C(13)	0.4901 (7)	−0.3210 (5)	0.0492 (5)	0.055 (2)
C(14)	0.3953 (6)	−0.2385 (5)	0.0196 (4)	0.046 (2)
C(15)	0.1473 (5)	0.1964 (4)	−0.2767 (4)	0.037 (2)
C(16)	0.1149 (6)	0.3205 (4)	−0.2568 (4)	0.041 (2)
C(17)	0.1262 (6)	0.3674 (4)	−0.1445 (4)	0.043 (2)
C(18)	0.0972 (7)	0.4818 (5)	−0.1283 (5)	0.058 (2)
C(19)	0.0560 (9)	0.5486 (5)	−0.2218 (6)	0.076 (3)
C(20)	0.0474 (11)	0.5036 (6)	−0.3324 (6)	0.099 (4)
C(21)	0.0769 (9)	0.3902 (5)	−0.3502 (5)	0.071 (3)
C(22)	0.2192 (7)	−0.0853 (5)	−0.5629 (4)	0.054 (2)
C(23)	0.3415 (6)	−0.0512 (5)	−0.4451 (4)	0.044 (2)
C(24)	0.4138 (7)	0.0014 (5)	−0.2324 (4)	0.060 (2)
C(25)	0.1736 (8)	−0.1357 (5)	−0.3353 (5)	0.063 (3)

Table 2. *Selected geometric parameters* (Å, °)

Cu—O(2)	1.976 (3)	C(3)—C(4)	1.384 (7)
Cu—O(3)	1.966 (4)	C(4)—C(5)	1.377 (9)
Cu—O(5)	2.117 (4)	C(5)—C(6)	1.381 (10)
Cu—Cu^i	2.670 (2)	C(6)—C(7)	1.380 (7)
Cu—O(1^i)	1.980 (3)	C(8)—C(9)	1.494 (7)
Cu—O(4^i)	1.976 (4)	C(9)—C(10)	1.399 (7)
O(1)—C(1)	1.260 (6)	C(9)—C(14)	1.390 (9)
O(2)—C(1)	1.259 (6)	C(10)—C(11)	1.385 (8)
O(3)—C(8)	1.258 (6)	C(11)—C(12)	1.383 (10)
O(4)—C(8)	1.263 (7)	C(12)—C(13)	1.388 (8)
O(5)—C(15)	1.240 (6)	C(13)—C(14)	1.378 (9)
O(6)—C(15)	1.263 (7)	C(15)—C(16)	1.508 (7)
O(7)—C(22)	1.413 (8)	C(16)—C(17)	1.390 (7)
N(1)—C(23)	1.497 (8)	C(16)—C(21)	1.376 (7)
N(1)—C(24)	1.477 (6)	C(17)—C(18)	1.383 (8)
N(1)—C(25)	1.492 (8)	C(18)—C(19)	1.359 (9)
C(1)—C(2)	1.495 (5)	C(19)—C(20)	1.371 (11)
C(2)—C(3)	1.375 (8)	C(20)—C(21)	1.377 (10)
C(2)—C(7)	1.404 (8)	C(22)—C(23)	1.491 (6)
O(2)—Cu—O(3)	89.6 (1)	C(4)—C(5)—C(6)	120.1 (5)
O(2)—Cu—O(5)	98.2 (1)	C(5)—C(6)—C(7)	120.5 (6)
O(3)—Cu—O(5)	96.8 (2)	C(2)—C(7)—C(6)	119.7 (6)
O(2)—Cu—Cu^i	83.3 (1)	O(3)—C(8)—O(4)	124.5 (5)
O(3)—Cu—Cu^i	87.8 (1)	O(3)—C(8)—C(9)	118.0 (5)
O(5)—Cu—Cu^i	175.2 (1)	O(4)—C(8)—C(9)	117.5 (4)
O(2)—Cu—O(1^i)	167.2 (2)	C(8)—C(9)—C(10)	119.4 (5)
O(3)—Cu—O(1^i)	88.0 (1)	C(8)—C(9)—C(14)	120.8 (4)
O(5)—Cu—O(1^i)	94.6 (1)	C(10)—C(9)—C(14)	119.7 (5)
O(2)—Cu—O(4^i)	91.6 (2)	C(9)—C(10)—C(11)	119.3 (5)
O(3)—Cu—O(4^i)	166.8 (2)	C(10)—C(11)—C(12)	120.8 (5)
O(5)—Cu—O(4^i)	96.0 (2)	C(11)—C(12)—C(13)	119.5 (6)
C(1)—O(1)—Cu^i	123.1 (3)	C(12)—C(13)—C(14)	120.4 (6)
Cu—O(2)—C(1)	124.3 (3)	C(9)—C(14)—C(13)	120.2 (5)
Cu—O(3)—C(8)	119.4 (4)	O(5)—C(15)—O(6)	123.2 (5)
C(8)—O(4)—Cu^i	128.8 (3)	O(5)—C(15)—C(16)	119.3 (5)
Cu—O(5)—C(15)	149.4 (4)	O(6)—C(15)—C(16)	117.4 (4)
C(23)—N(1)—C(24)	109.4 (4)	C(15)—C(16)—C(17)	121.0 (4)
C(23)—N(1)—C(25)	113.8 (4)	C(15)—C(16)—C(21)	120.0 (5)
C(24)—N(1)—C(25)	111.8 (4)	C(17)—C(16)—C(21)	119.0 (5)
O(1)—C(1)—O(2)	124.9 (4)	C(16)—C(17)—C(18)	120.0 (5)
O(1)—C(1)—C(2)	117.9 (4)	C(17)—C(18)—C(19)	120.5 (6)
O(2)—C(1)—C(2)	117.1 (4)	C(18)—C(19)—C(20)	119.7 (6)
C(1)—C(2)—C(3)	121.3 (5)	C(19)—C(20)—C(21)	120.7 (6)
C(1)—C(2)—C(7)	119.7 (5)	C(16)—C(21)—C(20)	120.1 (6)
C(3)—C(2)—C(7)	118.8 (4)	O(7)—C(22)—C(23)	106.2 (5)
C(2)—C(3)—C(4)	121.4 (6)	N(1)—C(23)—C(22)	113.5 (5)
C(3)—C(4)—C(5)	119.4 (6)		

