

THE CRYSTAL STRUCTURE OF DIBUTYL-BIS(PENTAMETHYLENEDI-THIOCARBAMATO)TIN (IV)

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The crystal and molecular structure of $\text{SnBu}_2(\text{pmdtc})_2$ has been solved by X-ray diffraction methods and refined by a block-diagonal least-squares procedure to $R = 0.083$ for 895 observed reflections. Monoclinic, space group $C2$, $a = 19.893(6)$, $b = 7.773(8)$, $c = 12.947(8) \cdot 10^{-10}$ m, $\beta = 129.07(5)^\circ$, $Z = 2$, $\text{C}_{20}\text{H}_{38}\text{N}_2\text{S}_4\text{Sn}$. Measured and calculated densities are $D_m = 1.38(2)$, $D_c = 1.36 \text{ Mg m}^{-3}$. Sn atom, placed on the twofold axes, is coordinated with four S atoms in the distances Sn—S 2.966(6) and 2.476(3) $\cdot 10^{-10}$ m. Coordination polyhedron is a strongly distorted octahedron. Ligand S_2CN is planar.

A great attention has been paid to the study of crystal structures of dithiocarbamate (dtc) complexes in several last years. A number of papers on crystal structures of dtc complexes with transition metals were published. Apparently, one of the reasons for that is a high biological activity of these complexes. In spite of that fact, low attention has been paid to dtc complexes of non-transition metals. One of the aims of this paper is to gain new information on the metal–ligand bonding in Sn complexes of dtc.

Non-transition metal complexes of dtc differ from analogical complexes of transition metals mainly by non-equivalency of metal–sulphur and sulphur–carbon bonds in the chelate ring. Assymetry of the chelate ring and the type of distortion of the coordination polyhedron in these complexes is determined either by stereochemical activity of lone electron pairs (as a consequence of high repulsion energy of bonding and non-boding electron pairs) or by formation of four-member chelate rings which are assymmetric because of rigidity of dtc (short interatomic distances S–S).

In the case of Sn(IV) complexes of dtc, the coordination geometry is dependent on the coordination number of the central atom to the large extend. The change of the coordination number is often achieved by exchange of dtc ligand by alkyl or aryl substituent.

There are three ways of coordination of dtc to Sn atom: 1) monodentate coordination — one Sn—S distance is approximately $2.5 \cdot 10^{-10}$ m (it corresponds to a single bond; the sum of Pauling's covalent radii¹ is $2.44 \cdot 10^{-10}$ m) and the second Sn—S distance is longer than the sum of van der Waals radii of Sn and S, *i.e.* $3.5 \cdot 10^{-10}$ m; 2) bidentate coordination — both Sn—S distances are in the interval 2.5 – $2.8 \cdot 10^{-10}$ m; 3) anisobidentate coordination — one of the Sn—S distances is approximately 2.5 and the second $3.0 \cdot 10^{-10}$ m.

EXPERIMENTAL

The white small crystals of $[\text{SnBu}_2(\text{pmdtc})_2]$ were prepared by dissolution of sodium salt of pentamethylenedithiocarbamic acid (pmdtc) in 150 ml of ethanol and adding the solution of chloride of tindibutylene in 50 ml of ethanol. Sodium chloride precipitated from the reaction mixture immediately. The reaction lasted four hours. After the end of the reaction, the reaction mixture was filtered. The alcohol was removed by distillation under vacuum and the product was recrystallized in *n*-heptan. Contents of C, H, and N was determined using microanalytical analyzer CHNO Carlo Erba 1102. For $[\text{SnBu}_2(\text{pmdtc})_2]$ (553.5) calculated: 43.32% C, 6.92% H, 5.06% N; found: 43.30% C, 7.04% H, 5.16% N.

The density of crystals was measured by flotation in aqueous ZnSO_4 solution, $D_m = 1.38(2) \text{ Mg m}^{-3}$. Calculated density for $Z = 2$ is $D_c = 1.36 \text{ Mg m}^{-3}$. Approximate values of lattice parameters found from rotation and Weissenberg photographs were refined by least squares method using 10 precisely centered reflections on the diffractometer Syntex P2₁ (interval of 2θ angles 20 – 45°): $a = 19.893(6)$, $b = 6.773(8)$, $c = 12.947(8) \cdot 10^{-10}$ m, $\beta = 129.07(5)^\circ$.

