Preparation and Spectroscopic Studies of Five-co-ordinate β-Diketonato-tri(organo)tin Compounds. Crystal Structure of (1,3-Diphenylpropane-1,3-dionato)triphenyltin(IV)

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A series of new five-co-ordinate complexes, R_3SnL [R = Me, (I)—(III) or Ph, (IV)—(VI); L = anions of acetylacetone (acac), benzoylacetone (bzac), or dibenzoylmethane (bzbz)], has been prepared and characterized by i.r., n.m.r., and Mössbauer spectroscopy. Compounds (I)—(III) have large quadrupole splittings (3·69—3·86 mm s^{-1}), while those of (IV)—(VI) are much smaller (1·38—2·25 mm s^{-1}). By use of partial quadrupole splittings, these splittings are shown to be consistent with the *mer*-structure for compounds (I)—(III), and the all-*cis*-structure for (IV)—(VI). The all-*cis*-structure has been confirmed for (VI), [Ph_3Sn(bzbz)], by a single-crystal *X*-ray diffraction study. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a = 13{\cdot}216(5)$, $b = 9{\cdot}443(4)$, $c = 22{\cdot}344(9)$ Å, and $\beta = 109{\cdot}42(2)°$. The structure was solved by the heavy-atom method from intensity data collected by diffractometric methods, and refined by full-matrix least-squares methods to *R* 0·051 for 2328 observed reflections. The co-ordination about the Sn atom is essentially a distorted trigonal bipyramid. The phenyl groups occupy one axial and two equatorial co-ordination sites with the chelating ligand bonded to one equatorial and one axial site. Sn–C(eq) Bond lengths are 2·149(7) and 2·181(6), and Sn–C(ax) 2·180(6) Å. The Sn–O(ax) distance [2·276(7) Å] is significantly longer than Sn–O(eq) [2·094(7) Å].

ALTHOUGH a fairly large number of five-co-ordinate organotin(IV) compounds is now known,[1] there is comparatively little structural information,[2] and *X*-ray structures are known for only seven monomeric five-co-ordinate species.[3-10] Since 1965, Mössbauer spectroscopy has been used as an indication of the co-ordination environment of tin(IV), and ρ values[11] (quadrupole splitting, q.s., divided by the centre shift, c.s.) have been used to indicate five-co-ordination. More recently, the additivity model[12] has been employed to distinguish between five-co-ordinate isomers.[13,14] However, as Clark *et al.*[15] have pointed out, a proper treatment of the five-co-ordinate q.s. treatment has been hampered by the paucity of structural data, as well as the difficulty of having to assign partial quadrupole splittings to both axial and equatorial groups.

We now report the preparation and characterization of six new five-co-ordinate complexes of β-diketonato-tri(organo)tin(IV) of the type R_3SnL [R = Me (I)—(III), or Ph (IV)—(VI); L = anions of acetylacetone (acac), benzoylacetone (bzac), and dibenzoylmethane (bzbz)]. The complete single-crystal *X*-ray study shows that (VI) [Ph_3Sn(bzbz)] has the all-*cis*-structure. The Mössbauer quadrupole splittings for (IV)—(VI) are consistent with this and strongly suggest that (I)—(III) have the hitherto unknown *mer*-structure.

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EXPERIMENTAL

The six compounds listed in Table 1 were prepared under dry nitrogen by use of the thallium(I) salt method.[16] The thallium(I) salts of the acetylacetonates were prepared by established techniques [16–18] and their purity checked by m.p.s. The organotin compounds were prepared by adding R_3SnCl (R = Me or Ph) in dry benzene to the stoicheiometric amount of the thallium(I) salt in benzene. Thallium chloride precipitated immediately. Except for (V), solvent was removed from the filtrate *in vacuo*. The crude products were recrystallized in warm benzene with the addition of a small amount of light petroleum. All yields were $>60\%$.

I.r. spectra of Nujol mulls were obtained by use of a Perkin-Elmer 621 spectrometer. N.m.r. spectra were recorded in benzene at room temperature with tetramethylsilane as standard by use of T 60 and HA 100 spectrometers.

