

THE CRYSTAL AND MOLECULAR STRUCTURE OF
TRIS-BUTYL-TIN(IV)-
(1-PYRROLIDINECARBODITHIOATO)-3-PROPIONATE

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The crystal and molecular structure of $\text{Bu}_3\text{Sn}(\text{pyrn-dtc-prop})$ was solved by the X-ray structural analysis method and refined by the block diagonal least squares method to $R = 0.053$ for 1 930 observed reflections. The compound crystallizes in the monoclinic system with a space group of $P2_1/c$, $Z = 4$, $F(000) = 1\ 056$, with unit cell dimensions of $a = 1.4758(5)$, $b = 0.9970(3)$, $c = 1.9166(6)$ nm, $\beta = 113.90(2)^\circ$. The measured and calculated crystal densities were $D_m = 1.32$ and $D_c = 1.31 \cdot 10^3 \text{ kg m}^{-3}$. The tin atom is coordinated by three carbon atoms at distances of $\text{Sn}-\text{C} 0.2117(8)$, $0.2133(8)$, $0.2158(11)$ nm and two oxygen atoms $\text{O}(1)$ and $\text{O}(2)$ at distances of $\text{Sn}-\text{O} 0.2210(5)$ and $0.2399(5)$ nm. The coordination polyhedron is a deformed trigonal bipyramid. The S_2CN ligand is approximately planar.

A great deal of attention has been paid in the literature to dithiocarbamates. Many papers have described their structures which are apparently connected with their biological activity. On the other hand, only a few papers have been published on the crystal structure of these complexes with a central nontransition metal ion¹⁻⁸. One of the purposes of this work was to make a contribution to understanding the metal-ligand bonds in these complexes.

EXPERIMENTAL AND RESULTS

Methods

White needle-like crystals were prepared by dissolving 0.2 mol 3-(pyrrolidinedithiocarbamate)-propionic acid in 100 ml benzene and addition of 0.1 mol dibutyltin oxide. The reaction mixture was distilled azeotropically with a mixture of $\text{H}_2\text{O} + \text{benzene}$ and was evaporated to dryness in a rotating distillation flask. White crystals were obtained by recrystallization from pentane. The percent contents of C, H, and N were found by using a CHNO microanalytical analyzer (Carlo Erba 1102). For $\text{C}_{20}\text{H}_{39}\text{NO}_2\text{S}_2\text{Sn}$ (508.4) calculated: 47.25% C, 7.73% H, 2.76% N; found: 47.09% C, 7.78% H, 2.78% N.

The crystal density was measured by the flotation method in saturated ZnSO_4 solution; $D_\theta = 1.32 \cdot 10^3 \text{ kg m}^{-3}$. The calculated value is in good agreement with the measured value assuming four formula units per unit cell, and equals $1.31 \cdot 10^3 \text{ kg m}^{-3}$. The approximate lattice parameter values found from rotation and Weissenberg photographs were refined by the least squares method on a Syntex P2₁ diffractometer. Fifteen precisely centred reflections yielded the following values: $a = 1.4758(5)$, $b = 0.9970(3)$, $c = 1.9166(6)$ nm, $\beta = 113.90(2)^\circ$.

The diffraction data were obtained on an automatic Syntex P2₁ diffractometer using a crystal with dimensions of $0.2 \times 0.1 \times 0.4$ mm. The integral intensity was measured using graphite monochromatized MoK_α radiation ($\lambda = 0.071069$ nm) and working conditions of 50 kV and 20 mA. The crystal was recentered after each 100 intensity measurements; no significant deviations in the measured intensities were found. The integral intensity was measured in the range $0^\circ < 2\theta < 55^\circ$ and only those values for which $I \geq 1.96\sigma(I)$ were classified as observed and used for final structure refinement. All the intensities were corrected for the Lorentz and polarization factors. Empirical correction was carried out for absorption but not for extinction. For the final structure refinement, only 1 930 of a total of 3 602 observed reflections (53.58%) were employed.

Structure Solution and Refinement

The structure was solved by the heavy atom method. The position of the tin atom was found from the Patterson map. The coordinates of the other nonhydrogen atoms were localized from Fourier maps. The positions of the individual atoms were refined in five cycles of the block diagonal least squares method using the minimization function $\sum w(|F_o| - |F_c|)^2$ and Cruickshank weighting scheme $w = 1/[a + |F_o| + b|F_c|^2]^{1/2}$ (constants a and b were assigned values of 25.0 and 0.003, respectively).