Diffraction data were measured on the automatic diffractometer Syntex P2₁ using crystal of dimensions $0.3 \times 0.15 \times 0.1$ mm. Integral intensities were measured using graphite monochromator, ($\text{MoK}\alpha$, $\lambda = 71.069$ pm) for $0^\circ < 2\theta < 55^\circ$. Reference reflections were measured after every 100 measured intensities. No systematic decrease of reference reflections was observed during measurement. Reflections classified as unobserved according to the criterion $I < 1.96 \cdot \sigma(I)$ were excluded from the structure refinement. The empirical correction for absorption, based on ψ SCAN of selected reflexions, was made using program system XTL. The minimum and maximum values of transmission factor were 0.69 and 1.0, respectively. All intensities were corrected for Lorentz and polarization factors with crystal monochromator perfection ratio 0.5.

Structure Determination and Refinement

Because of space group $C2$ and the number of formula units in the unit cell $Z = 2$, Sn atom has to lie on the twofold axes. Relative positions of two S atoms to Sn atom were found from three dimensional Patterson synthesis calculated using all 1 573 symmetrically independent reflections. The fragment SnS_2 was placed so that Sn atom lies in the origin of the unit cell. The subsequent Fourier synthesis calculated from the known fragment SnS_2 (with isotropic temperature coefficients 0.035 pm^2) revealed all the remaining non-hydrogen atoms. The structure was refined by block-diagonal least-squares method. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, where $w = 1$ for $|F_0| \leq 90$ and $w = 90/|F_0|$ for $|F_0| > 90$. Weighting scheme was chosen so that the average value of $\Sigma w(|F_0| - |F_c|)^2$ was approximately equal in different intervals of $|F_0|$ values. After 5 cycles of refinement with isotropic temperature coefficients, $R = \Sigma |F_0| - |F_c| / \Sigma |F_0| = 0.21$. Anisotropic refinement of non-hydrogen atoms led to $R = 0.083$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w |F_0|^2]^{1/2} = 0.09$. Shifts of all atomic coordinates were less than 0.1 and shifts

of temperature parameters less than 0.2 of corresponding estimated standard deviations in the last cycle of refinement. The scattering factors were taken from International Tables² (neutral atoms). The highest peak on the final difference map, $1.3 \cdot 10^{30} \text{ el m}^{-3}$, was localized near Sn atom. All crystallographic calculations were performed with program systems XTL and NRC on a computer EC-4030.

DISCUSSION

The final atomic coordinates are given in Table I, the interatomic distances and selected angles are shown in Table II and selected mean planes and deviations of atoms from them are in Table III. Projection of the crystal structure $[\text{SnBu}_2(\text{pmdtc})_2]$ along b axes is given in Fig. 1 and the projection of the complex along c axes in Fig. 2. Complex $[\text{SnBu}_2(\text{pmdtc})_2]$ has a twofold axes of symmetry. Tin atom located on the twofold axes is coordinated by four S atoms in distances $2.966(6)$ and $2.476(3) \cdot 10^{-10} \text{ m}$. Bond distances show that the dithiocarbamate ligand is bonded to the central atom anisobidentately. Coordination bond Sn-S(1) is very weak because the sum of covalent radii Sn and S is $2.44 \cdot 10^{-10} \text{ m}$ (ref.¹). Coordination polyhedron of the central atom is completed by further two bonds to carbon atoms C(7) and C(7)¹ of butyl substituents with bond length $2.226(12) \cdot 10^{-10} \text{ m}$. The lengths of bonds forming coordination polyhedron are in agreement with values found for different Sn(IV) dtc complexes (see Table IV).