Mössbauer spectra were obtained by use of a 5 mCi $BaSnO_3$ source at room temperature and an Austin Science Associates spectrometer. All absorbers were at 110 K. Velocity calibration was obtained by use of iron foil (New England Nuclear), and spectra were fitted to Lorentzian line-shapes, with the program written by A. J. Stone. All c.s. are reported with respect to the centre of a room-temperature $BaSnO_3$–$BaSnO_3$ spectrum by the scan-centre method.[19]

X-Ray Studies.—Compound (VI) crystallized from dry benzene as yellow crystals. A crystal was sealed in a capillary tube and preliminary photographic examination established the monoclinic space group $P2_1/c$ (C^5_{2h}, No. 14).[20] Accurate unit-cell dimensions were determined by a least-squares refinement of the angular settings of 23 reflections with $15 < 2\theta < 31°$, centred on a diffractometer by use of Mo-K_α radiation.

Crystal Data.—$C_{33}H_{26}O_2Sn$, $M = 573.3$, Monoclinic, $a = 13{\cdot}216(5)$, $b = 9{\cdot}443(4)$, $c = 22{\cdot}344(9)$ Å, $\beta = 109{\cdot}42(2)°$, $U = 2630$ Å^3, $D_m = 1{\cdot}46(1)$, $Z = 4$, $D_c = 1{\cdot}440$ g cm^{-3}, $F(000) = 1156{\cdot}5$. Mo-K_α radiation, $\lambda = 0{\cdot}70926$ Å; μ(Mo-K_α) = 9·1 cm^{-1}. Space group $P2_1/c$ from systematic absences: $h0l$ for $l = 2n + 1$, $0k0$ for $k = 2n + 1$. No crystallographic symmetry constraints.

For data collection a crystal of dimensions *ca.* 0·15 × 0·20 × 0·30 mm was mounted in a capillary such that the long dimension, [010], was offset from collinearity with the diffractometer-spindle axis. ω-Scans of a number of low-angle axial reflections showed an average width at half-height of 0·08°, which was considered acceptable.[21] Intensities were recorded on a Picker FACS 1 automatic four-circle diffractometer, by use of prefiltered (Nb foil, 0·07 mm) Mo radiation with a take-off angle of 1·6°. All reflections in the range $1{\cdot}5 \leqslant 2\theta \leqslant 45°$ in the octants hkl and $\bar{h}kl$ were collected in three shells. The θ—2θ scan technique was used at a scan rate of 1·0° min^{-1}, with a scan range of 0·8°, corrected for dispersion. Background counts were made for 10 s with a stationary crystal and counter at the ends of each scan. Coincidence losses were minimized for strong reflections by employing Cu foil attenuators. The intensities of five standard reflections monitored throughout data collection showed only random fluctuations of ±2%.

A total of 3833 reflections was measured and the recorded intensities were corrected for background, Lorentz, and polarization effects. A standard deviation, σ, was assigned to each reflection such that: $\sigma(I) = [\text{count} + \frac{1}{4}(t_c/t_b)^2(b_1 + b_2) + (pI)^2]^{\frac{1}{2}}$, where $I = \text{count} - \frac{1}{2}(b_1 + b_2)(t_c/t_b)$, count = total count measured in time t_c, and b_1 and b_2 are the background counts each measured in time t_b. The 'ignorance factor,' p, was initially chosen as 0·02,[22] but a statistical examination of the standard reflections suggested 0·013 to be more appropriate. In the final cycle of least-squares refinement p was chosen as 0·014 to give a value close to 1·0 for the error on an observation of unit weight. Absorption correction trials [23] with μ 9·1 cm^{-1} showed transmission factors ranging from 0·888 to 0·906, a variation of 2%. No absorption correction was made. Of the 3833 observations, 2104 having $I > 3\sigma(I)$ were used in the solution and initial refinement of the structure.

