The Crystal Structure of Calcium Bis[triacetatostannate(II)]: Evidence for an Unusual Regular Trigonal-pyramidal Environment for Tin

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An unusual *regular* trigonal-pyramidal environment is found for the tin atoms in the title compound. The structure has been determined by the heavy-atom method from 531 diffractometer reflections and refined by full-matrix least-squares methods to *R* 0.051. The crystals are trigonal, space group $P\bar{3}$ (C^{1}_{3i}, no. 147), with a = 8.31, c = 8.49 Å, and Z = 1. The environment of the tin atoms is unusual in that it is regular trigonal pyramidal with three Sn–O bonds of 2.14 Å and pyramidal bond angles of 83.5°.

IN most of its tin(II) compounds tin is in a distorted environment because of the presence of a stereochemically active lone pair of non-bonding electrons. The most common tin(II) environment consists of a trigonal-pyramidal arrangement of three nearest-neighbour tin-ligand bonds with three longer non-bonding contacts completing a distorted octahedral co-ordination. These longer contacts arise because close approach of ligands to the tin is prevented by the lone-pair orbitals. Tin(II) compounds in which this type of environment is found for oxygen-containing materials include $Sn[SO_4]$,[1] $Sn[HPO_4]$,[2] $K[Sn(O_2CH)_3]$,[3] $SnCl_2{\cdot}2H_2O$,[4] and one site in $Sn_3O(OH)_2(SO_4)$.[5] The dicarboxylate derivatives disodium bis(oxalato)stannate(II), $Na_2[Sn(C_2O_4)_2]$,[6] and tin maleate monohydrate, $Sn[O_4C_4H_2]{\cdot}H_2O$,[7] however, have tin in a distorted square-pyramidal environment which is also found in a few tin(II) derivatives of unidentate ligands such as $2K[SnF_3]{\cdot}H_2O$,[8] $Sn[SO_4]{\cdot}2CS(NH_2)_2$,[9] and two Sn sites in $Sn_3O(OH)_2(SO_4)$.[5]

The main structural feature found in all four-coordinate tin environments is the existence of two bonds of considerably greater length than those normally found in tin(II) compounds. It therefore appears probable that, if there are no specific solid-state effects such as the tin–tin interactions in blue-black tin(II) oxide,[10] the co-ordination about the tin atoms in tin(II) compounds can only be increased from the trigonal-pyramidal environment if one of the three bond lengths is increased.

Many simple and complex tin(II) carboxylates have been prepared with monocarboxylic acids, substituted monocarboxylic acids, and dicarboxylic acids. However, structures of only a few of these compounds are known.[3,6,7] The environment found for tin in $K[Sn(O_2CH)_3]$ is trigonal pyramidal with Sn–O distances of 2.18, 2.17, and 2.14 Å and bond angles of 82.9, 83.2, and 78.4°. We now describe the structure of a derivative of a tricarboxylatostannate(II) ion, *viz.* $Ca[Sn(O_2CMe)_3]_2$, in order to establish whether it has a four- or a three-coordinate tin environment.

TABLE 1

Atomic positional parameters, with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Sn	$\frac{1}{3}$	$\frac{2}{3}$	0.402 8(1)
Ca	0	0	$\frac{1}{2}$
O(1)	0.589 5(9)	0.481 2(8)	0.758 3(7)
O(2)	0.811 2(9)	0.731 9(9)	0.642 3(7)
C(1)	0.686 2(12)	0.658 2(11)	0.742 6(9)
C(2)	0.639 5(16)	0.771 7(14)	0.848 8(12)
H(1)	0.781 8(16)	0.882 4(14)	0.837 4(12)
H(2)	0.618 8(16)	0.709 8(14)	0.964 3(12)
H(3)	0.547 4(16)	0.827 1(14)	0.833 6(12)

EXPERIMENTAL

Tin(II) acetate (1 mol), prepared by the method of Donaldson *et al.*,[11] was dissolved in 60% w/w aqueous acetic acid (100 cm³), in a nitrogen atmosphere, and heated under reflux with an aqueous solution of calcium acetate (1 mol); 50—70% of the solvent was distilled off and the mixture filtered. The filtrate was allowed to cool and the white crystalline product filtered off, washed with acetone and diethyl ether, and dried *in vacuo* over potassium hydroxide (Found: Ca, 6.30; Sn, 37.5; acetate, 55.9. $C_{12}H_{18}CaO_{12}Sn_2$ requires Ca, 6.35; Sn, 37.6; acetate, 56.1%).

