

THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(1,3-DIPHENYLPROPANE-1,3-DIONATO)-DI-*n*-BUTYLTIN(IV)

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Summary

The crystal and molecular structure of bis(1,3-diphenylpropane-1,3-dionato)di-*n*-butyltin(IV) has been determined from three-dimensional X-ray data by the heavy-atom method. The space group is $P2_1/n$. Unit cell constants are a 1117.56(30), b 857.87(16), c 1758.36(51) pm, and β 99.398(20)°. The observed density of the yellow crystals (m.p. 92-94°C) is 1.38 g ml⁻³ and requires two molecules per unit cell. The molecule has a center of symmetry. Refinement converged to give final discrepancy indices, $R = 0.0481$, $R_w = 0.0607$; and goodness-of-fit (GOF) was 3.216 for 1688 observed reflections. The molecular skeleton about tin is a slightly distorted octahedron with bond distances: Sn-C, 212 pm; and Sn-O, 219 and 220 pm. The O(1)-Sn-O(2) bond angle is 83.8°, and C-Sn-O bond angles are very nearly 90°. The structural parameters are compared with those of other organotin complexes of similar stoichiometry.

Introduction

Organotin(IV) complexes exist in a variety of tetrahedral, trigonal bipyramidal and octahedral structures. Some of these are highly distorted, while others are very symmetrical. Because the structures are so varied, and because many are stereochemically non-rigid, the systems have been used to test several models [1-3] which semiquantitatively predict molecular shapes. Crystal structures which have been reviewed [4,5] provide valuable insights into the parameters affecting molecular geometry.

In this laboratory, special emphasis has been placed on the synthesis and study of complexes of type R_2SnCh_2 . "R" is an organic or halide substituent, and Ch^- is a bidentate chelate usually with oxygen or nitrogen donor atoms. Many such com-

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plexes have been synthesized [6–13] and subjected to study by a variety of physical techniques ranging from vibrational spectroscopy and Rayleigh light scattering to proton and ^{119}Sn NMR and the Kerr effect. Unfortunately, X-ray data are scarce.

Rapid ligand exchange ordinarily limits the usefulness of NMR to relations involving the coupling of ^1H , ^{13}C and ^{119}Sn nuclear spins. Coupling constants, however, do allow the estimation of C–Sn–C bond angles in solution [12–14]. Raman [9,11] and IR [15] spectra, when compared, do allow differentiation between regular *trans* and either *cis*, or distorted structures. Such spectra are not always helpful in assessing the degrees of distortion of octahedral complexes, though, since relatively small distortions from regular *trans* geometries result in IR-allowed symmetrical stretching modes [10,15] forbidden to highly symmetrical *trans* geometries, but very similar qualitatively to those predicted for regular *cis* structures.

Mössbauer studies have been highly successful in correlating the C–Sn–C bond angles with the magnitudes of the quadrupole splitting [4,16–22]. In several instances, X-ray crystallographic studies have confirmed the interpretations of the Mössbauer data.

A number of years ago, we demonstrated that the Kerr effect can be used easily to correctly identify molecular geometries of complexes in solution [7]. Very recently [23], it was shown by X-ray studies that $(\text{CH}_3)_2\text{Sn}(\text{trop})_2$ (trop = tropolonate) which we showed previously to be *cis* in solution by the Kerr effect, is *cis* in the solid state. We have continued our Kerr effect studies [10] and have demonstrated that $(\text{CH}_3)_2\text{Sn}(\text{oxinate})_2$ which is *cis* in the solid state [24] produces negatively birefringent solutions and Kerr constants of magnitude predicted for the *cis* structure also. In that same study [10], it was shown that a number of tropolonate and dibenzoylmethanate derivatives are of skew-trapezoidal bipyramidal shape, but that $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{dbzm})_2$ (dbzm = dibenzoylmethanate) is predicted to be of highly symmetrical *trans* geometry.

To confirm the Kerr effect findings reported earlier [10] and to supplement the meager X-ray data for complexes of type R_2SnCh_2 , we have prepared crystals of $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{dbzm})_2$ and have completed an X-ray structural analysis.

