TABLE I

Basic crystallographic data for $[Cu(alyl_2dtc)]_2$

Empirical formula	$C_{14}H_{20}N_2S_4Cu$
Relative molar mass	408·1
Melting point	105°C
Crystallographic system	triclinic
Space group	$P\bar{1}$
Dimensions of a unit cell and their standard deviations	$a = 10{\cdot}161(4)$ $b = 9{\cdot}294(4)$ $c = 10{\cdot}518(3)\,.\,10^{-10}$ m $\alpha = 76{\cdot}46(3)$ $\beta = 77{\cdot}10(3)$ $\gamma = 89{\cdot}02(3)°$
Volume of a unit cell	$938{\cdot}8\,.\,10^{-30}$ m^3
Number of formula units per unit cell	$Z = 2$
Number of electrons per unit cell	$F(000) = 422$
Measured crystal density	$D_0 = 1{\cdot}43(2)\,.\,10^3$ kg m^{-3}
Calculated crystal density	$D_c = 1{\cdot}44\,.\,10^3$ kg m^{-3}
Linear absorp. coef.	$\mu(\text{Mo K}_\alpha) = 1{\cdot}63$ mm^{-1}

with dimensions of 0·20 × 0·15 × 0·20 nm was selected for obtaining the basic crystallographic data and for intensity measurements. Preliminary Weissenberg patterns indicated the presence of a triclinic crystallographic system. The lattice parameters were refined on a Syntex P21 diffractometer by the least squares method on the basis of 10 centred reflections. The integral intensity was measured using graphite monochromated Mo K_α radiation. The intensity was recorded in the angle interval $0° < 2\Theta < 56°$. The crystal was recentred after each 100 intensity measurements. Of the total of 2 624 recorded independent reflections, 1 713 with $I < 1{\cdot}96\sigma(I)$ were classified as observed (65·3% of the observed reflections in the given diffraction sphere). All the intensities were corrected for the Lorentz and polarization factors and converted to the absolute scale by the Wilson method ($B = 3{\cdot}41 \,.\, 10^{-20}$ m^2). Correction was not carried out for absorption ($\mu = 1{\cdot}63$ mm^{-1}). All 1 713 observed reflections were employed in the final structure solution.

Solution and Refinement of the Structure

In the solution of the structure of the copper(II) bis(dialyldithiocarbamate) complex, the average statistical values $\langle |E_h|^2 \rangle$, $\langle |E_h|^2 - 1 \rangle$, and $\langle |E_h| \rangle$ and the E_h distribution unambiguously pointed to the *P1* space group. The position of the copper atom ($x = -0{\cdot}017$, $y = 0{\cdot}03$, $z = 0{\cdot}188$) and localization of the four sulphur atoms were found from the three-dimensional Patterson synthesis calculated from the contributions of all 1 713 independent reflections. The structure was further solved by the "heavy atom" method — three-dimensional Fourier synthesis of the electron density phased from the contribution of the CuS_4 fragment gradually indicated the positions of all the nonhydrogen atoms, where an isotropic thermal coeficient of $3{\cdot}5 \,.\, 10^{-20}$ m^2 was assumed for all the atoms. At this stage in the solution, factor R had a value of 0·21. The structure was refined in three cycles by the least squares method using the full matrix, isotropic thermal parameters of all the nonhydrogen atoms and a unit weighting scheme of all the 1 713 observed reflections to give a value of $R = 0{\cdot}14$. In the next 6 refinement cycles, anisotropic thermal vibration of all the atoms was assumed; together with the positional parameters refined by the least squares method in a 9 × 9 block diagonal approximation this led to a final value of $R = 0{\cdot}057$, where R is defined as $\Sigma||F_0| - |F_c||/\Sigma|F_0|$.

The correctness of the selection of the weights of the individual reflections in the minimized quantity $\Sigma w(|F_0| - |F_c|)^2$ according to the Hughes scheme (($\sqrt{w} = |F_0|/a$ for $|F_0| \leqq a$ or $\sqrt{w} = a/|F_0|$ for $|F_0| > a$, where $a = 35$) was confirmed by the approximately symmetrical distribution of the values of this quantity over the sin Θ/λ and $|F_0|$ intervals. In the last refinement cycle, the change in all the parameters was less than $0{\cdot}1\sigma$. Differential Fourier synthesis of the residual electron density had a greatest maximum of $0{\cdot}66 \,.\, 10^{30}$ em^{-3}. From this value, the positions of all the hydrogen atoms were found and were introduced into the last refinement cycle with the value of the thermal parameters identical to those for the carbon atoms to which they are bonded. The final value of factor R after localization of the hydrogen atoms attained a value of 0·049.