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Sn–Sn	4.250(5)	O(1)–H(2)	2.503(14)
Sn–O(1)	2.140(7)	O(1)–H(3)	3.130(16)
Sn–O(2)	2.930(7)	O(2)–C(1)	1.242(10)
Sn–C(1)	2.900(10)	O(2)–C(2)	2.386(15)
Sn–H(3)	3.994(11)	O(2)–H(1)	2.161(14)
Ca–O(2)	2.321(6)	O(2)–H(2)	3.126(13)
Ca–C(1)	3.421(8)	O(2)–H(3)	3.131(17)
Ca–C(2)	3.957(11)	C(1)–C(2)	1.489(17)
Ca–H(1)	3.268(11)	C(1)–H(1)	1.807(14)
Ca–Sn	6.248(9)	C(1)–H(2)	2.069(14)
O(1)–O(2)	2.206(8)	C(1)–H(3)	2.348(19)
O(1)–C(1)	1.283(3)	C(2)–H(1)	1.080(14)
O(1)–C(2)	2.364(14)	C(2)–H(2)	1.080(14)
O(1)–H(1)	2.965(12)	C(2)–H(3)	1.080(14)

(*b*) Angles [with reference to Figure 2(*a*), (*b*), and (*c*)]

O(1)–Sn–O(1$^{\mathrm{I}}$)	83.5(2)	O(1)–Sn–O(2$^{\mathrm{II}}$)	129.5(2)
O(1)–Sn–O(1$^{\mathrm{II}}$)	83.5(2)	O(1$^{\mathrm{I}}$)–Sn–O(2)	129.5(2)
O(1$^{\mathrm{I}}$)–Sn–O(1$^{\mathrm{II}}$)	83.5(2)	O(1$^{\mathrm{I}}$)–Sn–O(2$^{\mathrm{I}}$)	48.6(2)
O(2)–Sn–O(2$^{\mathrm{I}}$)	118.3(2)	O(1$^{\mathrm{I}}$)–Sn–O(2$^{\mathrm{II}}$)	77.0(2)
O(2)–Sn–O(2$^{\mathrm{II}}$)	118.3(2)	O(1$^{\mathrm{II}}$)–Sn–O(2)	129.5(2)
O(2$^{\mathrm{I}}$)–Sn–O(2$^{\mathrm{II}}$)	118.3(2)	O(1$^{\mathrm{II}}$)–Sn–O(2$^{\mathrm{I}}$)	77.0(2)
O(1)–Sn–O(2)	48.6(2)	O(1$^{\mathrm{IV}}$)–Sn–O(2$^{\mathrm{II}}$)	48.6(2)
O(1)–Sn–O(2$^{\mathrm{I}}$)	77.0(2)		
O(2)–Ca–O(2$^{\mathrm{I}}$)	84.6(2)	O(2$^{\mathrm{I}}$)–Ca–O(2$^{\mathrm{IV}}$)	84.6(2)
O(2)–Ca–O(2$^{\mathrm{II}}$)	95.4(2)	O(2$^{\mathrm{I}}$)–Ca–O(2$^{\mathrm{V}}$)	95.4(2)
O(2)–Ca–O(2$^{\mathrm{III}}$)	180.0(2)	O(2$^{\mathrm{II}}$)–Ca–O(2$^{\mathrm{IV}}$)	95.4(2)
O(2)–Ca–O(2$^{\mathrm{IV}}$)	95.4(2)	O(2$^{\mathrm{II}}$)–Ca–O(2$^{\mathrm{V}}$)	180.0(2)
O(2)–Ca–O(2$^{\mathrm{V}}$)	84.6(2)		
O(1)–C(1)–O(2)	121.7(9)	C(1)–C(2)–H(3)	131.4(1.1)
O(1)–C(1)–C(2)	116.8(8)	H(1)–C(2)–H(2)	109.5(1.3)
O(2)–C(1)–C(2)	121.5(8)	H(1)–C(2)–H(3)	109.5(1.3)
C(1)–C(2)–H(1)	87.9(1.1)	H(2)–C(2)–H(3)	109.5(1.3)
C(1)–C(2)–H(2)	106.1(1.3)		

Roman superscripts refer to the following equivalent positions:

I $-y, x-y, z$ IV $y, y-x, -z$
II $y-x, -x, z$ V $x-y, x, -z$
III $-x, -y, -z$

Crystal Data.—$C_{12}H_{18}CaO_{12}Sn_2$, *M* 631.7, $a = 8.31$, $c = 8.49$ Å, $U = 507.7$ Å³, $D_m = 2.06$ g cm⁻³, $Z = 1$, $D_c = 2.07$ g cm⁻³, $F(000) = 306$. Space group $P\bar{3}$ (C^{1}_{3i}, no. 147) or $P3$ (C^{1}_{3}, no. 143) from Laue symmetry of $\bar{3}$ and lack of systematic absences. The lower-symmetry space group was at first assumed but least-squares refinement showed convergence towards the centrosymmetric space-group positions ($P\bar{3}$) which were used in the final refinement. Mo-K_α radiation (λ 0.710 7 Å, μ 25.6 cm⁻¹).

Structure Determination.—Intensity data were collected about the *c* axis (layers *hk*0—8) with a Stoe two-circle computer-controlled semi-automatic diffractometer, by use of graphite-monochromated Mo-K_α radiation. The stationary-counter–moving-crystal method was used, with an ω-scan range of 2.0° on the lower levels, counting for

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0.15 s at 0.01° intervals. For reflections on the fourth and higher layers ($\mu > 7°$) a variable range was scanned, with $\Delta\omega$ defined by $[A + (B \sin\mu/\tan\nu)]$ where $A = 1.0$ and $B = 0.5$. Stationary background counts were measured at the extremities of each scan for 10 s. Within the range $0.1 < (\sin\theta)/\lambda < 0.65$, 531 independent reflections having $I > 2.5\sigma(I)$ were obtained and considered observed. Data were corrected for Lorentz and polarisation factors but not for absorption.

The structure could only be solved in the centrosymmetric space group and attempts at refining alternative solutions were unsuccessful. The usual heavy-atom Patterson and Fourier methods were used. Scattering factors used were those for the neutral atoms,[12] with corrections for the effects of anomalous dispersion ($\Delta f', \Delta f''$) [13] applied to those for calcium and tin. Initial refinement by full-matrix least-squares methods was with the layer-scale factors refined separately, and all the atoms vibrating isotropically. Refinement was continued with the layer-scale factors held constant and with the introduction of anisotropic thermal parameters for all the non-hydrogen atoms of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$. The methyl group was set up and refined as a rigid group (C–H 1.08 Å) as detailed in refs. 14 and 15, with U for each hydrogen fixed at 0.05 Å^2. In the final stages of refinement the weighting scheme $W = [\sigma^2(F_o) + (0.03|F_o|)^2]^{-1}$ was found appropriate, giving a satisfactory analysis of the variation of $W\Delta^2$ with increasing $(\sin\theta)/\lambda$ and with increasing fractions of $|F_o|$. At convergence, no parameter shift was $>0.001\sigma$ and a final difference-Fourier map showed no significant features. The final R was 0.051 and $R'\{=[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ was 0.056.

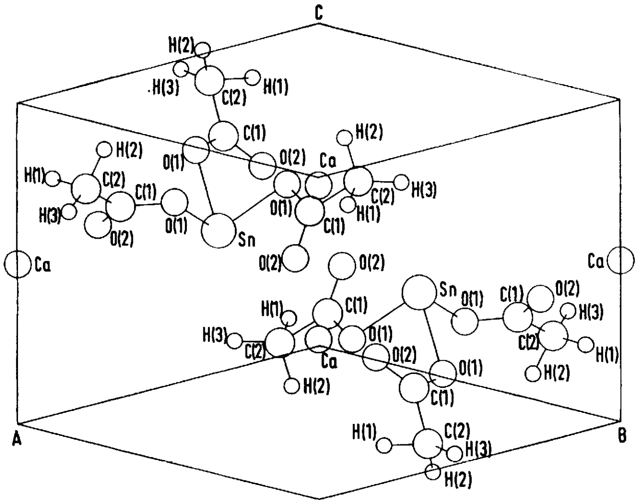

FIGURE 1 (232) Projection of the $Ca[Sn(O_2CMe)_3]_2$ structure

Most of the calculations were carried out on the ICL 1906A computer at the University of Birmingham Computer Centre using SHELX-76 [15] with BONDLA being used from '*X*-RAY '72' [16] on the CDC 7 600 computer at the University of Manchester Regional Computer Centre. Stereographic projections of the unit cell were obtained using CELLPLOT [17] on the ICL 4130 computer at the Chelsea College Computer Centre. Observed and calculated structure factors and anisotropic temperature factors are listed in Supplementary Publication No. SUP 22121 (6 pp.);* the final positional parameters, with their estimated stan-