In the next five refinement cycles, the anisotropic thermal vibrations of all nonhydrogen atoms were assumed; together with the positional parameters these values were refined by the least squares method in a 9×9 block diagonal approximation to a final value of $R = 0.063$. In the last refinement cycle, the maximal shift/error value was 0.15.

The positions of the hydrogen atoms were determined from the differential Fourier maps. Their coordinates were further refined together with the isotropic thermal parameters; after refinement, the R factor decreased to a value of $R = 0.053$. The differential Fourier synthesis of the electron density had the highest maximum of $0.64 \cdot 10^3 \text{ e nm}^{-3}$.

Table I gives the refined positional parameters of the nonhydrogen atoms and their equivalent isotropic thermal parameters. Table II lists the interatomic distances and valence and torsion angles. The deviations of some atoms from selected planes fitted by the least squares method are given in Table III. The structure of the complex is depicted in Fig. 1 in projection onto the (100) plane. The scattering curves for the neutral atoms were taken from the tables of ref.⁹.

All the calculations were carried out on an XTL module Syntex P2₁, instrument and EC-4030 computer using NRC system programs¹⁰.

DISCUSSION

The structure consists of polymer chains oriented in the XY plane mutually shifted by $1/2$ a unit cell in the direction of the z -axis. It has been demonstrated¹¹ on the basis of the IR spectra that a similar compound with 5-coordinated tin, $\text{Me}_3\text{Sn}-\text{OCO}-\text{NMe}_2$, also exhibits polymer structure. Each molecular unit in the chain contains 5-coordinated tin in a deformed trigonal bipyramid with tin atoms lying

0.0131(1) nm above the equatorial plane in the direction of the Sn—O bond, formed by three carbon atoms, C(9), C(13) and C(17) which coordinate the tin atom at distances of Sn—C(9) (0.2117 nm), Sn—C(13) (0.2123 nm), Sn—C(17) (0.2158 nm). These bonding distances are shorter than those found for other 5-coordinated tin compounds¹²⁻²⁰. The sum of the ligand—Sn—ligand angles in the trigonal plane of the compound is 358.8(11)°, which corresponds to the ideal value of 360° within experimental error. This is in good agreement with the slight deviation of the tin atoms from this plane. The O(1) and O(2)ⁱ oxygen atoms (from different molecules,

TABLE I

The positional parameters of the nonhydrogen atoms ($\cdot 10^4$) of Bu₃Sn(pyrn-dtc-prop) with standard deviations in brackets. $B_{\text{eq}} = 4/3(\sum_i \sum_j \beta_{ij} \cdot a_i \cdot a_j)$

Atom	x	y	z	$B_{\text{eq}} (\cdot 10^{-2} \text{ nm})$
Sn	577(0.3)	1 219(1)	2 846 (0.4)	5.28
O(1)	1 668(3)	—423(5)	3 286(3)	5.28
O(2)	492(4)	—1 873(5)	2 607(3)	6.01
C(1)	1 350(5)	—1 618(6)	3 060(4)	4.74
C(2)	2 110(6)	—2 726(9)	3 415(5)	5.95
C(3)	3 171(7)	—2 351(9)	3 667(4)	6.93
C(4)	3 737(6)	—3 442(9)	2 545(5)	6.55
C(5)	4 102(8)	—2 010(11)	1 623(6)	8.78
C(6)	4 360(11)	—2 407(13)	940(7)	11.86
C(7)	4 639(13)	—3 751(15)	1 060(9)	15.87
C(8)	4 244(9)	—4 512(12)	1 569(7)	9.91
C(9)	—362(5)	456(8)	3 343(4)	5.22
C(10)	—591(6)	1 420(9)	3 863(4)	6.59
C(11)	—1 256(7)	762(11)	4 222(5)	8.24
C(12)	—1 448(9)	1 736(15)	4 758(7)	11.65
C(13)	374(7)	963(9)	1 686(4)	7.18
C(14)	1 229(6)	600(10)	1 507(4)	8.04
C(15)	1 947(13)	1 529(21)	1 738(11)	19.60
C(16)	2 742(18)	1 754(21)	1 538(14)	24.19
C(17)	1 641(8)	2 677(10)	3 540(6)	9.23
C(18)	2 488(7)	2 250(10)	4 213(6)	9.07
C(19)	3 152(7)	3 478(15)	4 644(5)	10.79
C(20)	4 006(10)	2 998(16)	5 257(7)	13.28
S(1)	3 471(2)	—1 892(2)	2 855(1)	6.56
S(2)	3 615(5)	—4 934(7)	2 879(4)	9.20
N	3 986(5)	—3 306(7)	1 940(4)	7.19

