Derivatives of Divalent Germanium, Tin, and Lead. Part VI.[1] Crystal and Molecular Structure of Bis(1-phenylbutane-1,3-dionato)tin(II)

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The crystal structure of the title compound has been determined by Patterson and Fourier methods from *X*-ray diffractometer data. Crystals are monoclinic, space group *C*2/*c*, with a = 18·821(2), b = 10·102(3), c = 9·733(3) Å, β = 101·57(2)°, Z = 4. The tin atoms are chelated by two crystallographically equivalent benzoylacetonato-ligands resulting in distorted pseudotrigonal bipyramidal co-ordination with the lone pair of electrons occupying an equatorial site: r(Sn–O)(ax) 2·290(6), r(Sn–O)(eq) 2·135(1) Å, O(ax)–Sn–O(ax) 150·4(2), O(eq)–Sn–O(eq) 94·7(1)°.

FROM the structural data available for tin(II)–oxygen bonded compounds, it is clear that the classical pyramidal, three-co-ordinate stereochemistry for divalent tin is by no means universal. This geometry has been discerned in potassium tris(formato)stannate(II) [2] and tin(II) sulphate,[3] whilst in basic tin(II) sulphate, $Sn_3O(OH_2)SO_4$, two of the tin atoms are three- and the

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[1] Part V, P. F. R. Ewings, D. E. Fenton, and P. G. Harrison, *J.C.S. Dalton*, 1975, 821.

[2] A. Jelen and O. Lindquist, *Acta Chem. Scand.*, 1969, **23**, 3071.

[3] J. D. Donaldson and D. C. Puxley, *Acta Cryst.*, 1972, **B28**, 864.

third four-co-ordinate.[4] The tin atoms in the bis(thiourea) complex of tin(II) sulphate[5] are also four-co-ordinated by two sulphate oxygen atoms and by two thiourea sulphur atoms in distorted pyramidal sites. No less than three different types of six-co-ordination have been characterised. In dihydrogen ethylenediaminetetra-acetatostannate(II) the tin atom is centred in the rectangular face of a distorted trigonal prism.[6] The tin(II) atoms of the mixed-valence carboxylate, $Sn_2(O_2C{\cdot}C_6H_4{\cdot}NO_2\text{-}o)_4O$,thf, experience pentagonal pyramidal co-ordination, the tin lone pair of electrons occupying the remaining axial position.[7] However, in ditin(II) ethylenediaminetetra-acetate dihydrate, half the tin atoms are in similar pentagonal bipyramidal sites but with the lone pair now occupying an equatorial position. The remaining tin atoms in this compound are seven-co-ordinated in a complex way in which the lone pair is again stereochemically active.[8] Eight-co-ordination for tin(II) atoms has been observed in $SnHPO_4$.[9]

In Part V of this series[1] we described the synthesis and spectroscopic properties of tin(II) bis(β-diketonates). Here we present the results of an *X*-ray crystallographic investigation of one member of this family of compounds bis(1-phenylbutane-1,3-dionato)tin(II).

EXPERIMENTAL

Golden cubic crystals of $[Sn(PhCO{\cdot}CH{\cdot}COMe)_2]$ suitable for intensity measurements were obtained by recrystallisation from hot tetrahydrofuran. The crystals are air sensitive, but stable to *X*-rays, and a specimen of dimensions *ca.* 0·5 × 0·5 × 0·4 mm was mounted under nitrogen in a Lindemann capillary and used for both the initial photography and the subsequent intensity-data collection.

Crystal Data.—$C_{20}H_{18}O_4Sn$, $M = 441{\cdot}06$, $a = 18{\cdot}821(2)$, $b = 10{\cdot}102(3)$, $c = 9{\cdot}733(3)$ Å, $\beta = 101{\cdot}58(2)°$, $U = 1812{\cdot}9$ Å^3, $D_c = 1{\cdot}62$ g cm^{-3}, $Z = 4$, $F(000) = 880$. Space group $C2/c$ or Cc from systematic absences: hkl ($h + k = 2n + 1$) and $h0l$ ($l = 2n + 1$), $C2/c$ from successful refinement. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) = 14·41 cm^{-1}.