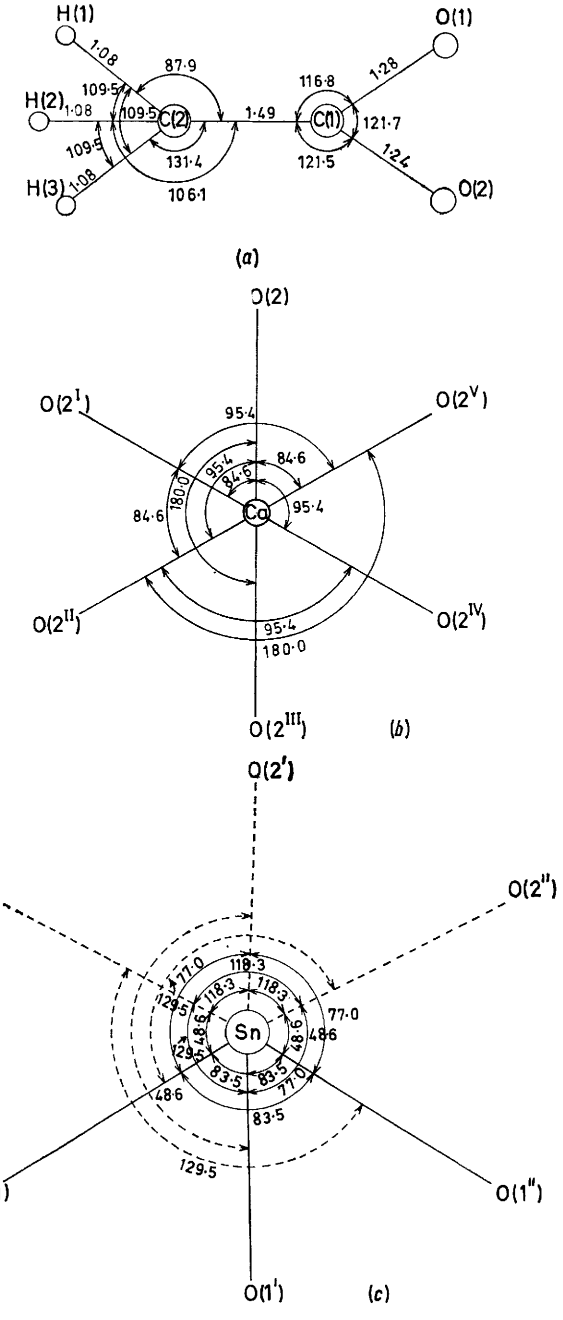

FIGURE 2 (*a*) Bond distances and angles in the acetate group. (*b*) View of the stereochemistry about the Ca atom. (*c*) View of the stereochemistry about the Sn atom

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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dard deviations, are given in Table 1, and interatomic distances and angles in Table 2.

DISCUSSION

The structure of calcium bis[triacetatostannate(II)] (Figure 1) consists of simple calcium cations and complex triacetatostannate(II) anions in a three-dimensional network. The bond distances and angles in the acetate group [Figure 2(*a*)] are typical of many acetates.[18,19] The calcium atoms in the structure are in distorted octahedral sites, with Ca–O bond lengths of 2.32 Å and O–Ca–O angles as shown in Figure 2(*b*).

The crystal structure confirms the suggestions from Mössbauer evidence [20] that tricarboxylatostannates(II) have tin in trigonal-pyramidal co-ordination. The tin co-ordination with oxygen is somewhat unusual in that the tin atom is at the apex of a regular trigonal pyramid with three equal Sn–O bond lengths of 2.14 Å and three equal O–Sn–O angles of 83.5° [Figure 2(*c*)].