TABLE I

Final positional parameters with their estimated standard deviations ($\cdot 10^4$) for non-hydrogen atoms of the complex $[\text{SnBu}_2(\text{pmdtc})_2]$ and $B_{\text{eq}} = 4/3 \sum_i \sum_j \beta_{ij} \cdot a_i \cdot a_j \cdot (\cdot 10^{-4} \text{ pm}^2)$

Atom	x	y	z	B_{eq}
Sn	0	0	0	7.57
S(1)	1 661(2)	1 320(5)	691(4)	10.77
S(2)	1 016(2)	2 661(4)	480(3)	7.06
C(1)	1 730(5)	1 295(8)	791(9)	4.61
N(1)	2 619(4)	1 793(12)	1 358(7)	6.41
C(2)	3 327(5)	556(16)	1 802(10)	7.83
C(3)	4 030(6)	653(24)	3 329(10)	11.72
C(4)	4 309(7)	2 981(26)	3 699(13)	13.24
C(5)	3 487(6)	4 454(39)	3 188(10)	16.04
C(6)	2 845(7)	3 944(16)	1 771(11)	8.27
C(7)	624(8)	-928(20)	2 076(12)	10.18
C(8)	692(10)	-3 206(24)	2 236(18)	13.83
C(9)	1 259(11)	-3 819(26)	3 827(14)	14.52
C(10)	1 232(10)	-6 046(23)	3 737(15)	13.25

The coordination polyhedron is a strongly distorted octahedron like in the complexes $[\text{SnMe}_2(\text{Me}_2\text{dte})_2]$ (ref.³) and $[\text{SnMe}_2(\text{Et}_2\text{dte})_2]$ (ref.⁴). It is indicated by angles of the coordination sphere SnS_4C_2 :

$$\begin{array}{ll} \text{S}(1)-\text{Sn}-\text{S}(1)^i & 144.9^\circ & \text{S}(1)-\text{Sn}-\text{C}(7) & 86.9^\circ \\ \text{S}(1)-\text{Sn}-\text{S}(2) & 64.3^\circ & \text{S}(2)-\text{Sn}-\text{S}(2)^i & 86.6^\circ \\ \text{S}(1)-\text{Sn}-\text{S}(2)^i & 150.8^\circ & \text{S}(7)-\text{Sn}-\text{C}(7)^i & 147.2^\circ, \end{array}$$

where index i denotes the atoms in symmetrically related position $-x, y, -z$.

TABLE II

Bond distances and their estimated standard deviations in parentheses ($\cdot 10^{10}$ m) and bond angles with their estimated standard deviations in parentheses in the symmetrically independent part of the molecule

Bond distances

Bond	Bond length	Bond	Bond length
Sn—S(1)	2.966(6)	C(3)—C(4)	1.640(24)
Sn—S(2)	2.476(3)	C(4)—C(5)	1.657(26)
Sn—C(7)	2.226(12)	C(5)—C(6)	1.471(16)
S(1)—C(1)	1.775(7)	C(7)—C(8)	1.551(21)
S(2)—C(1)	1.522(11)	C(8)—C(9)	1.661(23)
N(1)—C(2)	1.413(15)	C(9)—C(10)	1.511(24)
N(1)—C(6)	1.519(14)	Sn... C(1)	3.036(11)
C(1)—N(1)	1.464(5)	S(1)... S(2)	2.924(5)
C(2)—C(3)	1.544(15)		

Interbond angles

Atoms	Angle	Atoms	Angle
S(1)—Sn — S(2)	64.3(1)	N(1)—C(2)—C(3)	111.2(10)
S(1)—Sn — C(7)	86.9(4)	C(2)—C(3)—C(4)	106.4(11)
Sn—S(1)— C(1)	75.0(3)	C(3)—C(4)—C(5)	113.3(13)
Sn—S(2)— C(1)	95.9(4)	C(4)—C(5)—C(6)	102.6(13)
C(1)—N(1)—C(6)	113.2(8)	C(5)—C(6)—N(1)	119.7(17)
C(1)—N(1)—C(2)	130.3(8)	Sn—C(7)—C(8)	112.2(11)
C(2)—N(1)—C(6)	115.3(9)	C(7)—C(8)—C(9)	110.4(15)
S(1)—C(1)—S(2)	124.9(6)	C(8)—C(9)—C(10)	101.0(15)
S(2)—C(1)—N(1)	128.6(7)	S(1)—Sn — C(7)	86.9(4)
S(1)—C(1)—N(1)	106.2(6)	S(2)—Sn — C(7)	99.0(4)

The deformation is strongly influenced by interchange of dtc ligand with butyl substituent. The butyl radical is placed somewhere between *cis* and *trans* positions of octahedron (Fig. 2) what can be proved by angle C—Sn—C 147.2° (for complex [SnMe₂(Me₂dtc)₂] 136.5° and for complex [SnMe₂(Et₂dtc)₂] 141.0°). In spite of that fact the phenyl radicals are nearer to *cis* position in the complex [SnPh₂(Et₂dtc)₂] where angle C—Sn—C is 101.4°.