Structure Solution and Refinement.—The position of the Sn atom was located from a three-dimensional Patterson synthesis. Two cycles of least-squares refinement on F, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, and varying the Sn positional parameters led to R 0·259 and R' 0·296 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]$, where the weight, w, is defined as $w = 4F_o^2/\sigma^2(F_o)^2\}$.

Atomic scattering factors for neutral tin, oxygen, and carbon atoms were taken from ref. 24, and that for hydrogen from ref. 25. Anomalous dispersion contributions to the real and imaginary parts of the structure factor were included for tin, the values used being from ref. 26. All remaining 61 atoms (including the 26 hydrogen atoms) were readily located by a series of least-squares refinements and difference-Fourier syntheses.

The conditions for the final cycles of refinement were: (i) 2328 observed [$>2\sigma(I)$] reflections with $p = 0{\cdot}014$ and 115 variables; (ii) the phenyl rings were refined as groups [D_{6h} symmetry, C–C 1·392 Å (ref. 27)] with isotropic temperature factors for each carbon atom; (iii) the six non-group non-hydrogen atoms were assigned anisotropic thermal parameters; (iv) phenyl ring hydrogen-atom contributions to F_c were calculated and included (C–H 1·00 Å, B 4·0 Å^2); (v) positional and thermal parameters of the hydrogen atom of the propanedionato-ligand were not refined, but the atom was included in the refinement. Refinement then converged at R 0·051 and R' 0·063. No evidence for extinction was observed. An examination of the observed and calculated structure factors, in terms of magnitude, $\lambda^{-1} \sin\theta$, indices, and diffractometer setting

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angles (χ and ϕ) showed no unusual trends. A final difference-Fourier synthesis showed the largest residual peak to be 0·53(16) e$Å^{-3}$ in the vicinity of 3C(5), a phenyl ring carbon atom. The standard deviation of an observation of unit weight is 0·99 electrons. Observed and calculated structure factors and derived phenyl hydrogen atom positional parameters are listed in Supplementary Publication No. SUP 21255 (14 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Analytical and physical data for the compounds are summarized in Table 1, along with the n.m.r. spectra and i.r. ν(Sn–C) bands for the trimethyl compounds. A reproducible analysis could not be obtained for (II) owing to its instability both in solution and in the solid state. (II) tended to disproportionate, as indicated, in

$$2[Me_3Sn(bzac)] \longrightarrow [Me_2Sn(bzac)_2] + Me_4Sn$$

solution by the presence of Me_4Sn [τ 9·9, $^2J(^{119}Sn–CH_3)$ 54 Hz][1] in a benzene solution of (II) shortly after preparation. Similar disproportionation reactions have been found[28] for $Me_3Sn(oxin)$ (oxin = 8-hydroxyquinolinato) and $Cl_3Sn(acac)$.[29] In contrast, (I) and (III) were stable in solution for several weeks. The triphenyl compounds are more stable than the corresponding methyl compounds, although a really satisfactory analysis could not be obtained for (IV).

TABLE 1

M.p.s, analyses, proton n.m.r. and i.r. data

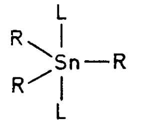
Compound	No.	M.p./°C	Analyses * % C	Analyses * % H	τ	$^2J(^{119}Sn–CH_3)$/Hz	$\nu(Sn–C)/cm^{-1}$
$[Me_3Sn(acac)]$	(I)	176—177	36·03 (36·5)	4·99 (5·1)	9·68	60·8	574m, 556s
$[Me_3Sn(bzac)]$	(II)	126—128	48·05 (56·7)	5·58 (5·2)	9·62	60·5	589m, 550s
$[Me_3Sn(bzbz)]$	(III)	164d	56·66 (55·85)	4·69 (4·95)	9·62	59·2	585w, 548w
$[Ph_3Sn(acac)]$	(IV)	98—100d	58·95 (61·4)	4·42 (4·45)			
$[Ph_3Sn(bzac)]$	(V)	63—65	65·52 (65·8)	4·67 (4·75)			
$[Ph_3Sn(bzbz)]$	(VI)	135—136	68·38 (69·1)	4·47 (4·55)			

* Found, in parentheses.