Symmetry code: (i) $-x, -y, -z$.

All non-H atoms were refined anisotropically. H atoms attached to C and N atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The H atom of the alcoholic group was located from a ΔF map.

Data collection and cell refinement: Nicolet *P*3 diffractometer system. Structure solution, refinement, other calculations and graphics: *SHELXTL/PC* (Sheldrick, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1186). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Kawata, T., Uekusa, H., Ohba, S., Furukawa, T., Tokii, T., Muto, Y. & Kato, M. (1992). *Acta Cryst.* B**48**, 253–261.
Niekerk, J. N. van & Schoening, F. R. L. (1953). *Acta Cryst.* **6**, 227–232.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Porter, L. C. & Doedens, R. J. (1984). *Inorg. Chem.* **23**, 997–999.
Sheldrick, G. M. (1990). *SHELXTL/PC*. Realease 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Turpeinen, U., Hämäläinen, R. & Ahlgrén, M. (1980). *Acta Cryst.* B**36**, 927–930.
Turpeinen, U., Hämäläinen, R. & Ahlgrén, M. (1985). *Acta Cryst.* C**41**, 1728–1730.
Turpeinen, U., Hämäläinen, R. & Reedijk, J. (1987). *Inorg. Chim. Acta*, **134**, 87–93.
Turpeinen, U., Hämäläinen, R. & Reedijk, J. (1988). *Inorg. Chim. Acta*, **154**, 201–207.

Acta Cryst. (1995). C**51**, 2546–2548

Tribenzyltin Acetate, a Redetermination

GEORGE FERGUSON

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

TREVOR R. SPALDING, ANNA T. O'DOWD AND KAREN C. O'SHEA

Department of Chemistry, University College, Cork, Ireland

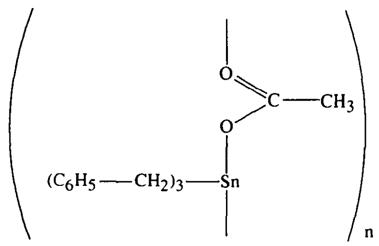
(*Received* 14 *February* 1995; *accepted* 20 *June* 1995)

Abstract

This redetermination of the structure of tribenzyltin acetate, $[Sn(C_2H_3O_2)(C_7H_7)_3]$, has confirmed the structure determined previously from photographic data [Alcock & Timms (1968). *J. Chem. Soc. A*, pp. 1873–1876], but the molecular dimensions reported here are an order of magnitude more precise. The structure is polymeric with bridging unsymmetric acetate groups [Sn—O 2.1309 (15) and 2.5592 (16) Å, O—Sn—O 169.54 (5)°, and C—O 1.281 (3) and 1.239 (2) Å]. Distorted trigonal bipyramidal coordination at Sn is completed by three benzyl groups [Sn—C 2.139–2.161 (2) Å].