The sulphur atoms are not arranged exactly square planar because S—Sn—S angles are in the range 64.3—150.8°. The lowest is the chelate angle S(1)—Sn—S(2). The interligand angle formed by shorter Sn—S bonds is substantially lower (86.6°) than the angle formed by longer Sn—S bonds (144.9°). Thus, the interligand interaction S(2)—S(2)¹ (3.399 · 10⁻¹⁰ m) is formed.

TABLE III

Coefficients of mean plane equations $Ax + By + Cz = D$ and the deviations of selected atoms from these planes ($\cdot 10^{10}$ m) for complex [SnBu₂(pmdtc)₂]

fragment Sn S(1) C(1) N(1) C(2) C(6)	$A = 0.3912; B = 0.1128; C = -0.9134; D = 0.4039$
Sn	-0.402(0), S(1) -0.066(5), S(2) -0.004(3), C(1) 0.062(9)
N(1)	0.089(8), C(2) -0.001(10), C(3) -1.337(11)
fragment N(1) C(2) C(3) C(4) C(5) C(6)	$A = 0.8447; B = 0.3150; C = -0.4326; F = 3.4476$
N(1)	-0.191(9), C(2) 0.236(12), C(3) -0.278(14), C(4) 0.271(17),
C(5)	-0.222(16), C(6) 0.189(15);

TABLE IV

Review of bond distances ($\cdot 10^{10}$ m) and valence angles (°) in Sn(II) and Sn(IV) dithiocarbamate complexes

Complex	Space group	Sn—C	Sn—S	Sn...S	S—Sn—S	C—Sn—C	Ref.
[SnMe ₃ (Me ₂ dtc)]	<i>Pba</i> 2	2.220	2.470	3.160	63.0	117.0	5
[SnMe ₃ (Me ₂ dtc)]	<i>Pba</i> 2	2.210	2.470	3.330	60.0	119.0	5
[SnMe ₃ (Me ₂ dtc)]	<i>P2</i> ₁ / <i>c</i>	2.190	2.470	3.160	62.0	119.0	6
[SnMe ₂ (Cl)(Me ₂ dtc)]	<i>P2</i> ₁ / <i>c</i>	2.190	2.480	2.790	68.2	128.0	7
[SnMe ₂ (Me ₂ dtc) ₂]	<i>Fdd</i> 2	2.140	2.506	3.007	82.7	136.0	3
[SnMe ₂ (Et ₂ dtc) ₂]	<i>C2</i> / <i>c</i>	2.130	2.519	2.957	83.0	140.0	4
[SnMe ₂ (Et ₂ dtc) ₂]	<i>P</i> $\bar{1}$	2.108	2.527	2.943	83.2	142.3	4
[SnPh ₂ (Et ₂ dtc) ₂]	<i>P2</i> ₁ / <i>c</i>	2.170	2.580	2.710	93.1	101.4	8
[SnPh(Cl)(Et ₂ dtc) ₂]	<i>P2</i> ₁ / <i>n</i>	2.154	2.528	2.661	90.5	94.0	9
[Sn(Et ₂ dtc) ₂]	<i>P2</i> ₁ / <i>a</i>	—	2.580	2.790	96.2	—	10