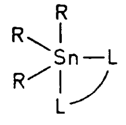
The n.m.r. coupling constants $^2J(^{119}Sn–CH_3)$ are characteristic of five-co-ordinate trimethyltin compounds.[1] Thus the J values for our trimethyl compounds are similar to those for other known five-co-ordinate trimethyl species such as $[Me_3SnBr(Ph_3PO)]$ (66 Hz),[30] and much smaller than those for six-co-ordinate dimethyl compounds such as $[Me_2Sn(acac)_2]$ (99·2 Hz)[31] or $[Me_2SnCl_2(Ph_3PO)_2]$ (88 Hz).[30] The multiple i.r. Sn–C frequencies show that the three methyl groups are not in equivalent equatorial positions, and that the two oxygen atoms in the ligands are not in axial positions, as one would expect from the steric properties of the ligands. In contrast, trimethyltin compounds such as $[Me_3SnBr(Ph_3PO)]$ which contain only unidentate ligands have only the one Sn–C band characteristic of three equatorial methyl groups.

It is perhaps surprising that the trimethyl compounds show only one set of proton resonances when the three methyl groups are not equivalent. Similar one-peak resonances have been observed[28] for $[Me_3Sn(oxin)]$ and other trimethyltin cations.[30] This is probably due to fast intra- or inter-molecular interconversion processes.

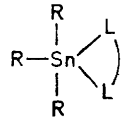
Since the structural data for $[Me_2Sn(acac)_2]$ and $[Cl_2Sn(acac)_2]$[32] and now our structure of $[Ph_3Sn(bzbz)]$ indicate that diketonates act as chelating ligands, it seems reasonable to rule out dimeric structures in which the ligand bridges two moieties. The three possible R_3SnL_2 isomers are then (A)—(C). However, steric requirements for the diketonato-ligand along with the i.r. evidence rule out structure (A).



(A)



(B)



(C)

The Mössbauer quadrupole splittings (Table 2) enable us to assign structures with reasonable confidence. It

TABLE 2

Mössbauer parameters (mm s^{-1} at 110 K) *

Compound	C.s.	Q.s.
$[Me_3Sn(acac)]$ [a]	1·21	3·81
$[Me_3Sn(bzac)]$ [a]	1·13	3·69
$[Me_3Sn(bzbz)]$ [a]	1·15	3·86
$[Me_2Sn(acac)_2]$ [b]	1·16	4·02
$[Me_2Sn(bzac)_2]$ [b]	1·06	3·87
$[Me_2Sn(bzbz)_2]$ [b]	1·18	4·08
$[Me_4Sn]$ [c]	1·31	0
$[Ph_3Sn(acac)]$ [a]	1·09	1·38
$[Ph_3Sn(bzac)]$ [a]	1·08	2·25
$[Ph_3Sn(bzbz)]$ [a]	1·13	2·25
$[Ph_2Sn(acac)_2]$ [b]	0·71	2·07
$[Ph_2Sn(bzac)_2]$ [b]	0·73	2·23
$[Ph_2Sn(bzbz)_2]$ [b]	0·73	2·15
$[Ph_4Sn]$ [c]	1·22	0

* Errors ±0·02 mm s^{-1}; linewidths 1·10 ± 0·10 mm s^{-1}. χ^2 Values for all spectra 505 ± 40 for *ca.* 500 degrees of freedom.

[a] This work. [b] G. M. Bancroft and T. K. Sham, ref. 31. [c] G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1973, **15**, 59, Table 42.