Tables of the observed and calculated structural factors are available on request to the authors. Scatter curves for the neutral atoms were taken from the Tables[32]. The basic crystallographic data for substance $[Cu(alyl_2dtc)_2]_2$ are given in Table I. The refined positions of the nonhydrogen atoms are given in Table II and the coordinates of the hydrogen atoms in Table III. The bonding distances and bond angles in the $[Cu(alyl_2dtc_2]_2$ molecule are given in Table IV. The values of the coefficients in equation $AX + BY + CZ = D$ fitted by the least squares method through selected atoms and the deviations of the atoms from selected planes are given in Tables V and VI. Fig. 1 depicts projection of the structure of substance $[Cu(alyl_2dtc)_2]_2$ onto the 010 plane.

All the calculations were carried out on an XTL module from Syntex $P2_1$ and on a Siemens 4004/150 computer using a system of programs obtained from individual authors (A. Zalkin, O. Lingren and F. Wengelin). The positions of the atoms were refined by the least squares method using the NRC crystallographic program for the IBM/360 system[33].

Description of Structure and Discussion

The crystal structure of $[Cu(alyl_2dtc)_2]_2$ consists of dimers, where the formation of a dimer between two parallel molecules of the copper complex depends on interaction of the copper atom in each molecule with a sulphur atom in the neighbouring molecule with formation of a 5-fold, tetragonal pyramidal configuration. Each copper atom is coordinated by five sulphur atoms, of which one bond, Cu-S'4 = 2·888 . . 10^{-10} m, is much longer and corresponds to the interaction leading to dimer formation.

TABLE II

Positional parameters (. 10^4) and isotropic temperature parameters* for the nonhydrogen atoms in the crystal structure of $[Cu(alyl_2dtc)_2]_2$ with standard deviations given in brackets

Atom	x/a	y/b	z/c	$B(.\ 10^{-10}\ m)^2$
Cu	− 67(1)	275(1)	1 804(1)	3·59
S1	1 412(1)	624(1)	3 889(1)	4·13
S2	− 65(1)	−2 065(1)	2 202(1)	3·88
S3	− 531(1)	2 710(1)	1 782(1)	3·86
S4	−1 828(1)	17(1)	− 97(1)	3·68
C1	1 022(5)	−1 237(5)	3 691(5)	3·35
C2	−1 768(5)	1 935(5)	377(5)	3·05
C3	1 091(7)	−3 502(7)	4 514(7)	6·11
C4	−3 598(5)	2 027(6)	−1 557(5)	4·30
C5	2 497(6)	−1 194(7)	5 905(5)	4·72
C6	−2 673(6)	4 343(6)	211(5)	4·48
C7	2 219(8)	−4 474(7)	4 445(7)	7·01
C8	−2 158(6)	5 185(6)	− 632(5)	4·57
C9	3 929(6)	−1 271(7)	5 792(7)	6·28
C10	−5 025(6)	1 914(7)	−1 395(7)	5·99
C11	2 531(10)	−5 416(8)	5 313(9)	9·34
C12	−2 868(7)	6 144(6)	−1 192(6)	5·61
C13	4 848(8)	−1 739(8)	6 555(10)	10·33
C14	−6 012(7)	2 518(9)	−2 082(9)	9·22
N1	1 535(4)	−1 950(5)	4 644(4)	4·13
N2	−2 635(4)	2 708(4)	− 287(4)	4·11

* $B = \frac{4}{3}\sum_i \sum_j B_{ij}\bar{a}_i, \bar{a}_j$.