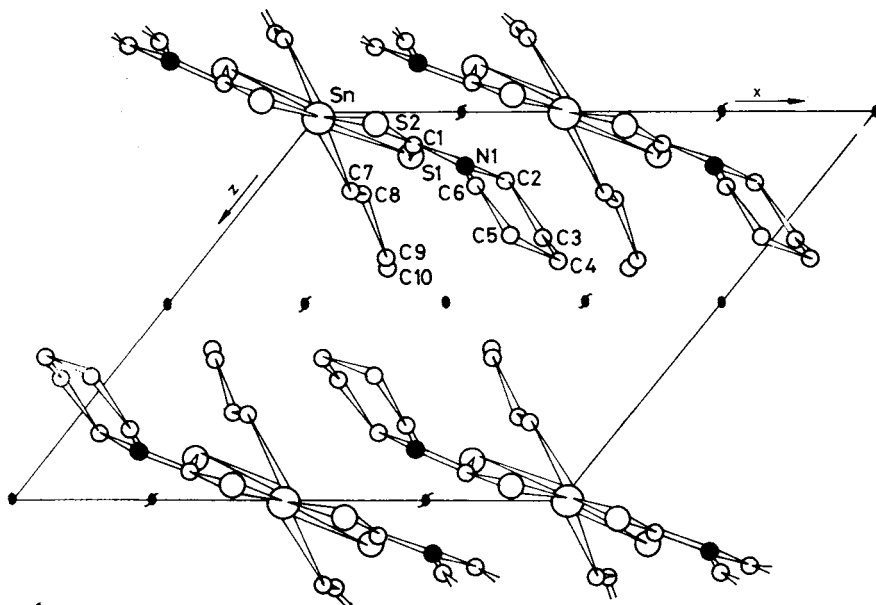


FIG. 1

Numbering of atoms in the structure $[\text{SnBu}_2(\text{pmdtc})_2]$. Projection along b axes

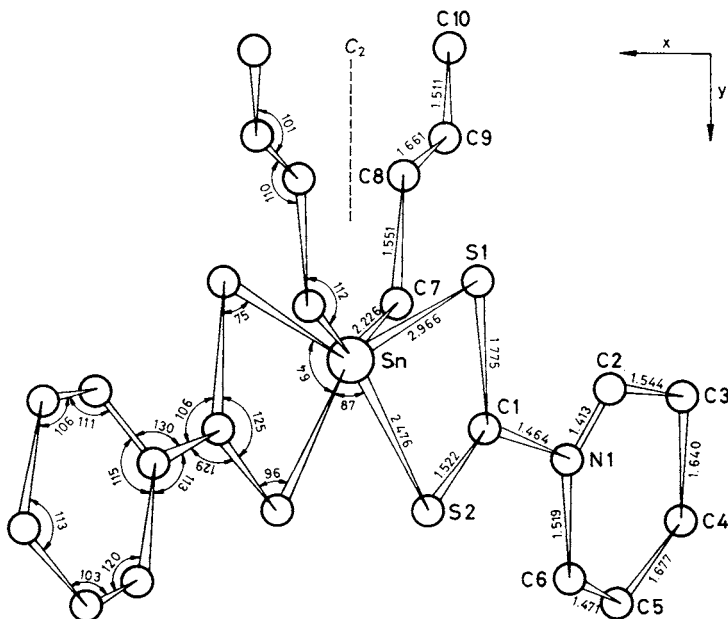


FIG. 2

Projection of the molecule $[\text{SnBu}_2(\text{pmdtc})_2]$ along the c axes

The anomal bond length $S(2)-C(1)$ in dithiocarbamate part of ligand may be caused by neglecting the secondary extinction or by approximative character of empirical correction for absorption. It influences probably also the bond length $C(1)-N(1)$ ($1.464 \cdot 10^{-10}$ m). The bond lengths $C-C$ correspond to single bonds and the angles to sp^3 hybridization of C atoms in the pentamethylene ring.

It follows from Table III that unlike the most of the dithiocarbamate complexes of transition metals the fragment S_2CNC_2 of the title compound shows deviations from the planarity. Cyclohexamethylene substituent has a chair conformation. In addition to interligand interactions $S-S$, also intermolecular interactions were reported for most of $Sn(IV)$ complexes. The lengths of these intermolecular distances are comparable with the sum of the corresponding van der Waals radii. It can be expected that these interactions have no influence on the structure of the molecule and that the geometry of the coordination of the central atom results from the intermolecular steric and electron factors.

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