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

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is apparent that the trimethyl compounds have much larger splittings than their triphenyl analogues. Also, the triphenyl compounds have similar quadrupole splittings to their *cis*-diphenyl analogues, while the trimethyl compounds have similar splittings to their *trans*-dimethyl analogues (Table 2). These results are readily rationalized if the triphenyl compounds have structure (B), and the trimethyl compounds structure (C). In Table 3, the e.f.g. components are given in terms of partial field gradients for the relevant ideal structures. We have assumed here that axial and equatorial ligands have the same partial field gradients. To enable rough calculations of quadrupole splittings for these species, we assume [33] that the five-co-ordinate partial quadrupole splittings are given by the octahedral values calculated previously, *i.e.* $(\text{p.q.s.})_{\text{Me}}$ $-1{\cdot}03$ and $(\text{p.q.s.})_{\text{Ph}}$ $-0{\cdot}95$ mm s^{-1} [15] and that $(\text{p.q.s.})_{\text{L}}$ is zero. The calculated quadrupole splittings for the five structures of interest are also given in Table 3. The calculations indicate that structure (C) should give a q.s. about twice that of structure (B), and that the q.s. of (C) should be slightly smaller than that for the *trans*-R_2SnL_4 compound. The results (Table 3) show that these calculations are consistent with the observed quadrupole splittings if the triphenyl compounds have structure (B), and the trimethyl compounds have structure (C). The small quadrupole splittings for (IV) relative to those of (V) and (VI) is surprising and cannot be readily rationalized.

TABLE 3

Electric field gradient components and predicted quadrupole splittings for five- and six-co-ordinate isomers

Species *	E.f.g. components	Predicted q.s./mm s^{-1}	
		R = Me	R = Ph
(A)	$V_{zz}/e = 4[L] - 3[R]$ $\eta = 0$	$-3{\cdot}09$	$-2{\cdot}85$
(B)	$V_{11}/e = -\frac{3}{2}[R] + [L]$ $V_{22}/e = +\frac{3}{2}[R] - 2[L]$ $V_{33}/e = +[L]$	$1{\cdot}75$ $(\eta = 1)$	$1{\cdot}65$ $(\eta = 1)$
(C)	$V_{11}/e = -\frac{1}{2}[L]$ $V_{22}/e = -3[R] + \frac{5}{2}[L]$ $V_{33}/e = 3[R] - 2[L]$	$3{\cdot}55$ $(\eta = 1)$	$3{\cdot}28$ $(\eta = 1)$
(D)	$V_{zz}/e = 4[R] - 4[L]$	$+4{\cdot}12$	$+3{\cdot}80$
(E)	$V_{zz}/e = -2[R] + 2[L]$	$-2{\cdot}06$	$-1{\cdot}90$

* (A), (B), (C) defined in text; (D) *trans*-R_2SnL_4, (E) *cis*-R_2SnL_4.

TABLE 4

Atomic (Sn $\times 10^5$, H $\times 10^3$, others $\times 10^4$) and thermal parameters * ($\times 10^4$)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	21697(5)	35626(7)	35640(3)	411(4)	414(4)	356(4)	45(4)	113(2)	$-20(4)$
O(1)	3598(5)	2396(8)	3856(3)	537(41)	746(49)	483(43)	217(39)	$-5(36)$	$-231(38)$
O(2)	2976(6)	4385(8)	4568(3)	588(45)	675(45)	422(39)	179(38)	2(36)	$-95(37)$
C(1)	4377(7)	2232(10)	4382(4)	406(55)	436(55)	410(59)	$-111(46)$	111(48)	$-26(47)$
C(2)	4474(8)	2914(11)	4937(4)	455(55)	557(59)	364(56)	18(51)	128(45)	$-28(49)$
C(3)	3781(8)	3962(9)	5016(5)	428(57)	424(64)	398(55)	$-37(45)$	101(48)	1(43)
HC(2)	525	269	530	4·0 †					

* In the form: $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$ where the thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. † Anisotropic, $B/\text{Å}^2$.

The quadrupole splittings calculated in Table 3 are obviously dependent on the choice of p.q.s. values, but the trends in q.s. are independent of the choice of p.q.s. values for R between $-0{\cdot}9$ and $-1{\cdot}2$ mm s^{-1} and L between $-0{\cdot}2$ mm s^{-1} and $0{\cdot}2$ mm s^{-1}. We are preparing a complete treatment of five-co-ordinate systems, in which we derive separate p.q.s. values for axial and equatorial ligands.[33]

There is a marked increase in c.s. for the triorganotin species relative to the six-co-ordinate diorganotin species (Table 2) especially for the triphenyl compounds. These centre shifts reflect the very large tin 5*s* character in the R–Sn bonds in the five-co-ordinate species.