The coordination polyhedron of the Cu atom is a tetragonal pyramid, where the S1, S2, S3 and S4 atoms lie roughly in a plane from which the Cu atom lies at a distance of $0{\cdot}26 \,.\, 10^{-10}$ m. The long bond from the copper atom, Cu-S'4 is roughly perpendicular to the plane of the base. Deviations of the sulphur atoms, S1, S2, S3 and S4 from the best plane drawn through them are a result of the difference between angles S1CuS4 170·6° and S2CuS3 163·3° and those for precise square pyramidal coordination (Fig. 2).

Compound $[Cu(alyl_2dtc)_2]_2$ can be included in the group of structures containing a Cu atom with coordination number of 5, similarly as for $[Cu(n\text{-}Pr_2dtc)_2]_2$ (ref.[7]), $[Cu(Et_2dtc)_2]_2$ (ref.[6]), $[Cu_2(Et_2dtc)_2Cl_2]_2$ (ref.[12]), $[Cu_3(n\text{-}Bu_2dtc)_6][Cd_2Br_6]$ (ref.[13]). Table VII gives some of the geometric dimensions of the CuS_2CNC_2 fragment for all Cu(II)–dtc complexes that thave so far been studied. It can be seen from the table that two of the solved structures form dimers in which the intermolecular interactions Cu—S'4 2·851 (ref.[6]) and $2{\cdot}741 \,.\, 10^{-10}$ m (ref.[7]) are similar to the Cu—S'4 value of $2{\cdot}888 \,.\, 10^{-10}$ m found for the compound $[Cu(alyl_2dtc)_2]_2$. Dimer

TABLE III

The positional parameters (. 10^4) for the hydrogen atoms in the crystal structure of $[Cu(alyl_2dtc)_2]_2$

Atom	x/a	y/b	z/c
H31	440	−4 090	5 012
H32	130	−3 320	3 800
H41	−3 249	1 147	−2 153
H42	−3 634	2 542	−2 244
H51	2 188	−1 589	6 619
H52	2 269	31	6 254
H61	−2 350	4 423	1 177
H62	−3 580	4 509	211
H71	3 268	−4 281	4 371
H81	−1 063	4 972	− 749
H91	3 835	− 453	5 258
H101	−4 717	2 095	− 511
H111	2 180	−5 270	4 600
H112	2 900	−4 670	5 570
H121	−3 794	6 004	−1 239
H122	−2 570	5 850	2 500
H131	5 696	−1 217	6 927
H132	5 218	−2 409	6 645
H141	−6 673	2 402	−1 440
H142	−6 371	3 565	−2 050

formation is a result of an attempt of the Cu atom to increase its coordination number by out-of-plane interaction of the d_z2 orbital of the Cu atom in the 5th coordination position with the p_π orbital of the sulphur atom in the neighbouring molecule[34] (π-bonds in out-of-plane interactions are weaker than strong planar σ-bonds). This

TABLE IV

The bonding distances (. 10^{-10} m) and bond angles (°) in the symmetrically independent part of the unit cell of $[Cu(alyl_2dtc)_2]_2$ with standard deviations given in brackets

Bonding distances			
Bond	Bond length	Bond	Bond length
Cu—S1	2·314(2)	N1—C3	1·470(8)
Cu—S2	2·309(2)	N1—C5	1·473(7)
Cu—S3	2·324(2)	N2—C4	1·463(7)
Cu—S4	2·328(2)	N2—C6	1·492(7)
Cu—S4′	2·888(2)	C3—C7	1·476(10)
S1—C1	1·722(5)	C5—C9	1·487(9)
S2—C1	1·703(5)	C6—C8	1·480(8)
S3—C2	1·710(5)	C4—C10	1·502(8)
S4—C2	1·731(5)	C7—C11	1·398(11)
C1—N1	1·343(6)	C9—C13	1·244(1)
C2—N2	1·327(6)	C8—C12	1·319(8)
Cu—Cu′	3·742(2)	C10—C14	1·315(10)