The space-group and initial cell parameters were determined from oscillation and zero- and first-layer Weissenberg photographs obtained on an equi-inclination Weissenberg camera. Relative intensities were collected up to θ 30·0° with Mo-K_α radiation by use of a Hilger and Watts Y290 single-crystal four-circle diffractometer, accurate cell dimensions being obtained by least-squares refinement of *ca.* 20 reflections. Each reflection was counted for 30 s and the two associated background counts for 10 s. The reflections were brought to the same relative intensities by reference reflections taken for every one hundred reflections recorded; the diffractometer orientation was referenced every two hundred reflections.

All reflections with a corrected count of $<3\sigma$ of the total counts were considered as non-observed and were not used further. The total number of reflections was thus reduced from 5173 to 4677, and further reduced to 2459 by averaging equivalent reflections. Finally, 352 reflections of lowest intensity were discarded in order to enable adequate computer storage for refinement. The intensities were corrected for Lorentz and polarisation effects, but not for absorption.

Structural Determination and Refinement.—The four tin atoms in the unit cell lie on two-fold axes in the special positions $0,y,\frac{1}{4}$, $0,y,\frac{3}{4}$, $\frac{1}{2},y + \frac{1}{2},\frac{1}{4}$, and $\frac{1}{2},\frac{1}{2} - y,\frac{3}{4}$. The value of y was obtained from a three-dimensional Patterson synthesis, and the positional parameters of the tin atom thus obtained were used to phase the initial structure-factor calculation. A Fourier synthesis produced the remaining twelve non-hydrogen light atoms. Eight cycles of isotropic block-diagonal refinement followed by four cycles of anisotropic block-diagonal refinement gave R of 0·048. At this stage a weighting scheme of the form $w = (A/F_o)^2$, where $F_o > A$ and $A = 67{\cdot}00$, was applied. Two further cycles of anisotropic block-diagonal refinement gave a final R value of 0·041. The scattering factors used were those for neutral atoms.[10] Calculations were performed using the '*X*-Ray '70' suite of programmes. The results are collected in Tables 1—4. Final observed and calculated structure factors, and thermal parameters are listed in

TABLE 1

Fractional atomic co-ordinates, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Sn	0	0·05553(4)	$\frac{1}{4}$
O(1)	−0·0574(1)	0·1994(3)	0·1088(3)
O(2)	0·0914(1)	0·1134(3)	0·1373(3)
C(1)	−0·1003(2)	0·3413(4)	−0·0805(3)
C(2)	−0·0844(2)	0·4564(4)	−0·1501(4)
C(3)	0·0886(2)	0·1837(4)	0·0314(4)
C(4)	−0·0400(2)	0·2600(3)	0·0032(3)
C(5)	−0·1723(2)	0·3010(4)	−0·0874(4)
C(6)	0·0258(2)	0·2557(4)	−0·0372(4)
C(7)	−0·2296(2)	0·3737(5)	−0·1663(4)
C(8)	−0·1431(3)	0·5302(4)	−0·2294(5)
C(9)	−0·2145(3)	0·4885(5)	−0·2364(5)
C(10)	0·1558(2)	0·1931(7)	−0·0311(5)

TABLE 2

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bond lengths			
Sn–O(1)	2·135(1)	C(4)–C(1)	1·497(4)
Sn–O(2)	2·290(6)	C(1)–C(2)	1·408(5)
O(1)–C(4)	1·286(4)	C(2)–C(8)	1·392(6)
O(2)–C(3)	1·248(5)	C(8)–C(9)	1·385(7)
C(3)–C(10)	1·508(6)	C(9)–C(7)	1·398(7)
C(3)–C(6)	1·419(5)	C(7)–C(5)	1·396(6)
C(6)–C(4)	1·378(5)	C(5)–C(1)	1·399(5)
(*b*) Bond angles			
O(1)–Sn–O(1′)	94·7(1)	O(1)–C(4)–C(1)	114·5(3)
O(2)–Sn–O(2′)	150·4(2)	C(1)–C(4)–C(6)	119·0(3)
O(1)–Sn–O(2)	81·2(1)	C(4)–C(1)–C(2)	121·6(3)
Sn–O(2)–C(3)	128·9(3)	C(4)–C(1)–C(5)	119·0(3)
O(2)–C(3)–C(10)	117·9(3)	C(2)–C(1)–C(5)	119·3(3)
O(2)–C(3)–C(6)	125·0(3)	C(1)–C(5)–C(7)	120·5(4)
C(6)–C(3)–C(10)	117·2(4)	C(5)–C(7)–C(9)	119·6(4)
C(3)–C(6)–C(4)	126·2(3)	C(7)–C(9)–C(8)	120·2(4)
Sn–O(1)–C(4)	131·5(4)	C(9)–C(8)–C(2)	120·6(4)
O(1)–C(4)–C(6)	126·4(3)	C(8)–C(2)–C(1)	119 8(4)

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[4] S. Grimvall, *Acta Chem. Scand.*, 1973, **27**, 1447.