Experimental

Reagents

$(\text{C}_4\text{H}_9)_2\text{Sn}(\text{dbzm})_2$ was prepared as described earlier [6]. Yellow crystals were formed from a filtered saturated cyclohexane solution by slow evaporation (for about a week) in a desiccator which was sealed, except for an exit port connected to a CaCl_2 filled tube.

X-Ray crystallography

A suitable data crystal, approximately $0.4 \times 0.3 \times 0.5$ mm was glued to a glass fiber and mounted on a Nicolet R3M/E auto-diffractometer. Lattice parameters, a 1117.56(30), b 857.87(16) c 1758.36(51) pm, β 99.398(20) $^\circ$ of a monoclinic primitive cell were determined by automatic centering of 25 reflections between 25 and 27 $^\circ$ 2θ . The observed systematic absences ($0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$) were consistent with space group $P2_1/n$, $Z = 4$. The density determined by flotation in aqueous KI solution, (d_{obs} 1.38(1), d_{calc} 1.36 g ml $^{-3}$) indicated that there were only two molecules in the unit cell, requiring the molecule to possess a

TABLE 1
 ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	u^a
Sn	0	0	0	55(1)
O(1)	1411(4)	58(5)	-737(2)	63(2)
O(2)	1363(4)	-1301(6)	787(2)	68(2)
C(1)	2430(5)	-661(7)	-646(3)	48(2)
C(2)	2900(5)	-1526(7)	3(3)	52(2)
C(3)	2379(5)	-1830(7)	660(3)	48(2)
C(4)	3021(5)	-2853(7)	1279(3)	46(2)
C(5)	2355(6)	-3600(8)	1769(3)	61(2)
C(6)	2913(8)	-4582(8)	2343(4)	76(3)
C(7)	4134(7)	-4831(8)	2446(4)	74(3)
C(8)	4799(7)	-4083(11)	1964(4)	85(3)
C(9)	4255(6)	-3112(10)	1388(4)	72(3)
C(10)	3128(5)	-469(7)	-1297(3)	46(2)
C(11)	2705(6)	580(8)	-1883(4)	59(2)
C(12)	3311(6)	755(10)	-2506(4)	74(3)
C(13)	4330(7)	-93(9)	-2554(4)	85(3)
C(14)	4767(7)	-1127(10)	-1982(4)	86(3)
C(15)	4166(6)	-1318(9)	-1353(4)	68(3)
C(16)	606(7)	2081(10)	585(4)	85(3)
C(17)	1890(10)	2730(12)	499(50)	134(5)
C(18)	1840(11)	3669(12)	-181(5)	140(6)
C(19)	3182(10)	3992(14)	-304(7)	145(6)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

center of symmetry. A total of 2434 reflections were collected, using graphite monochromated Mo- K_α radiation (λ 0.71069 \AA), of which 1688 had $I > 2.0\sigma(I)$ and were considered observed and used in refinement. No absorption corrections were applied ($\mu(\text{Mo-}K_\alpha)$ 8.05 cm^{-1}).

TABLE 2
 BOND LENGTHS (μm)

Sn-O(1)	219.9(8)	Sn-O(2)	218.9(8)
Sn-C(16)	211.5(10)	Sn-O(1a)	219.9(8)
Sn-O(2a)	218.9(8)	Sn-C(16a)	211.5(10)
O(1)-C(1)	128.1(8)	O(2)-C(3)	127.6(9)
C(1)-C(2)	139.0(9)	C(1)-C(10)	149.6(10)
C(2)-C(3)	140.0(10)	C(3)-C(4)	148.9(9)
C(4)-C(5)	138.5(10)	C(4)-C(9)	137.8(10)
C(5)-C(6)	138.3(10)	C(6)-C(7)	136.4(12)
C(7)-C(8)	137.4(12)	C(8)-C(9)	137.4(11)
C(10)-C(11)	139.2(10)	C(10)-C(15)	138.7(10)
C(11)-C(12)	138.6(11)	C(12)-C(13)	136.6(12)
C(13)-C(14)	136.9(11)	C(14)-C(15)	139.4(11)
C(16)-C(17)	157.0(15)	C(17)-C(18)	143.5(14)
C(18)-C(19)	157.4(18)		

TABLE 3
BOND ANGLES (°)