Bond angles			
Atoms	Angle	Atoms	Angle
S1—Cu—S2	76·8(1)	N2—C4—C10	112·4(5)
S3—Cu—S4	76·6(1)	N2—C6—C8	112·5(4)
Cu—S1—C1	84·3(2)	C3—C7—C11	120·9(7)
Cu—S2—C1	84·8(2)	C5—C9—C13	125·4(7)
Cu—S3—C2	85·0(2)	C6—C8—C12	123·0(6)
Cu—S4—C2	84·5(2)	C4—C10—C14	122·1(6)
S1—C1—S2	114·1(3)	C1—N1—C3	121·3(4)
S3—C2—S4	113·9(3)	C1—N1—C5	121·9(4)
S1—C1—N1	122·1(4)	C5—N1—C3	116·7(5)
S2—C1—N1	123·8(4)	C2—N2—C6	121·7(4)
S3—C2—N2	124·1(4)	C2—N2—C4	122·7(4)
S4—C2—N2	122·1(4)	C6—N2—C4	115·6(4)
N1—C3—C7	111·4(5)	N1—C5—C9	112·4(5)

is ensured by sufficient planarity of the whole complex, permitting approach of the two molecules to a distance of ($<2{\cdot}9 \,.\, 10^{-10}$ m), required for interaction. Thus the structure of $Cu(pm\ dtc)_2$ (pm denotes pentamethylene)[10] consists of monomeric units in which the *trans*-configuration (apparently with better total lattice energy) of the piperidine rings sterically prevents sufficiently close approach of the mole-

TABLE V

The values of the coefficients in the equation AX + BY + CZ = D fitted by the least squares method through selected atoms

Plane	Atoms	*A*	*B*	*C*	*D*
1	S1S2C1N1	0·8985	−0·1404	−0·4158	−1·0966
2	S3S4C2N2	0·7911	0·1960	−0·5795	−1·3784
3	S1S2C1N1C3C5	0·8906	−0·1697	−0·4219	−1·0666
4	S3S4C2N2C4C6	0·8039	0·2300	−0·5487	−1·3333
5	S1S2S3S4	0·8623	0·0241	−0·5059	−1·6044

TABLE VI

The deviations of some atoms (. 10^{-10} m) from planes 1—5 defined in Table V. The designation of the atoms and planes is the same as in Table V and Fig. 1

Plane 1		S1S2C1N1
Deviations	Cu −0·071, S1 0·0, S2 0·0, C1 0·003, N1 −0·001, C3 −0·127, C5 0·032	
Plane 2		S3S4C2N2
Deviations	Cu −0·093, S3 −0·003, S4 −0·003, C2 0·009, N2 −0·004, C4 0·135, C6 −0·140	
Plane 3		S1S2C1N1C3C5
Deviations	Cu −0·103, S1 −0·046, S2 0·033, N1 0·026, C1 0·010, C3 −0·056, C5 0·035	
Plane 4		S3S4C2N2C4C6
Deviations	Cu −0·095, S3 0·065, S4 −0·072, N2 −0·003, C2 0·010, C4 0·078, C6 −0·079	
Plane 5		S1S2S3S4
Deviations	Cu 0·262, S1 0·075, S2 −0·073, S3 −0·074, S4 0·073	

Angles between planes (°): (1)—(3) 1·8, (2)—(4) 2·7.

cules. There are similar steric hindrances to dimerization in $Cu(MePh\ dtc)_2$ (ref.[9]), where the benzene rings do not lie in the plane of the complex but are rotated by an angle of 82° around the S_2CN–C bond (as a result of the steric effect of the methyl substituents).

As can be seen from Table VII, all the bonds of Cu—S with C atoms with sp^2 hybridization vary in length from 2·28 to 2·34 . 10^{-10}m and the S—C bonds equal 1·72 . 10^{-10} m (average value) irrespective of the type of coordination polyhedron. The values found for the studied complex did not differ significantly from these values. The S—C bonds are shorter than the distance of 1·76 – 1·78 . 10^{-10} m, assumed for a single bond as found from the structures of substances of the monothiocarbamate type $\{M[SOCN(C_3H_7)_2]_2\}_6$ (M = Cu, Zn, Ag)[35–37] and for substances containing a thiourea molecule, $Zn(tu)_2Cl_2$ (ref.[38]) and $Ni(tu)_2(NCS)_2$ (ref.[39]). In contrast to dithiocarbamate complexes, delocalization of the π-electrons