[5] J. D. Donaldson, D. G. Nicholson, D. C. Puxley, and R. A. Howie, *J.C.S. Dalton*, 1973, 1810.

[6] K. G. Shields, R. C. Seccombe, and C. H. L. Kennard, *J.C.S. Dalton*, 1973, 741.

[7] P. F. R. Ewings, P. G. Harrison, T. J. King, and A. Morris, *J.C.S. Chem. Comm.*, 1974, 53.

[8] F. P. van Remoortere, J. J. Flynn, F. P. Boer, and P. P. North, *Inorg. Chem.*, 1971, **10**, 1511.

[9] A. F. Berndt and R. Lamberg, *Acta Cryst.*, 1971, **B27**, 1092.

[10] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

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TABLE 3

Principal intermolecular contacts (Å), with estimated standard deviations in parentheses

Sn · · · C(6)	3·74(1)	Sn · · · O(1)	4·63(1)
Sn · · · C(3)	3·78(1)	Sn · · · C(1)	4·85(1)
Sn · · · O(2)	4·18(1)	C(3) · · · C(10)	4·97(1)
Sn · · · C(4)	4·18(1)	Sn · · · Sn	4·99(1)
Sn · · · C(10)	4·60(1)		

TABLE 4

Equations of least-squares planes, and, in square brackets, deviations (Å) of atoms from these planes

Plane (1): O(1), O(2), C(3), C(4), C(6)

$$3{\cdot}6152x + 7{\cdot}9913y + 5{\cdot}1652z - 1{\cdot}9475 = 0$$

[Sn −0·212(2)]

Plane (2): C(1), C(2), C(5), C(7)—(9)

$$-3{\cdot}9989x + 5{\cdot}5307y + 8{\cdot}1322z - 1{\cdot}6369 = 0$$

[Sn 0·703(3), O(2) −0·258(3), C(3) 0·047(3), C(4) 0·751(3) C(10) −0·313(3)]

Dihedral angles (°):

(1)–(2)	30·42
(3)–(3′) *	88·30

* Planes (3) and (3′) are defined by atoms Sn, O(1), O(2), and Sn, O(1′), O(2′), respectively.

TABLE 5

Comparison of valence-bond angles (°) in [(PhCO·CH·COMe)$_2$Sn] with those in structurally related compounds

Compound	X–M–X(eq)	X–M–X(ax)
[Sn(PhCO·CH·COMe)$_2$] [a]	150·4	94·7
[Sn(S$_2$CNEt$_2$)$_2$] [b]	139·2	96·2
[Pb(S$_2$CNEt$_2$)$_2$] [c]	133·2	96·2
[Pb(S$_2$COEt)$_2$] [d]	137·2	98·2
[Pb[S$_2$P(OEt)$_2$]$_2$] [e]	138·2	94·1
[Pb(S$_2$COPr^i)$_2$,C$_5$H$_5$N] [f]	127·7	95·0
[Pb(S$_2$COBu^n)$_2$] [g]	141·2	91·7

[a] This work. [b] J. Potenza and D. Mastropaolo, *Acta Cryst.*, 1973, **B29**, 1830. [c] H. Iwasaki and H. Hagihara, *Acta Cryst.*, 1972, **B28**, 507. [d] H. Hagihara and S. Yamashita, *Acta Cryst.*, 1966, **21**, 350. [e] T. Ito, *Acta Cryst.*, 1972, **B28**, 1034. [f] H. Hagihara, N. Yoshida, and Y. Watanabe, *Acta Cryst.*, 1969, **B25**, 1775. [g] H. Hagihara, Y. Watanabe, and S. Yamashita, *Acta Cryst.*, 1968, **B24**, 910.

