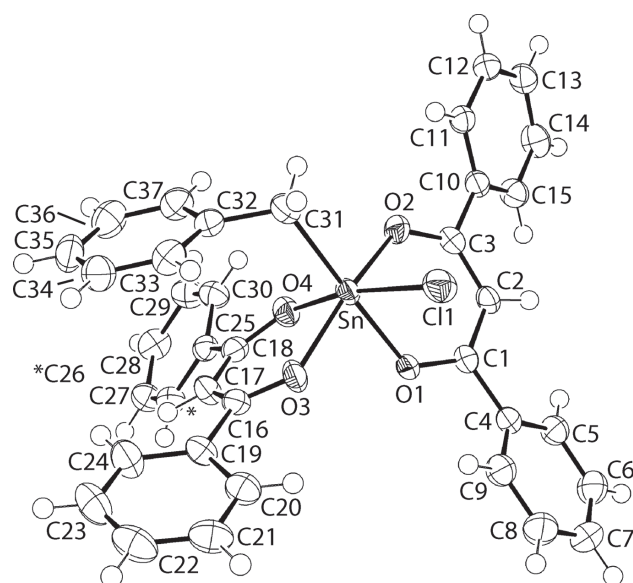


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Crystal structure of benzylbis(1,3-diphenylpropane-1,3-dionato- κ^2O,O')chloridotin(IV), $C_{37}H_{29}ClO_4Sn$



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Abstract

$C_{37}H_{29}ClO_4Sn$, monoclinic, $P2_1/c$ (no. 14), $a = 10.4233(3)$ Å, $b = 19.5060(6)$ Å, $c = 14.8084(5)$ Å, $\beta = 94.148(2)^\circ$, $V = 3002.91(16)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0432$, $wR_{ref}(F^2) = 0.1036$, $T = 296(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.26 × 0.16 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.98 mm ⁻¹
Diffractometer, scan mode:	CCD, φ and ω
θ_{max} , completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	29202, 7468, 0.043
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 6485
$N(param)_{refined}$:	388
Programs:	Bruker [1], SHELX [2–4], WinGX/ORTEP [5]

Source of material

The melting point (uncorrected) was measured on an electrothermal digital melting point apparatus. The IR spectrum was recorded using a Perkin-Elmer RX1 spectrophotometer in a Nujol mull between KBr plates. The ¹H and ¹³C{¹H} NMR spectra were recorded in CDCl₃ solution on a Bruker AVN FT-NMR spectrometer with chemical shifts relative to Me₄Si for ¹H and CDCl₃ for ¹³C{¹H}.

Dibenzyltin dichloride was prepared from the direct synthesis method using tin powder (Sigma-Aldrich) and benzyl chloride (Sigma-Aldrich) in toluene [6]. The ligand, dibenzoylmethane (Sigma-Aldrich; 0.31 g, 2.0 mmol) and dibenzyltin dichloride (0.37 g, 1 mmol) were heated in 95% ethanol (50 mL) for 30 min. After filtration, the filtrate was evaporated slowly until colourless crystals formed. Yield: 0.30 g (43%). M. pt: 525–527 K. IR (cm⁻¹): 541 (*m*) ν (Sn–O), 1515, 1531 (*s*) ν (C=O). ¹H NMR (CDCl₃, p.p.m.): 6.87–8.17 (25*H*, Ph–H), 7.04 (2*H*, CH), 3.05 (2*H*, Ph–CH₂). ¹³C NMR (CDCl₃, p.p.m.): 37.4 (Ph–CH₂), 95.8 (CH), 128.2, 128.4, 128.8, 133.4, 133.6, 136.7, 136.8, 138.2 (CPh), 187.7 (C=O).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.93–0.97 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. Owing to poor agreement, the (1 0 0) reflection was omitted from the final cycles of refinement.