TABLE II

The bonding distances (nm) and bonding and torsion angles ($^{\circ}$) with standard deviations in brackets

Bond	Bond length	Bond	Bond length
Sn —O(9)	0.2117(8)	C(2) —C(3)	0.1488(14)
Sn —C(17)	0.2158(11)	C(5) —C(6)	0.1554(18)
Sn —C(13)	0.2133(8)	C(6) —C(7)	0.1394(20)
Sn —O(1)	0.2210(5)	C(7) —C(8)	0.1525(22)
O(1)—C(1)	0.1290(8)	C(9) —C(10)	0.1518(12)
N —C(4)	0.1357(11)	C(11)—C(12)	0.1522(17)
N —C(8)	0.1522(15)	C(14)—C(15)	0.1341(22)
S(1)—C(13)	0.1839(9)	C(15)—C(16)	0.1391(35)
S(1)—C(4)	0.1756(9)	C(17)—C(18)	0.1450(15)
S(2)—C(4)	0.1657(9)	C(18)—C(19)	0.1576(17)
C(1)—C(2)	0.1524(11)	C(19)—C(20)	0.1414(18)

Atoms	Angle	Atoms	Angle
Bonding angles			
Sn —C(9) —C(10)	115.4(5)	C(1) —C(2) —C(3)	116.7(7)
Sn —C(17)—C(18)	120.1(8)	C(2) —C(3) —S(1)	111.8(6)
Sn —C(13)—C(14)	119.8(6)	C(3) —S(1) —C(4)	103.4(4)
Sn —O(1) —C(1)	116.5(4)	C(4) —N —C(8)	121.8(8)
O(1)—C(1) —O(2)	123.7(7)	C(4) —N —C(5)	124.0(8)
O(2)—C(1) —C(2)	121.5(7)	C(9) —C(10)—C(11)	111.8(7)
N —C(5) —C(6)	103.6(9)	C(10)—C(11)—C(12)	110.7(9)
N —C(8) —C(7)	97.9(9)	C(13)—C(14)—C(15)	113.0(10)
S(1)—C(4) —S(2)	125.8(5)	C(14)—C(15)—C(16)	131.6(19)
S(1)—C(4) —N	112.1(6)	C(17)—C(18)—C(19)	111.5(9)
O(1)—C(1) —C(2)	114.7(6)	C(18)—C(19)—C(20)	109.0(10)
		C(6) —C(7) —C(8)	114.0(10)
Surroundings of the Sn atom			
C(13)—Sn—C(9)	125.7(3)	C(9) —Sn—O(1)	94.0(3)
C(13)—Sn—C(17)	118.9(4)	C(9) —Sn—C(7)	114.2(4)
C(13)—Sn—O(1)	94.7(3)	C(17)—Sn—O(1)	91.6(3)
Torsion angles			
S(1)—C(4)—N—C(8)	—179.7(8)	Sn—O(1)—C(1)—C(2)	—176.4(5)
S(1)—C(4)—N—C(5)	4.8(12)	C(2)—C(3)—S(1)—C(4)	—85.8(7)

related to the basic molecule by the transformation relationship $-x, 1/2 + y, 1/2 - z$ occupy the axial position. The Sn—O(2) bond is slightly longer (0.2399 nm) than the Sn—O(1) bond (0.2210 nm).

No significant anomalies were observed in the (pyrn-dtc-prop) ligand. Most of the lengths of the C—C and C—N bonds in the pyrrolidine ring corresponded to single bonds (0.154 and 0.147 nm) and the angles to sp^3 hybridization of the carbon and nitrogen atoms. The S_2CN and O_2C_2 ligand fragments were tested for planarity by fitting mean planes through selected atoms; the results are given in Table III. It follows that the S_2CN and O_2C_2 ligand fragments are planar (within experimental

TABLE III

Deviations ($\cdot 10^{-7}$ m) of some atoms from the planes and the dihedral angles between the planes ($^\circ$)