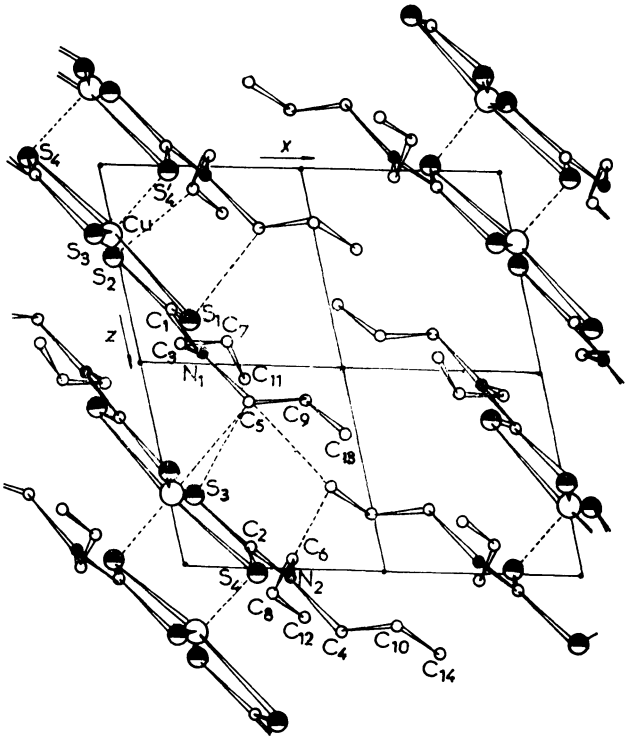

FIG. 1

Projection of the structure of $[Cu(alyl_2dtc)_2]_2$ onto the (010) plane

in monothiocarbamate of this type is limited primarily to the C = O and C = NR_2 bonds; thus the length of the C—S bond indicates that these are primarily single bonds. This information is in agreement with the results of IR spectra where the ν(C—O) and ν(C—N) vibration bands lie in the region between 1 450 and 1 550 cm^{-1} (ref.[40]).

The determined S—C bond lengths in dialylderivatives confirm that the C=S π-electron bonds in the dtc–ion are completely delocalized to form a four-membered ring. The inclusion of the lone electron pair of the nitrogen atom in conjugation with the chelate ring is demonstrated by the lengths of the C1—N1 and C2—N2 bonds, which correspond to a double bond (1·34, 1·33 . 10^{-10} m). The average length of the N1—C3, N1—C5, N2—C6 and N2—C4 bonds, 1·47 . 10^{-10} m indicates that this is a type of single bond. Measurement of the IR spectra of the studied compound reveals the presence of a ν(C—N) band at 1 490 cm^{-1}, indicating the double character of the C—N bond.

No marked anomalies in bond lengths or angles were found in the two alyl parts of the dithiocarbamate ligand. All the C—C bonds have an average length of 1·49 . . 10^{-10} m and C=C, 1·32 . 10^{-10} m. The size of the bond angles for the given bonds corresponds to sp^3 or sp^2 hybridization (Table IV). The lengths of the C7—C11 (1·398 . 10^{-10} m) and C9—C13 (1·244 . 10^{-10} m) bonds differ slightly from that for the theoretical length of a C=C bond (1·33 . 10^{-10} m). This fact is apparently connected with the highest value of thermal parameter B for the terminal carbon atoms of the alyl groups, C11 and C13, reflecting their high rotational (or also vibrational) flexibility, probably as a result of rotation around the C—C single bond in the —CH_2—CH=CH_2 group.

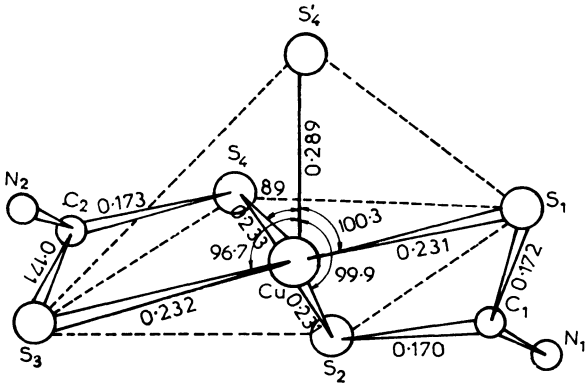

FIG. 2

Interatomic distances (nm) and angles in the coordination polyhedron of the Cu(II) atom

TABLE VII

Comparison of the bonding distances (. 10^{-10} m) and chelating S—Cu—S angles (°) in various substituted Cu(II)-dtc complexes