O(1)–Sn–O(2)	83.8(2)	O(1)–Sn–C(16)	93.7(3)
O(2)–Sn–C(16)	89.4(3)	O(1)–Sn–O(1a)	180.0(2)
O(2)–Sn–O(1a)	96.2(2)	C(16)–Sn–O(1a)	86.3(3)
O(1)–Sn–O(2a)	96.2(2)	O(2)–Sn–O(2a)	180.0(2)
C(16)–Sn–O(2a)	90.7(3)	O(1a)–Sn–O(2a)	83.8(2)
O(1)–Sn–C(16a)	86.3(3)	O(2)–Sn–C(16a)	90.7(3)
C(16)–Sn–C(16a)	180.0(2)	O(1a)–Sn–C(16a)	93.7(3)
O(2a)–Sn–C(16a)	89.3(3)	Sn–O(1)–C(1)	128.6(4)
Sn–O(2)–C(3)	128.1(4)	O(1)–C(1)–C(2)	124.7(6)
O(1)–C(1)–C(10)	114.5(5)	C(2)–C(1)–C(10)	120.8(6)
C(1)–C(2)–C(3)	128.6(6)	O(2)–C(3)–C(2)	125.5(5)
O(2)–C(3)–C(4)	114.7(5)	C(2)–C(3)–C(4)	119.8(6)
C(3)–C(4)–C(5)	118.9(6)	C(3)–C(4)–C(9)	123.3(6)
C(5)–C(4)–C(9)	117.8(6)	C(4)–C(5)–C(6)	120.8(7)
C(5)–C(6)–C(7)	120.9(7)	C(6)–C(7)–C(8)	118.4(7)
C(7)–C(8)–C(9)	121.2(7)	C(4)–C(9)–C(8)	120.9(7)
C(1)–C(10)–C(11)	118.8(6)	C(1)–C(10)–C(15)	122.9(6)
C(11)–C(10)–C(15)	118.3(6)	C(10)–C(11)–C(12)	120.3(7)
C(11)–C(12)–C(13)	120.8(7)	C(12)–C(13)–C(14)	120.0(8)
C(13)–C(14)–C(15)	119.9(8)	C(10)–C(15)–C(14)	120.8(6)
Sn–C(16)–C(17)	118.5(6)	C(16)–C(17)–C(18)	111.6(9)
C(17)–C(18)–C(19)	107.7(9)		

TABLE 4
ANISOTROPIC TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^3$)^a

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn	42(1)	73(1)	53(1)	12(1)	18(1)	14(1)
O(1)	49(2)	87(3)	56(2)	21(3)	17(2)	19(3)
O(2)	62(3)	92(4)	57(3)	10(3)	29(2)	18(3)
C(1)	41(3)	55(3)	49(3)	–1(3)	13(3)	8(3)
C(2)	40(3)	64(4)	54(4)	10(3)	13(3)	17(3)
C(3)	53(4)	52(4)	43(3)	3(3)	17(3)	4(3)
C(4)	48(3)	52(4)	38(3)	1(3)	9(3)	8(3)
C(5)	60(4)	68(5)	56(4)	9(4)	15(3)	19(4)
C(6)	95(6)	80(6)	57(4)	23(4)	26(4)	19(4)
C(7)	90(5)	73(5)	56(4)	15(4)	3(4)	22(5)
C(8)	64(5)	113(7)	76(5)	21(5)	5(4)	21(5)
C(9)	58(4)	100(6)	58(4)	21(4)	9(3)	7(4)
C(10)	46(3)	51(4)	43(3)	–3(3)	13(3)	–7(3)
C(11)	54(4)	73(5)	51(4)	5(4)	13(3)	–2(4)
C(12)	68(5)	100(6)	59(4)	19(4)	22(4)	–1(5)
C(13)	90(6)	108(6)	67(4)	14(5)	46(4)	9(5)
C(14)	88(6)	94(6)	88(5)	12(5)	52(5)	27(5)
C(15)	71(5)	75(5)	68(4)	15(4)	37(4)	22(4)
C(16)	72(5)	94(6)	92(5)	29(5)	22(4)	24(5)
C(17)	183(11)	114(8)	102(7)	–45(6)	18(7)	5(8)
C(18)	238(15)	83(7)	110(7)	–3(6)	60(9)	18(9)
C(19)	131(10)	129(9)	194(11)	–50(9)	79(9)	–35(9)

^a The anisotropic temperature factor exponent takes the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \dots + 2hka^*b^*U_{12})]$.