Comment

There has been much discussion in the literature about the coordination number of tin in triorganotin carboxylates (Britton & Dunitz, 1981; Harrison, Lambert, King & Majee, 1983; Molloy, Purcell, Quill & Nowell, 1984; Amini, Ng, Fidelis, Heeg, Muchmore, van der Helm & Zuckermann, 1989). One of the key compounds in this discussion has been tribenzyltin acetate, which is generally taken to contain five-coordinate tin, R_3SnO_2. The structure of tribenzyltin acetate, (I), was reported in 1968, derived from photographic data, but the *R* factor was only 13% (Alcock & Timms, 1968). We decided to reassess the structure and obtain more precise dimensions for this compound.



(I)

Fig. 1 is an *ORTEP*II (Johnson, 1976) plot of the structure showing the numbering scheme. The overall structural features determined by Alcock & Timms (1968) are confirmed, but our analysis yields molecular dimensions which are an order of magnitude more precise than those reported previously. As before, we find that the structure is polymeric with tribenzyltin acetate moieties linked to form an infinite chain about a 2_1 screw axis by Sn—O interactions involving bridging acetate groups [Sn—O1 2.1309 (15) and Sn—O2^i 2.5992 (16) Å] [symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$]. The Sn coordination is distorted trigonal bipyramidal with O1—Sn1—C*n*7 (*n* = 1–3) in the range 91.06 (7)–96.97 (9)° and O2^i—Sn1—C*n*7 79.39 (7)–93.12 (9)° (*n* = 1–3).

The difference in Sn—O distances (0.468 Å) is almost three times the corresponding differences in Ph_3SnOAc (0.164 Å; Molloy, Purcell, Quill & Nowell, 1984) and $Me_2PhSnOAc$ (0.169 Å; Amini, Ng, Fidelis, Heeg, Muchmore, van der Helm & Zuckermann, 1989), and more than three times the difference in trivinyltin acetate (0.131 Å; Valle, Peruzzo, Marton & Ganis, 1982). However, the non-bonded intramolecular contact distance in (I) [Sn1···O2 3.2916 (16) Å], is only slightly (0.086–0.107 Å) longer than the equivalent distances in the triphenyl- (3.206 Å) and dimethylphenyltin acetates (3.185 Å). The O1—Sn—O2^i angle in (I) is 169.54 (5)°, only slightly reduced from the values of 173.6 (1) and 174.0 (1)° in the triphenyl- and dimethylphenyltin acetates, respectively.

The accuracy of the present structure allows us to confirm that the acetate is unsymmetrically C—O bonded with the longer distance [C1—O1 1.281 (3) Å] correlating with the shorter Sn—O bond and the shorter distance [C1—O2 1.239 (2) Å] associated with the longer Sn—O bond. The O1—C1—O2 angle is 124.2 (2)°. Atoms Sn, O1, C1 and O2 are almost coplanar with a torsion angle of 6.2 (3)°. The Sn—CH_2 distances in (I) are in the range 2.139 (2)–2.161 (2) Å; in tetrakis(2-methoxybenzyl)tin, the unique Sn—CH_2 distance is 2.165 (5) Å (Ross, Wardell, Ferguson & Low, 1994). The CH_2—Sn—CH_2 angles vary considerably [108.58 (9)–126.85 (11)°], doubtless as a consequence of intermolecular packing effects. The mean phenyl C—C and C_{arom}—CH_2 distances are 1.374 (16) and 1.493 (8) Å, respectively.