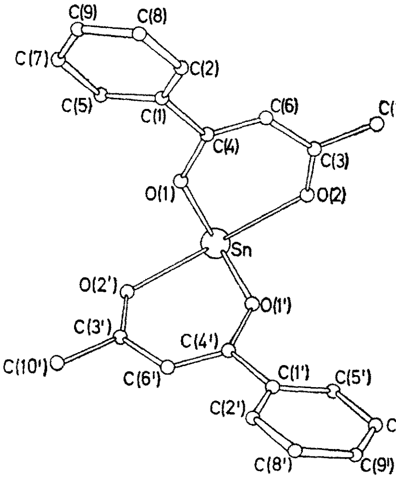

FIGURE 1 View of the molecule down the two-fold axis; symmetry-related atoms are primed

DISCUSSION

As may be seen from Figures 1—3, crystals of [Sn(PhCO·CH·COMe)$_2$] consist of discrete molecules. The two crystallographically equivalent β-diketonate rings chelate the tin in an unsymmetrical fashion, resulting in a distorted trigonal bipyramidal geometry at tin with the lone pair of electrons occupying an equatorial site. Confirmation of the stereochemical activity of the lone pair is readily apparent from the stacking of the molecules in the crystal (Figure 2). In

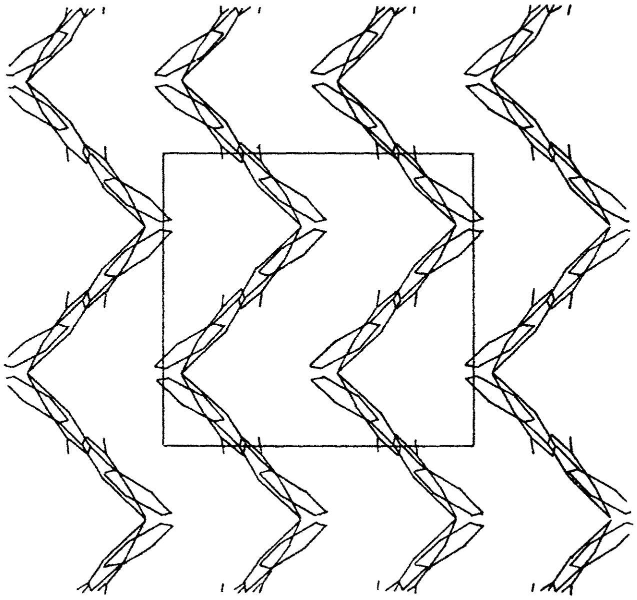

FIGURE 2 Projection of the unit cell on the *bc* plane

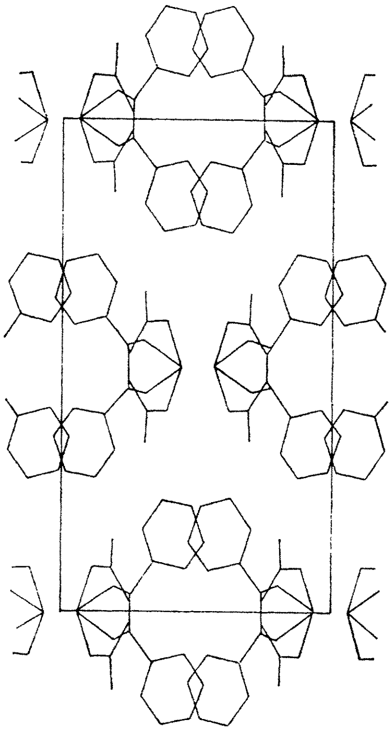

FIGURE 3 Projection of the unit cell on the *ab* plane

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

addition, the O(eq)–Sn–O(eq) and O(ax)–Sn–O(ax) bond angles are reduced to 94·7 and 150·4°, respectively, owing to lone-pair–bond-pair repulsions. Similar structures, but generally with a greater degree of distortion, have been observed for tin(II) and lead(II) dithiocarbamates, -carbonates, and -phosphoridates (Table 5).