The tin(II) co-ordination and bond distances in $Ca[Sn(O_2CMe)_3]_2$ are compared in Table 3 with other tin(II)–oxygen compounds of known structure. Two types of Sn–O environment are found in tin(II) compounds: (*i*) those with trigonal-pyramidal oxygen sites in which there are three short Sn–O bonds and in which the next-nearest Sn–O distance is too long to be a bonding distance; and (*ii*) those with square-pyramidal environments in which there are usually two long and two short Sn–O bond lengths. The tin site in $Ca[Sn(O_2CMe)_3]_2$ falls within the first category showing that the acetate groups are acting as unidentate ligands; any acetate chelation or bridging would give rise to square-pyramidal environments like those found for tin(II) maleate monohydrate.[7] Even within the group of compounds with trigonal-pyramidal oxygen co-ordination of the tin, the $[Sn(O_2CMe)_3]^-$ group in $Ca[Sn(O_2CMe)_3]_2$ is unusual in that all three bond lengths and O–Sn–O angles are equal. The Sn–Sn distances are too long to permit solid-state effects [10] of the type found in SnO which also has a regular tin(II) environment. The unique regular environment in $Ca[Sn(O_2CMe)_3]_2$ must arise because of the constraints of crystal packing in the high-symmetry space group. Of the known structures with tin in a trigonal-pyramidal environment, only $K[Sn(O_2CH_2)_3]$, both tin(II) sites in $Sn_2(OH)(PO_4)$, and one of the sites in $Sn_2(edta)\cdot 2H_2O$ (edta = ethylenediaminetetra-acetate) have Sn–O bonds as short as that in $Ca[Sn(O_2CMe)_3]_2$. The pyramidal site in $Sn_2(edta)\cdot 2H_2O$, however, has only two very short Sn–O distances with the third contact at 2.30 Å. The tin(II) environment most similar to that of $Ca[Sn(O_2CMe)_3]$, not surprisingly, is that found in $K[Sn(O_2CH)_3]$ but even in this compound the average Sn–O bond length is greater. The shorter average bond length for $Ca[Sn(O_2CMe)_3]$ results in a smaller Mössbauer chemical isomer shifts than those found for most other oxygen-containing tin(II) compounds.

The ^{119}Sn Mössbauer chemical shift (0.80 mm s^{-1}) is smaller than that for tin(II) acetate (1.21 mm s^{-1}) as would be expected in view of the formation of three short Sn–O bonds in the $[Sn(O_2CMe)_3]^-$ species. The large quadrupole splitting (2.03 mm s^{-1}) can be explained by the presence of a stereochemically active lone pair of electrons on the tin atom. Figure 2(*c*) shows that there is no close approach of oxygen atoms to the tin on the side opposite the three short Sn–O bonds. This must be due to the lone pair preventing the approach of ligands in the direction in which it points. The principal axis of the field gradient at the Sn atom is likely to lie in the direction of the lone pair.

TABLE 3

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

Compound	Three nearest Sn–O distances	Next-nearest neighbour
$Ca[Sn(O_2CMe)_3]_2$ [a]	2.14, 2.14, 2.14	2.93
$K[Sn(O_2CH)_3]$ [b]	2.14, 2.17, 2.18	2.89
$Sn[WO_4]$ [c]	2.21, 2.21, 2.21	2.81
$Sn[SO_4]$ [d]	2.25, 2.27, 2.27	2.95
$Ph_3Sn^{IV}Sn^{II}(NO_3)$ [e]	2.38, 2.53, 2.54	2.84
$Sn[H_2edta]$ [f]	2.20, 2.34, 2.64	3.06
$Sn_2(OH)(PO_4)$ [g]		
Sn^{I}	2.08, 2.16, 2.18	3.01
Sn^{II}	2.11, 2.13, 2.15	2.92
$Sn_2(edta)\cdot 2H_2O$ [h]		
Sn^{I}	2.14, 2.18, 2.30	3.10
Sn^{II}	2.29, 2.45, 2.64	2.70
$Sn[HPO_4]$ [i]	2.26, 2.26, 2.26	2.66
SnO [j]	2.21, 2.21, 2.21	2.21
$Sn(O\cdot CPh\cdot CH\cdot COMe)_2$ [k]	2.14, 2.14, 2.29	2.29
$[Sn_2(O_2CC_6H_4NO_2)_4O\cdot thf]_2$ [l]	2.11, 2.41, 2.43	2.44
$Na_2[Sn(C_2O_4)_2]$ [m]	2.25, 2.25, 2.36	2.36
$Sn[O_4C_2H_4]\cdot H_2O$ [n]	2.18, 2.20, 2.31	2.44

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