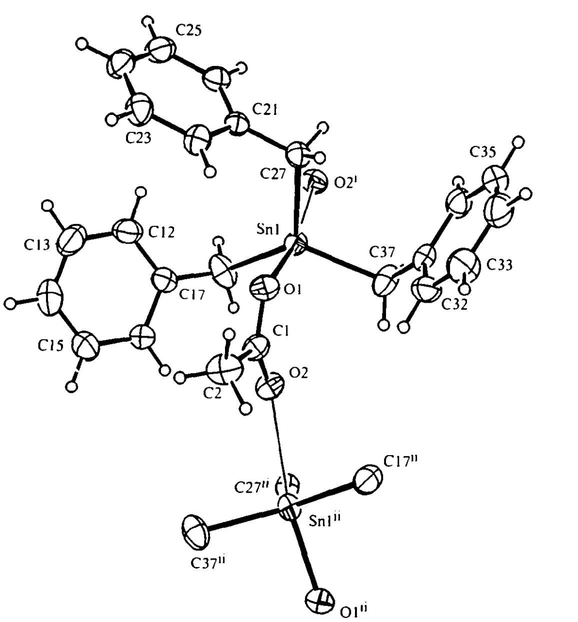


Fig. 1. A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Experimental

Compound (I) was synthesized from the reaction between bis(tribenzyltin) oxide and glacial acetic acid. Suitable crystals for the X-ray study were grown from acetic acid solution.

Crystal data

$[Sn(C_2H_3O_2)(C_7H_7)_3]$	Mo $K\alpha$ radiation
$M_r = 451.11$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/c$	$\theta = 9.4$–$17.3°$
$a = 11.3031$ (8) Å	$\mu = 1.296$ mm^{-1}
$b = 10.9569$ (12) Å	$T = 294$ (1) K
$c = 16.7039$ (14) Å	Block cut from larger piece
$\beta = 105.644$ (6)°	0.39 × 0.35 × 0.27 mm
$V = 1992.1$ (3) Å^3	Colorless
$Z = 4$	
$D_x = 1.504$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: six ψ-scans at 4° steps (North, Phillips & Mathews, 1968)
$T_{min} = 0.524$, $T_{max} = 0.677$
6043 measured reflections
5786 independent reflections
4595 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.013$
$\theta_{max} = 29.9°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 23$
3 standard reflections frequency: 120 min intensity decay: 1.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0261$
$wR(F^2) = 0.0693$
$S = 1.153$
5786 reflections
238 parameters
H atoms refined as riding (C—H 0.93–0.97 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.3107P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.779$ e Å^{-3}
$\Delta\rho_{min} = -0.519$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0240 (7)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sn1	0.48839 (1)	0.21840 (1)	0.19770 (1)	0.04553 (6)
O1	0.54148 (15)	0.06441 (13)	0.13758 (9)	0.0565 (4)
O2	0.54280 (15)	−0.07406 (14)	0.23542 (9)	0.0578 (4)
C1	0.5615 (2)	−0.0430 (2)	0.16860 (13)	0.0502 (4)
C2	0.6118 (3)	−0.1307 (2)	0.1170 (2)	0.0742 (7)
C11	0.7629 (2)	0.1763 (2)	0.28461 (12)	0.0503 (4)
C12	0.8292 (3)	0.2445 (2)	0.2411 (2)	0.0743 (8)
C13	0.9332 (3)	0.1980 (3)	0.2246 (2)	0.0887 (10)
C14	0.9757 (2)	0.0860 (3)	0.2512 (2)	0.0819 (8)
C15	0.9135 (3)	0.0188 (3)	0.2942 (2)	0.0818 (8)
C16	0.8089 (2)	0.0628 (2)	0.3107 (2)	0.0628 (6)
C17	0.6491 (2)	0.2229 (3)	0.3016 (2)	0.0694 (7)
C21	0.5901 (2)	0.3687 (2)	0.07374 (10)	0.0453 (4)
C22	0.6582 (2)	0.2907 (2)	0.03798 (14)	0.0577 (5)
C23	0.7658 (2)	0.3298 (3)	0.02275 (15)	0.0663 (6)
C24	0.8088 (2)	0.4461 (3)	0.0438 (2)	0.0713 (7)
C25	0.7431 (2)	0.5236 (2)	0.0797 (2)	0.0689 (6)
C26	0.6343 (2)	0.4858 (2)	0.09392 (13)	0.0558 (5)
C27	0.4716 (2)	0.3282 (2)	0.08933 (12)	0.0500 (4)
C31	0.2279 (2)	0.1426 (2)	0.11033 (14)	0.0523 (5)
C32	0.2247 (2)	0.0364 (2)	0.0645 (2)	0.0658 (6)
C33	0.1533 (3)	0.0277 (3)	−0.0165 (2)	0.0816 (8)
C34	0.0824 (3)	0.1239 (3)	−0.0539 (2)	0.0783 (8)
C35	0.0843 (2)	0.2274 (3)	−0.0118 (2)	0.0757 (8)
C36	0.1556 (2)	0.2390 (2)	0.0702 (2)	0.0671 (6)
C37	0.3081 (2)	0.1527 (3)	0.19764 (15)	0.0685 (6)