Unlike $[Me_2Sn(acac)_2]$,[11] in which the Sn–O bonds are equivalent, the Sn–O(eq) bond distance (2·135 Å) is significantly shorter than Sn–O(ax) (2·290 Å). These values fall in the rather wide range observed for other tin(II)–oxygen bonds (Table 6), but, moreover, are similar to the Sn–O bond distances in $[Ph_3Sn(ONPhCOPh)]$ [12] which contains both covalent (2·091 Å) and co-ordinate (2·308 Å) Sn–O interactions. The contribution of the PhC(OSn)**:**CH·C(**:**O)Me enolate form to the overall structure is manifest in the endocyclic C–C and C–O bond distances. The (Ph)C–O distance (1·286 Å) approaches that of a single bond, whilst the (Me)C–O distance (1·248 Å) is only marginally longer than that in simple carbonyl compounds. Similarly, the (Ph)C–CH distance (1·378 Å) is appreciably shorter, and hence with a greater double-bond character, than the corresponding (Me)C–CH distance (1·419 Å). Both, however, are shorter than the two exocyclic C–C distances (1·508 and 1·497 Å) which are as expected (Table 7). The twist of the phenyl group from the plane of the chelate ring (30·4°) is most probably due to crystal-packing forces.

TABLE 6

Comparison of tin–oxygen bond distances (Å) in various tin(II) derivatives

Compound	Co-ord. no.	Geometry *	r(Sn–O)
$[Sn(C_{10}H_9O_2)_2]$ [a]	4	Dist. ψ-trig. bipy.	2·290 (ax,) 2·135 (eq)
$K[Sn(O_2CH)_3]$ [b]	3	Trig. bipy.	2·139—2·182
$Sn[SO_4]$ [c]	3	Trig. bipy.	2·25—2·27
$Sn[SO_4],2(H_2N)_2CS$ [d]	4	Dist. py.	2·24, 2·41
$[Sn(edtaH_2)]$ [e]	6	Dist. trig. prism	2·196, 2·343, 2·635, 3·057
$[Sn_2(edta)],2H_2O$ [f]			
Sn^{I}	6	Dist. ψ-pentag. bipy.	2·14, 2·18, 2·30, 3·10, 3·14, 3·18
Sn^{II}	7	2 Dist. interlocking tetrahedra	2·29, 2·45, 2·64, 2·70
$[Sn_2(O_2C{\cdot}C_6H_4{\cdot}NO_2)_4O]$,thf [g]	6	Pentag. py.	2·12 (ax), 2.40—2·59 (eq)

[a] This work. [b] Ref. 2. [c] Ref. 3. [d] Ref. 5. [e] Ref. 6. [f] Ref. 8. [g] Ref. 7.

* Dist. = distorted, trig. = trigonal, bipy. = bipyramidal, py. = pyramidal, tri. = triangular, pentag. = pentagonal.

TABLE 7

Comparison of bond distances (Å) and angles (°) of the chelate ring in $[Sn(PhCO{\cdot}CH{\cdot}COMe)_2]$ with those in other metal β-ketoenolates

Compound	O–M–O	M–O–C	O–C–C	C–C–C	r(C–O)	r(C–C)
$[Sn(PhCO{\cdot}CH{\cdot}COMe)_2]$ [a,b]	81·2	128·9, 131·5	117·9, 126·5	126·4	1·248, 1·286	1·378, 1·419
$[Pd(acac)_2]$ [a,c]	95·6	123, 124	125·5	126	1·31, 1·32	1·39, 1·44
$[(acac)_2SnCo_2(CO)_7]$ [d]						
Ring (1):	84·4	125·5, 130·7	123·9, 130·0	123·1	1·27, 1·28	1·35, 1·45
Ring (2):	84·4	128·8, 128·9	122·6, 124·1	130·8	1·32, 1·33	1·32, 1·34
$[Me_2Sn(acac)_2]$ [a,e]	86	126, 127	124, 130	130	1·27, 1·28	1·36, 1·44

[a] Chelate rings crystallographically equivalent. [b] This work. [c] A. N. Knyazeva, E. A. Shugan, and L. M. Shkol'nikova, *J. Struct. Chem.*, 1972, **11**, 875. [d] R. D. Ball and D. Hall, *J. Organometallic Chem.*, 1973, **56**, 209. [e] Ref. 11; acac = acetylacetonato.

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[11] G. A. Miller and E. O. Schlemper, *Inorg. Chem.*, 1973, **12**, 677.

[12] P. G. Harrison and T. J. King, *J.C.S. Chem. Comm.*, 1972, 815.