Description of the Structure.—The structure consists of discrete monomers; the shortest intermolecular distance of approach (2·42 Å) is between phenyl ring hydrogen atoms bonded to 1C(5) and 5C(5). The shortest intermolecular distance of approach not involving hydrogen atoms is 3·80 Å between phenyl carbon atoms 1C(1) and 2C(3).

Final positional and thermal parameters are given in Tables 4 and 5. An overall view of the molecule is shown in the Figure. Selected bond distances and angles are given in Table 6.

Co-ordination about tin. The co-ordination about the tin atom is best described as a slightly distorted trigonal bipyramid. O(2) And 2C(1) occupy axial positions, the equatorial positions being occupied by 1C(1), 3C(1), and O(1) (Figure). The largest departure from an ideal trigonal bipyramidal geometry is that of O(2). The Sn–O(2)(ax) distance is 2·276(7) whilst the Sn–O(1)-(equatorial) distance is 2·094(7) Å. These distances differ by 20σ and the difference is clearly significant. The angle subtended at the tin atom by the two axial ligands [O(2)–Sn–2C(1) 163·7(2)°] is far removed from the ideal value of 180°. The Sn–C distances to the co-ordinated phenyl rings are Sn–1C(1) 2·181(6), and Sn–3C(1) 2·149(7) (both equatorial), and Sn–2C(1) 2·180(6) Å (axial). Although the two Sn–C (equatorial) distances are just significantly different (3·5σ) no chemical significance is attached to this observation. There is thus no structural evidence for a lengthening of the Sn–C(ax) relative to the Sn–C(eq) bond.

A series of least-squares planes has been calculated and is shown in Table 7. The four atoms in the equatorial plane (2) [Sn, 1C(1), 3C(1), and O(1)] are

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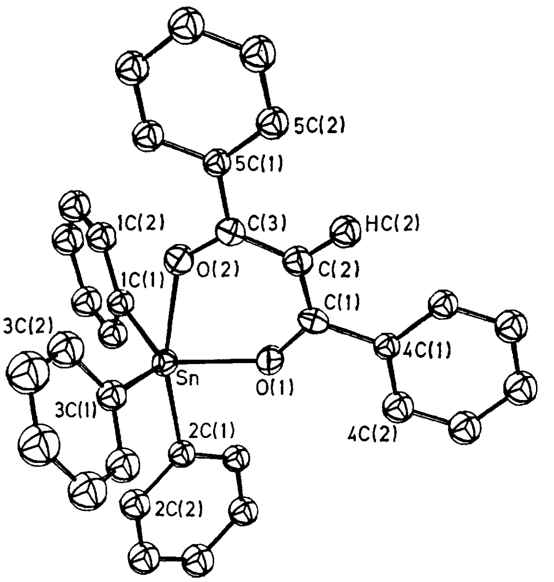
[33] G. M. Bancroft, M. G. Clark, V. G. Kumar Das, and T. K. Sham, *J.C.S. Chem. Comm.*, 1974, 236; *J.C.S. Dalton*, to be published.