Comment

The deprotonated dibenzoylmethane (DBM) molecule is known to react with many metal ions to form chelate

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Sn	0.27229(2)	0.09507(2)	0.27112(2)	0.01816(7)
Cl1	0.11610(8)	0.18193(4)	0.30827(5)	0.02837(16)
O1	0.16399(19)	0.08983(10)	0.14846(14)	0.0201(4)
O2	0.16152(19)	0.00964(11)	0.30488(14)	0.0221(4)
O3	0.38511(19)	0.16388(11)	0.20157(14)	0.0235(4)
O4	0.3835(2)	0.01801(11)	0.21249(14)	0.0229(4)
C1	0.0472(3)	0.06736(14)	0.13463(19)	0.0183(5)
C2	−0.0090(3)	0.01950(15)	0.1897(2)	0.0207(6)
H2	−0.092661	0.005580	0.172978	0.025*
C3	0.0518(3)	−0.00901(14)	0.2683(2)	0.0195(5)
C4	−0.0254(3)	0.09661(14)	0.0538(2)	0.0197(5)
C5	−0.1239(3)	0.06059(15)	0.0060(2)	0.0233(6)
H5	−0.146434	0.017079	0.025111	0.028*
C6	−0.1881(3)	0.08949(17)	−0.0697(2)	0.0286(7)
H6	−0.253205	0.065078	−0.101765	0.034*
C7	−0.1561(3)	0.15448(18)	−0.0981(2)	0.0318(7)
H7	−0.200286	0.173921	−0.148625	0.038*
C8	−0.0577(3)	0.19060(18)	−0.0510(2)	0.0328(7)
H8	−0.035926	0.234243	−0.069997	0.039*
C9	0.0076(3)	0.16177(16)	0.0240(2)	0.0261(6)
H9	0.074088	0.185887	0.054942	0.031*
C10	−0.0125(3)	−0.06398(14)	0.3180(2)	0.0196(5)
C11	0.0127(3)	−0.06828(15)	0.4120(2)	0.0205(6)
H11	0.071244	−0.038400	0.441564	0.025*
C12	−0.0497(3)	−0.11708(15)	0.4613(2)	0.0236(6)
H12	−0.035193	−0.118832	0.523955	0.028*
C13	−0.1336(3)	−0.16323(15)	0.4168(2)	0.0252(6)
H13	−0.175174	−0.195938	0.449842	0.030*
C14	−0.1559(3)	−0.16085(16)	0.3232(2)	0.0272(7)
H14	−0.210335	−0.192765	0.293698	0.033*
C15	−0.0968(3)	−0.11067(15)	0.2735(2)	0.0242(6)
H15	−0.113422	−0.108317	0.211038	0.029*
C16	0.4953(3)	0.15090(15)	0.1690(2)	0.0212(6)
C17	0.5455(3)	0.08614(15)	0.1531(2)	0.0225(6)
H17	0.624863	0.084295	0.128335	0.027*
C18	0.4871(3)	0.02408(15)	0.17121(19)	0.0201(5)
C19	0.5665(3)	0.21337(15)	0.1453(2)	0.0227(6)
C20	0.4972(3)	0.27234(16)	0.1219(2)	0.0263(6)
H20	0.407821	0.271482	0.119154	0.032*
C21	0.5609(4)	0.33272(17)	0.1025(2)	0.0318(7)
H21	0.513938	0.371750	0.085398	0.038*
C22	0.6939(4)	0.33475(18)	0.1085(2)	0.0354(8)
H22	0.736239	0.375325	0.096253	0.043*
C23	0.7643(4)	0.27654(19)	0.1326(3)	0.0364(8)
H23	0.853669	0.278223	0.137563	0.044*
C24	0.7012(3)	0.21558(18)	0.1496(2)	0.0316(7)
H24	0.748574	0.176132	0.163720	0.038*
C25	0.5430(3)	−0.04168(14)	0.1419(2)	0.0201(5)
C26	0.6193(3)	−0.04502(15)	0.0682(2)	0.0240(6)
H26	0.636453	−0.005228	0.036662	0.029*
C27	0.6698(3)	−0.10700(17)	0.0417(2)	0.0274(6)
H27	0.719558	−0.108686	−0.007950	0.033*
C28	0.6462(3)	−0.16630(16)	0.0889(2)	0.0284(7)
H28	0.681468	−0.207725	0.071905	0.034*
C29	0.5693(3)	−0.16377(16)	0.1621(2)	0.0287(7)
H29	0.552974	−0.203639	0.193753	0.034*