Table 2. *Selected geometric parameters* (Å, °)

Sn1—O1	2.1309 (15)	Sn1—C37	2.161 (2)
Sn1—O2^i	2.5992 (16)	O1—C1	1.281 (3)
Sn1—O2	3.2916 (16)	O2—C1	1.239 (2)
Sn1—C17	2.148 (2)	C1—C2	1.502 (3)
Sn1—C27	2.139 (2)		
O1—Sn1—O2^i	169.54 (5)	C37—Sn1—O2^i	93.12 (9)
O1—Sn1—C17	96.59 (8)	C1—O1—Sn1	125.33 (13)
O1—Sn1—C27	91.06 (7)	C1—O2—Sn1^{ii}	134.73 (14)
O1—Sn1—C37	96.97 (9)	O2—C1—O1	124.2 (2)
C17—Sn1—C27	122.27 (10)	O2—C1—C2	121.7 (2)
C17—Sn1—C37	126.85 (11)	O1—C1—C2	114.1 (2)
C27—Sn1—C37	108.58 (9)	C11—C17—Sn1	115.20 (15)
C17—Sn1—O2^i	79.39 (7)	C21—C27—Sn1	115.72 (13)
C27—Sn1—O2^i	83.12 (7)	C31—C37—Sn1	110.34 (14)

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Molecules of (I) crystallized in the monoclinic system; space group $P2_1/c$ was determined from the systematic absences. The coordinates of the C2 methyl H atoms were determined using the *AFIX* 133 option in *SHELXL*93 (Sheldrick, 1993) and an overall isotropic displacement parameter was refined for these three H atoms. The structure was solved by the Paterson heavy-atom method. Examination of the structure with the *SOLV* routine in *PLATON* (Spek, 1994*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM CAD*-4 (Enraf–Nonius, 1992). Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*94. Program(s) used to refine structure: *NRCVAX*94; *SHELXL*93. Molecular graphics: *NRCVAX*94, *PLATON*; *PLUTON* (Spek, 1994*b*); *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX*94; *SHELXL*93.

GF thanks NSERC (Canada) for research grants.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Alcock, N. W. & Timms, R. E. (1968). *J. Chem. Soc. A*, pp. 1873–1876.

Amini, M. M., Ng, S. W., Fidelis, K. A., Heeg, M. J., Muchmore, C. R., van der Helm, D. & Zuckerman, J. J. (1989). *J. Organomet. Chem.* **365**, 103–110.

Britton, D. & Dunitz, J. (1981). *J. Am. Chem. Soc.* **103**, 2971–2979.

Enraf–Nonius (1992). *CAD-4-PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Harrison, P. G., Lambert, K., King, T. J. & Majee, B. (1983). *J. Chem. Soc. Dalton Trans.* pp. 363–369.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molloy, K. C., Purcell, T. G., Quill, K. & Nowell, I. W. (1984). *J. Organomet. Chem.* **267**, 237–247.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Ross, J.-N., Wardell, J., Ferguson, G. & Low, J. N. (1994). *Acta Cryst.* C**50**, 1703–1707.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Spek, A. L. (1994*a*). *PLATON*. *Molecular Geometry Program*. July 1994 version. Univ. of Utrecht, Utrecht, The Netherlands.

Spek, A. L. (1994*b*). *PLUTON*. *Molecular Graphics Program*. July 1994 version. Univ. of Utrecht, Utrecht, The Netherlands.

Valle, G., Peruzzo, V., Marton, D. & Ganis, P. (1982). *Cryst. Struct. Commun.* **11**, 595–600.