Atom ^a	Plane ^b	Deviation from the plane
C(9)*	1	0
C(13)*	1	0
C(17)*	1	0
O(1)	1	-2.340(5)
Sn	1	0.131(1)
S(1)*	2	0.009(3)
S(2)*	2	0.010(4)
C(4)*	2	-0.030(9)
N*	2	0.011(8)
C(5)	2	-0.021(11)
C(8)	2	-0.005(13)
O(1)*	3	-0.003(5)
O(2)*	3	-0.003(6)
C(1)*	3	0.009(8)
C(2)*	3	-0.002(8)
C(3)	3	0.584(9)

Plane ^b	Plane ^b	Dihedral angle
1	2	53.63(3)
1	3	93.20(4)
2	3	90.47(3)

^a *Designates the atoms through which the plane is fitted. ^b $1 - 0.5611X + 0.7609Y - 0.3260Z = 0$; $\chi^2 = 15.5$; $2 - 0.7598X - 0.0583Y - 0.6476Z = -5.3456$; $\chi^2 = 12.4$; $3 - 0.6491X + 0.0812Y - 0.7563Z = -4.4448$; $\chi^2 = 10.4$.

error, $\chi^2 = 15.5$ and 10.1). The dihedral angle between the planes is $90.5(2)^\circ$, also confirmed by the value of the torsion angle $C(2)-C(3)-S(1)-C(4)$ $85.8(7)^\circ$ (Table III). The length of the $C(4)-S(2)$ bond (0.1657 nm) is significantly shorter than that of the $C(4)-S(1)$ bond (0.1756 nm), indicating that the π -electrons in the $C(4)-S(2)$ bond are partly delocalized into the S_2CN ligand fragment together with the lone electron pair on the nitrogen atom, appearing in partial shortening of the single bonds $C(4)-N$ and $C(4)-S(1)$. The lengths of the $C(1)-O(1)$ (0.1290 nm) and $C(1)-O(2)$ (0.1237 nm) bonds correspond to double bonds.

Certain anomalies were observed in the butyl ligands in the lengths of the $C(14)-C(15)$ (0.1341 nm) and $C(15)-C(16)$ (0.1391 nm) bonds, probably as a result of the considerable flexibility of this part of the chain, leading to uncertain positions of these terminal carbon atoms. The remaining bond lengths corresponded to single bonds (0.154 nm) and angles for sp^3 hybridization of the carbon atoms.

No intermolecular interactions were observed in the crystal structure between the individual polymer chains up to a distance of 0.35 nm. There is thus only a small contribution to the stability of the crystal structure provided by van der Waals forces.

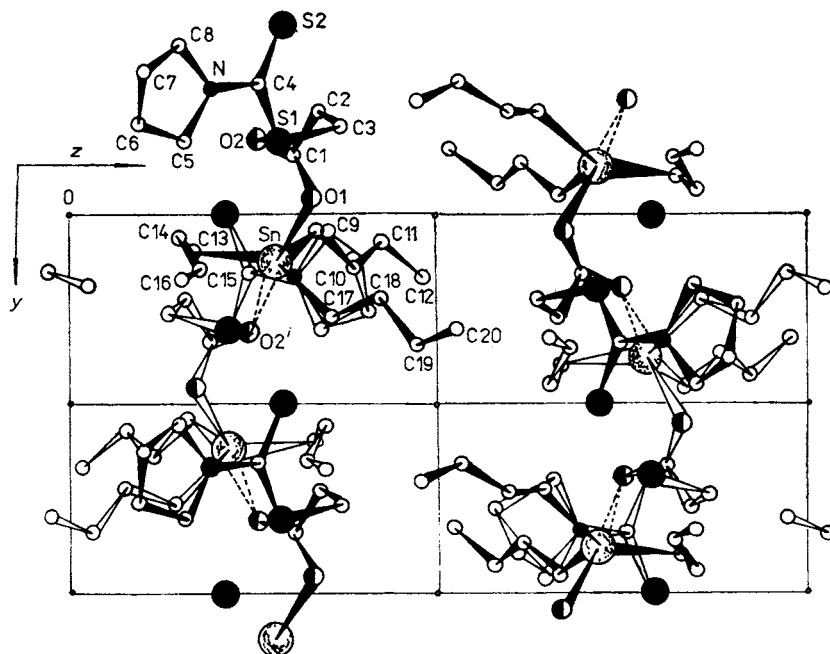


FIG. 1

Projection of the $Bu_3Sn(pyrn-dtc-prop)$ structure to the (100) plane

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