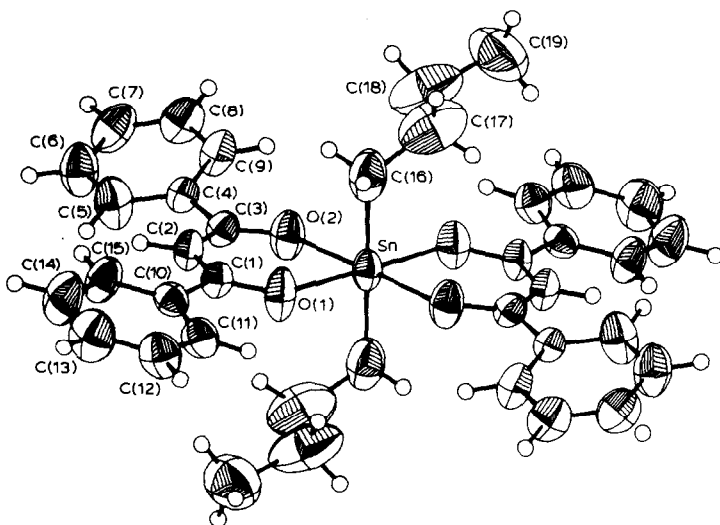


Fig. 1. ORTEP drawing of bis(1,3-diphenylpropane-1,3-dionato)di-n-butyltin(IV). Only the unique atoms in the asymmetric unit are labeled. Thermal ellipsoids are drawn at the 50% probability level, while isotropic hydrogen thermal parameters are represented by spheres of arbitrary size.

The structure was solved by the heavy-atom method. The tin atom was placed at the origin, and subsequent difference-Fourier maps revealed the non-hydrogen atom positions. Hydrogen atoms were placed at idealized positions (C–H 96 pm) and assigned fixed isotropic thermal parameters equal to 1.2 times the equivalent

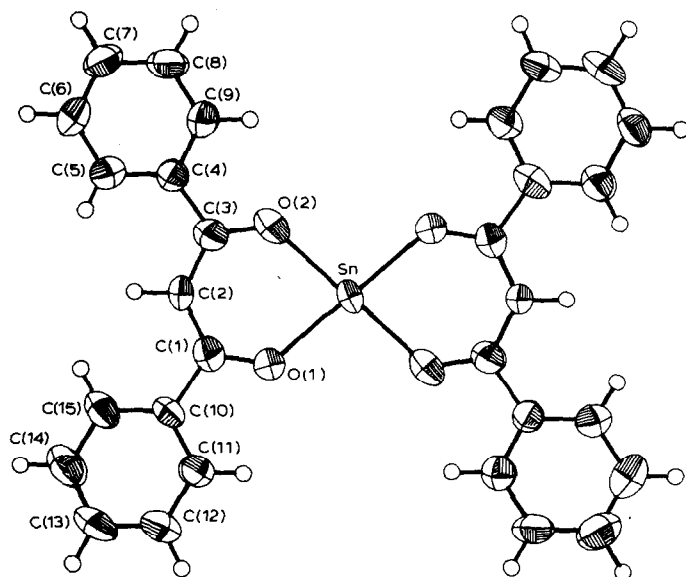


Fig. 2. ORTEP view of the atoms in the equatorial plane of bis(1,3-diphenylpropane-1,3-dionato)di-n-butyltin(IV). The butyl chain has been removed for clarity.

isotropic thermal parameters of the atoms to which they were attached, and not refined. Refinement converged to give final discrepancy indices, $R = 0.0481$, $R_G = 0.0607$, and $GOF = 3.216$ for 1688 reflections [25]. The maximum shift/error on the final least-squares cycle was -0.049 . The final difference Fourier map showed maxima and minima of 0.592 and $-1.179 \text{ e } \text{\AA}^{-3}$, respectively. All calculations were performed using a Data General Eclipse computer with the SHELXTL [26] programs, which use complex neutral atom scattering factors from International Tables for X-ray Crystallography (1974) [27]. Final atomic parameters are listed in Table 1, bond lengths in Table 2, bond angles in Table 3, and thermal parameters in Table 4 [28]. Figures 1 and 2 present ORTEP [29] plots of the complex.