Substance	Point symmetry of the Cu atom	Cu—S	S—Cu—S	C—S	C—N	Lit.
$Cu(Me_2dtc)_2$[a]	$\bar{1}$	2·302; 2·319; 3·159	77·0	1·716; 1·726	1·31	5
$Cu_2(Et_2dtc)_4$[b]	*1*	2·317; 2·297 2·851 2·301; 2·339	77·3 76·5	1·711; 1·710 1·710; 1·740	1·35 1·33	6
$Cu_2(n\text{-}Pr_2dtc)_4$[b]	*1*	2·323; 2·332 2·740 2·322; 2·324	76·6 76·3	1·711; 1·735 1·715; 1·724	1·34 1·32	7
$Cu(i\text{-}Pr_2dtc)_2$[c]	$\bar{1}$	2·279; 2·291(B) 2·283; 2·286(A)	77·3 76·7	1·718; 1·725 1·710; 1·727	1·33 1·32	8
$Cu_2(alyl_2dtc)_4$[b]	*1*	2·314; 2·309 2·888 2·324; 2·328	76·8 76·6	1·722; 1·703 1·710; 1·731	1·34 1·33	this paper this paper
Cu(MePh dtc)$_2$[c]	$\bar{1}$	2·274; 2·329	77·2	1·72; 1·73	1·31	9
Cu(pm dtc)$_2$[c]	$\bar{1}$	2·286; 2·303	77·7	1·71; 1·74	1·33	10
$Cu(pmdtc)_2(CuBr)_4$[a]	*2/m*	2·316	77·1	1·74	1·32	11
$Cu(pmdtc)_2(CuBr)_6$[a]	*2/m*	2·306	77·3	1·75	1·32	11
$[Cu_2(Et_2dtc)_2Cl_2]_2$[b]	*1*	2·274; 2·261 2·882 2·275; 2·286	—	—	—	12

[a] Layered polymeric structure; [b] tetragonal-pyramidal complex; [c] planar monomeric complex; A, B designations for two independent molecules in the cell.

TABLE VIII

Intermolecular interactions $<4 \cdot 10^{-10}$ m of the van der Waals type in the crystal structure of $[Cu(alyl_2dtc)_2]_2$[a]

Cu—S′4[I]	2·888(2) . 10^{-10} m	S2—H81[II]	3·985(6)
Cu—C2[I]	3·576(5)	C1—H41[II]	3·072(5)
Cu—H51[II]	3·102(1)	C5—C14[IV]	3·695(10)
S2—C2[I]	3·639(5)	C5—H141[IV]	3·763(6)
S3—H51[II]	2·962(2)	C7—C12[II]	3·626(10)
S1—H41[II]	3·122(2)	C6—H142[III]	3·925(6)

[a] Transformation of the atoms in the various asymmetric units with respect to the atoms of a unit cell (with positions x, y, z) in Table II. I: $1 - x, - y, - z$; II: $- x, - y, - z$; III: $x, y, 1 + z$; IV: $- x, 1 - y, - z$.

Table VIII lists the intermolecular interactions less than $4 \cdot 10^{-10}$ m, yielding information on the positioning of the molecules in the crystal lattice. In some Cu–dtc complexes[6,7,10], interactions of the Cu...H type have been observed, where the hydrogen atom occupied the 6th coordination position in a deformed octahedral coordination around the copper atom. In the studied compound, the closest interaction with the copper atom, with the exception of the Cu—S′4 interaction described above, was the Cu—H51 interaction, at a distance of $3{\cdot}1 \cdot 10^{-10}$ m, corresponding to a weak van der Waals bond.

It follows from the deviations of some atoms from the planes of the $[Cu(alyl_2-dtc)_2]_2$ molecule (Table VI) that the S_2CN fragment is highly planar in this molecule. The C3, C5, C4 and C6 atoms lie slightly outside planes 1 and 2. The observed deviations of these atoms from the S_2CN plane are in agreement with the results obtained by testing S_2CN fragments for planarity in bis–dtc complexes. In bis–dtc complexes, the planarity of this fragment is strongly affected by the monomeric nature of the molecule and by the presence of intermolecular interactions of the M...H or S...H types, found for the studied substance. The M...S interactions remain most important as they lead to dimer formation.

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