TABLE 5

Phenyl group positional and thermal parameters

	x	y	z	B/Å^2
Ph (1)				
1C(1)	0·2182(5)	0·5771(5)	0·3281(3)	3·5(2)
1C(2)	0·2384(5)	0·6901(6)	0·3705(2)	4·2(2)
1C(3)	0·2365(6)	0·8283(5)	0·3484(3)	4·9(2)
1C(4)	0·2145(6)	0·8534(5)	0·2839(3)	5·3(2)
1C(5)	0·1943(6)	0·7404(7)	0·2415(2)	5·0(2)
1C(6)	0·1961(6)	0·6023(6)	0·2636(3)	4·2(2)
Ph (2)				
2C(1)	0·1855(4)	0·2555(7)	0·2642(2)	3·3(2)
2C(2)	0·0804(4)	0·2244(8)	0·2270(3)	4·4(2)
2C(3)	0·0590(4)	0·1682(8)	0·1665(3)	4·9(2)
2C(4)	0·1428(5)	0·1431(8)	0·1431(2)	5·2(2)
2C(5)	0·2479(4)	0·1742(7)	0·1803(3)	4·0(2)
2C(6)	0·2692(3)	0·2304(7)	0·2409(3)	3·3(2)
Ph (3)				
3C(1)	0·1013(5)	0·2680(7)	0·3945(3)	3·7(2)
3C(2)	0·0663(6)	0·3433(6)	0·4375(4)	5·3(2)
3C(3)	−0·0076(7)	0·2828(9)	0·4620(4)	6·9(2)
3C(4)	−0·0465(6)	0·1469(9)	0·4436(4)	6·5(2)
3C(5)	−0·0115(6)	0·0717(7)	0·4005(4)	5·9(2)
3C(6)	0·0624(6)	0·1322(7)	0·3760(3)	4·8(2)
Ph (4)				
4C(1)	0·5200(4)	0·1165(6)	0·4334(3)	3·0(2)
4C(2)	0·5037(4)	0·0448(7)	0·3765(2)	4·3(2)
4C(3)	0·5825(5)	−0·0457(7)	0·3700(3)	4·9(2)
4C(4)	0·6777(5)	−0·0645(7)	0·4204(3)	5·0(2)
4C(5)	0·6940(4)	0·0072(7)	0·4773(3)	4·4(2)
4C(6)	0·6151(5)	0·0977(7)	0·4838(2)	3·6(2)
Ph (5)				
5C(1)	0·3963(5)	0·4652(6)	0·5648(2)	3·1(2)
5C(2)	0·4831(5)	0·4296(6)	0·6181(3)	3·9(2)
5C(3)	0·4987(5)	0·4995(7)	0·6753(2)	4·7(2)
5C(4)	0·4276(5)	0·6050(7)	0·6792(2)	4·8(2)
5C(5)	0·3407(5)	0·6405(7)	0·6259(3)	4·4(2)
5C(6)	0·3251(4)	0·5706(7)	0·5687(2)	3·9(2)



A view of the molecule showing the atom labelling scheme. The phenyl carbon atoms are numbered sequentially. Atoms are shown as 50% probability ellipsoids. Phenyl ring hydrogen atoms have been omitted

situated such that the tin atom is below the least-squares plane, on the side of the axial phenyl ring, and the other three atoms are above the plane. The two equatorial phenyl rings are tilted differently with respect to the equatorial plane, ring (3) making an angle of 80·2° and ring (1) one of 54·0° with this plane. The angle between rings (1) and (3) is 50·1°. Ring (4) and ring (5), the phenyl substituents on the bzbz ligand, are approximately coplanar with the plane of the ligand, ring (4) making an angle of 6·1, and ring (5) one of 3·7° with the plane. This is in contrast to results from three studies of solvated alkaline-earth complexes containing the bzbz ligand,[34-36] in which the rings subtended angles varying from 5·6 to 47·6° with the plane of the ligand,

TABLE 6

Selected bond distances and angles

(*a*) Co-ordination about Sn

(i) Distances

Sn–O(2)	2·276(7)	Sn–2C(1)	2·180(6)
Sn–O(1)	2·094(7)	Sn–1C(1)	2·181(6)
Sn–3C(1)	2·149(7)		

(ii) Angles

3C(1)–Sn–O(1)	111·0(3)	O(2)–Sn–O(1)	78·1(2)
3C(1)–Sn–1C(1)	124·1(2)	O(2)–Sn–1C(1)	85·0(2)
1C(1)–Sn–O(1)	120·1(3)	2C(1)–Sn–1C(1)	99·3(2)
O(2)–Sn–2C(1)	163·7(2)	2C(1)–Sn–O(1)	86·2(3)
O(2)–Sn–3C(1)	84·5(3)	2C(1)–Sn–3C(1)	105·5(2)