Discussion

The data presented in Tables 2 and 3 clearly show that $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{dbzm})_2$ adopts a highly regular *trans* octahedral structure. The C–Sn–C bond angle is 180° , as required by symmetry, and the chelate rings are very nearly coplanar with the tin atom which lies only 18 pm out of the O(1), O(2), C(1), C(2), C(3) least-squares plane. Also, the phenyl rings do not lie quite in the same plane with the chelate ring. One phenyl group (C(4)–C(9)) is rotated 23.2° out of the plane, while the other (C(10)–C(15)) is rotated only 8.6° out of the same plane. In addition, the phenyl rings are deflected slightly from the chelate plane; the line connecting C(10) and C(13) is bent 1.8° out of the chelate plane while the corresponding line connecting C(4) and C(7) is bent 4.6° out of the chelate plane.

If the bond lengths and angles of $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{dbzm})_2$ are compared with those of $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$ [4,5] (acac = acetylacetonate), as they are in Table 5, it is apparent that the basic bonding about the tin atom is nearly identical in both complexes. Within experimental error, Sn–C, Sn–O, and O–C bond lengths are identical. Only the enolate ring C–C bonds show small differences, as do O–Sn–O bond angles. In this study, O(1)–Sn and O(2)–Sn bonds are equal to within 1σ . The C(1)–C(2) and C(2)–C(3) bonds are similarly nearly of equal length, indicating that bonding in the chelate ring is delocalized. Our values of 140 and 139 pm for the dibenzoylmethanate contrast with 136 and 144 pm, respectively, for corresponding bonds in the acetylacetonate. Regardless of the minor difference in C–C enolate bond lengths, both structures must possess a high degree of delocalization in the enolate ring. All in all, the two structures are remarkably similar and in marked contrast with the structure of $(\text{CH}_3)_2\text{Sn}(\text{trop})_2$, the bond lengths and angles of which are also listed in Table 5.

It is clear that the bulk of the butyl group has no apparent effect on the structure. Of added interest is the fact that C(18) is approximately *gauche* to the tin in the Sn–C(16)–C(17)–C(18) (torsion angle 84.9°), whereas the butyl side chain is nearly *anti* (C(16), C(17), C(18), C(19) torsion angle is 169.2°).

Certainly, the results of this study are consistent with the predictions of Kepert [3] who noted that ligands of large normalized “bite” such as acetylacetonates and dibenzoylmethanates should give rise to regular octahedral structures in compounds of type R_2SnCh_2 . It is especially notable that the acetylacetonate and dibenzoylmethanate derivatives, which have identical “bites”, have essentially identical structures even though substituents, R, and chelates vary markedly in bulk.

TABLE 5

A COMPARISON OF BOND DISTANCES AND ANGLES FOR $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$ (I), $(\text{CH}_3)_2\text{Sn}(\text{trop})_2$ (II) AND $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{dbzm})_2$ (III)

	Distance (pm)		
	I	II	III
Sn-C(16)	214	217	212
Sn-O(1)	220	214	220
Sn-O(2)	218	218	219
O(1)-C(1)	127	129	128
O(2)-C(3)	128	129	128
C(2)-C(3)	136	-	140
C(1)-C(2)	144	-	139
C(1)-C(10)	152	-	150
C(3)-C(4)	153	-	150
	Angles (°)		
	I	II	III
C(16)-Sn-O(2)	90	87-160	89.4
O(1)-Sn-O(2)	86	73.5	83.2
C(16)-Sn-C(16a)	180	109	180.0
C(1)-C(2)-C(3)	130	-	128.6
O(2)-C(3)-C(2)	124	-	125.5
C(11)-O(1)-Sn	128	-	127

As a note of caution, it must be pointed out that factors other than bite may be of significance. Factors such as steric angle [2], ligand electronegativity and symmetry may be significant, as well as electronic effects related to covalent bonds of tin. Full assessment of the relative importance of the various factors affecting the geometry of R_2SnCh_2 -type compounds awaits the structural determination of related compounds which differ predictably in chelate steric angle, electronegativity and symmetry, as well as the electronegativity and size of the monodentate substituents.

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