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C30	0.5173(3)	−0.10229(15)	0.1877(2)	0.0241(6)
H30	0.464745	−0.101163	0.235857	0.029*
C31	0.3802(3)	0.09965(17)	0.4006(2)	0.0269(6)
H31A	0.363039	0.142974	0.429520	0.032*
H31B	0.351756	0.063156	0.438899	0.032*
C32	0.5218(3)	0.09285(15)	0.3922(2)	0.0227(6)
C33	0.5994(3)	0.15029(16)	0.3814(2)	0.0271(6)
H33	0.563600	0.193937	0.382228	0.032*
C34	0.7293(3)	0.14273(18)	0.3692(2)	0.0312(7)
H34	0.779901	0.181166	0.360979	0.037*
C35	0.7836(3)	0.07801(19)	0.3695(2)	0.0322(7)
H35	0.870789	0.072901	0.361602	0.039*
C36	0.7082(3)	0.02107(18)	0.3814(2)	0.0334(7)
H36	0.744657	−0.022447	0.381374	0.040*
C37	0.5789(3)	0.02846(16)	0.3933(2)	0.0274(6)
H37	0.529227	−0.010233	0.402140	0.033*

complexes. Indeed, the DBM anion is a common chelating reagent used in solvent extraction for the spectroscopic determination of metal ions [7]. In continuation of on-going work on the syntheses and structural studies of organotin compounds, the reactions of diorganotin dichlorides with DBM were investigated. These reactions might be expected to lead to the formation of either a mono- or a bis-DBM compound by the replacement of one or two chloride anions [8–10]. In the present study, the reaction of dibenzyltin dichloride with two molar equivalents of DBM was found to produce a benzylbis(dibenzoylmethane)chloridotin compound as the predominant product, where one chloride and a benzyl group of the organotin precursor have been substituted by two DBM molecules.

The molecular structure is shown in the figure (70% displacement ellipsoids) and shows the tin atom to be coordinated by four oxygen atoms, derived from two chelating DBM anions, as well as benzyl-C and chloride atoms. The benzyl-C and chloride atoms are mutually *cis* in the resulting CClO₄ donor set which defines a distorted octahedron with the range of angles being a narrow 82.06(8)°, for O2–Sn–O4, to a wide 178.38(9)°, for O1–Sn–C31. The Sn–O bond lengths are experimentally distinct with the shortest Sn–O1 bond [2.071(2) Å] having the O1 atom *trans* to the benzyl-C atom. The longest Sn–O4 bond [2.122(2) Å] sees the O4 atom *trans* to the Cl1 atom. The remaining Sn–O2 [2.108(2) Å] and Sn–O3 [2.102(2) Å] bonds are experimentally equivalent. These systematic variations follow the expected trends [11]. There is evidence that the disparity in the Sn–O bonds is reflected in differences in the associated C–O bonds. Thus, the oxygen atom forming the shorter Sn–O bond of each chelating ligand forms the longer C–O bond [C–O1, O2 = 1.296(3) and 1.282(4) Å, and C–O3, O4 = 1.303(3) and

1.284(3) Å]. The six-membered chelate rings are non-planar and are best described as having envelope conformations. Thus, for the O1-DBM ligand, the tin atom lies 0.547(3) Å out of the plane defined by the remaining five atoms of the six-membered ring, which have a r.m.s. deviation of 0.035 Å; the comparable values for the O3-DBM ligand are 0.343(4) and 0.030 Å, respectively. The dihedral angle between the planar regions of the chelate rings is 72.30(8)°, indicating an almost orthogonal relationship. Finally, the dihedral angles between the planar regions of the O1-chelate ring and the pendant C4- and C10-phenyl rings are 26.73(16) and 31.74(14)°, respectively, and the dihedral angle between the outer rings is 30.51(14)°. The equivalent angles for the O3-chelate and the C19- and C25-rings are 31.24(9), 27.44(16) and 27.44(16)°, respectively.

In the crystal, supramolecular chains along the *a* axis are sustained by phenyl-C—H···O1 [C27—H27···O1ⁱ: H27···O1ⁱ = 2.51 Å, C27···O1ⁱ = 3.428(4) Å with angle at H27 = 169° for symmetry operation (i) 1 - *x*, - *y*, - *z*] and benzyl-phenyl-C—H···π(phenyl) [C36—H36···Cg(C10—C15)ⁱ: H36···Cg(C10—C15)ⁱ = 2.63 Å, C36···Cg(C10—C15)ⁱ = 3.503(4) Å and angle at H36 = 157°] interactions. The chains assemble into a three-dimensional architecture with no directional interactions between them.

According to a search of the Cambridge Structural Database [12], there are no examples of mixed organo/halotin(acetylacetonate)₂ structures related to the title structure in the crystallographic literature. However, there is a related diorganotin(DBM)₂ molecule, e.g. for *R* = *n*-Bu [9]. In the same way, there is also a related Sn(DBM)₂Cl₂ molecule [13]. In the former, the *n*-butyl groups are *trans* and in the latter, the chloride atoms are *cis*.

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