(*b*) The chelating ligand

(i) Distances

O(2)–C(3)	1·260(11)	C(3)–5C(1)	1·499(11)
C(3)–C(2)	1·399(13)	C(1)–4C(1)	1·512(11)
C(2)–C(1)	1·365(13)	C(2)–HC(2)	1·09
C(1)–O(1)	1·290(11)		

(ii) Angles

Sn–O(1)–C(1)	135·3(6)	5C(1)–C(3)–O(2)	116·1(8)
O(1)–C(1)–C(2)	125·3(9)	4C(1)–C(1)–O(1)	113·0(8)
C(1)–C(2)–C(3)	125·5(9)	4C(1)–C(1)–C(2)	121·8(8)
C(2)–C(3)–O(2)	122·6(9)	C(3)–C(2)–HC(2)	122·3
C(3)–O(2)–Sn	132·1(6)	C(1)–C(2)–HC(2)	111·3
5C(1)–C(3)–C(2)	121·3(8)		

TABLE 7

(*a*) Equations of selected least-squares planes in the form $Ax + By + Cz = D$, and in square brackets distances (Å) of relevant atoms from the plane

	A	B	C	D
Plane (1): Sn, O(1), O(2), C(1)—(3)	8·454	6·705	−10·953	0·3806
Plane (2): Sn, O(1), 3C(1), 1C(1)	1·041	3·650	18·78	8·423

Plane (1): [Sn −0·061, O(2) 0·073, C(1) 0·016, C(2) −0·052, C(3) −0·021, O(1) 0·044]

Plane (2): [Sn −0·205, O(1) 0·066, 3C(1) 0·067, 1C(1) 0·072]

(*b*) Equations of planes through the phenyl rings *

Plane	Ring	A	B	C	D
(3)	(1)	13·086	−0·577	−4·703	0·9785
(4)	(2)	0·322	8·723	−8·220	0·117
(5)	(3)	6·976	−3·635	12·033	4·479
(6)	(4)	7·334	7·194	−11·166	−0·188
(7)	(5)	9·021	6·479	−10·372	0·731

* Calculated using the positions of atoms *n*C(1), *n*C(3), and *n*C(5) of ring *n*.

(*c*) Interplanar angles (°)

(2)–(3) 80·21, (2)–(5) 53·95, (2)–(4) 89·51, (3)–(5) 50·10, (1)–(6) 6·14, (1)–(7) 3·73

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[34] F. J. Hollander, D. H. Templeton, and A. Zalkin, *Acta Cryst.*, 1973, **B29**, 1289.

[35] F. J. Hollander, D. H. Templeton, and A. Zalkin, *Acta Cryst.*, 1973, **B29**, 1295.

[36] F. J. Hollander, D. H. Templeton, and Z. Zalkin, *Acta Cryst.*, 1973, **B29**, 1303.

although the intra-atomic distances and angles within the diketonato-ligand were comparable. The ligand geometry is also not significantly different from that of the free ligand in the enolate form.[37,38]

Although structural data for the previously reported triphenyl(*N*-phenylhydroxamato)tin were incomplete,[8] the geometry of the SnC_3O_2 core appears to be similar to that of the present structure [Sn–C(ax) 2·18, Sn–O(ax) 2·31, Sn–C(eq) 2·13 and 2·14, and Sn–O(eq) 2·09 Å, ref. 8].

From presently known structural data for organotin compounds[3,4,8,10] and $SnCl_5^-$,[39] it is not yet possible to rationalize the axial–equatorial Sn–O bond length differences in terms of bonding differences, *trans*-influence, or the steric requirements of the ligands.

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[38] D. H. Templeton and A. Zalkin, *Acta Cryst.*, 1973, **B29**, 1552.

[39] R. F. Bryan, *J. Amer. Chem. Soc.*, 1964, **86**, 733.