Acetates and Acetato-complexes. Part 3.[1] The Crystal and Molecular Structure of Tetramethylammonium Penta-acetatostannate(IV)

By **Nathaniel W. Alcock** * and **Valerie L. Tracy**, Department of Molecular Sciences, University of Warwick, Coventry CV4 7AL

The crystal and molecular structure of the title compound has been determined. Crystals are orthorhombic, space group $P2_12_12_1$, a = 19.62(1), b = 14.60(1), c = 14.55(1) Å, Z = 8, from 1 500 reflections. The data have been measured by diffractometer and the structures solved by the heavy-atom method (R 0.090). There are two independent $[NMe_4]^+$ and $[Sn(O_2CMe)_5]^-$ ions in the asymmetric unit. The anions contain seven-co-ordinate tin atoms in pentagonal-bipyramidal geometry, with two bi- and one uni-dentate acetate group around the equator: Sn–O(bidentate) = 2.21 Å (mean) and Sn–O(unidentate) = 2.02 Å (mean).

TETRAMETHYLAMMONIUM PENTA-ACETATOSTANNATE(IV) (1) was prepared during studies [1] of the acceptor behaviour of metal acetates dissolved in acetic anhydride, and its structure has now been determined by X-ray methods in order to obtain information on the co-ordination of the tin atom and to assist in infrared spectral assignments.

EXPERIMENTAL

Compound (1) was prepared by the reaction of tetramethylammonium chloride, silver(I) acetate, and tin(IV) iodide in acetic anhydride.[1] The needle-shaped crystals produced on filtration and evaporation were recrystallized from acetic anhydride (m.p. 127 °C). The very hygroscopic crystals were handled in a dry-box and mounted in capillary tubes that had been heated to 150 °C *in vacuo*. Only freshly recrystallized samples were used.

Crystal Data.—$C_{14}H_{27}NO_{10}Sn$ (1), M = 487.63, Orthorhombic, a = 19.62(1), b = 14.60(1), c = 14.55(1) Å, U = 4 165 Å^3, Z = 8 (assumed), D_c = 1.75 g cm^{-3}, F(000) =

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[1] Parts 1 and 2, N. W. Alcock, V. M. Tracy, and T. C. Waddington, *J.C.S. Dalton*, 1976, preceding papers.

1 184, Cu-K_α radiation, graphite monochromator, λ = 1.541 8Å, μ = 6.78 cm^{-1}. No density measurement could be made. Systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$; indicating space group $P2_12_12_1$ with two independent molecules in the asymmetric unit. Data for layers $hk0$—6 and $hk7$—12 were collected on a Stoe Weissenberg diffractometer, using two crystals, to give 1 500 observed reflections [$I/\sigma(I) > 3.0$]. Unit-cell constants were determined from the positions of axial reflections, and their accuracy was estimated from the accuracy of the measurements. Lorentz-polarization and absorption corrections (with ABSCOR)[2] were applied. The tin atoms were located from a Patterson synthesis and the structure was solved by Fourier methods. Refinement by least squares gave a final R of 0.090, with anisotropic temperature factors for tin atoms only. [U_{33} was fixed for Sn(1) because individual layer scale factors were refined, and no data about a or b were available.] The atom numbering is systematic, with the atoms of one acetate group numbered O(mn1), O(mn2), C(mn1), and C(mn2) with m = 1 or 2 for Sn(1) or Sn(2), n = 1—5 for the various acetate groups with n = 1 or 2 for bidentate, 3 or 4 for unidentate axial, and 5 for unidentate equatorial groups. The cations have N(1) and N(2) attached to C(11)–C(14) and C(21)–C(24). Final atomic co-ordinates and temperature factors are in Table 1, bond lengths and angles in Table 2. Table 3 contains information on the molecular planes. Because of the high individual standard deviations, only average values are quoted for distances and angles involving only light atoms. The high temperature factors of O(221) and O(222) suggest that these sites may be slightly disordered; their bond lengths and angles are less accurate than the remainder and are shown in square brackets in Table 2, and excluded from the averages. Final structure factors are listed in Supplementary Publication No. SUP 21854 (12 pp., 1 microfiche).* Computing was with the 'X-ray' system.[3]

TABLE 1

Atomic co-ordinates ($\times 10^3$), isotropic and anisotropic * temperature factors ($\times 10^3$) with standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	173.5(1)	14.5(2)	107.8(2)	34(1)	51(2)	38	1(2)	−2(1)	−1(2)
Sn(2)	96.2(1)	504.5(3)	−51.3(2)	48(1)	48(1)	34(2)	0(2)	−5(2)	6(2)
Atom	x	y	z	U	Atom	x	y	z	U
O(111)	79(1)	71(2)	173(2)	51(8)	O(211)	58(1)	533(2)	85(2)	51(9)
O(112)	125(1)	134(2)	57(2)	49(8)	O(212)	16(2)	612(2)	−28(2)	48(9)
C(111)	78(2)	132(3)	110(4)	51(13)	C(211)	20(2)	598(3)	58(4)	54(12)
C(112)	26(2)	208(3)	103(4)	60(13)	C(212)	−18(2)	661(3)	125(4)	62(14)
O(121)	264(1)	−68(2)	69(2)	41(8)	O(221)	134(3)	469(4)	−187(4)	183(24)
O(122)	243(2)	55(2)	−13(2)	60(10)	O(222)	77(3)	562(5)	−192(5)	221(30)
C(121)	279(2)	−16(3)	1(3)	47(11)	C(221)	110(3)	512(5)	−225(4)	88(18)
C(122)	340(2)	−36(3)	−59(4)	66(17)	C(222)	120(2)	507(4)	−334(3)	78(13)
O(131)	126(2)	−64(2)	14(2)	58(9)	O(231)	164(1)	606(2)	−43(2)	47(8)
O(132)	23(1)	−11(3)	−3(2)	80(9)	O(232)	215(2)	561(3)	87(4)	14(2)
C(131)	61(2)	−78(3)	−22(4)	58(15)	C(231)	197(2)	632(3)	35(4)	65(14)
C(132)	56(3)	−164(3)	−58(4)	76(16)	C(232)	225(4)	727(5)	41(6)	126(27)
O(141)	241(2)	88(2)	192(2)	58(9)	O(241)	18(2)	409(2)	−56(3)	53(9)
O(142)	179(2)	192(2)	252(3)	86(12)	O(242)	−85(2)	330(3)	−81(4)	120(16)
C(141)	233(2)	151(3)	238(3)	43(12)	C(241)	−235(3)	435(6)	−193(5)	75(17)
C(142)	300(2)	175(3)	290(4)	76(16)	C(242)	−23(4)	390(4)	−109(7)	147(36)
O(151)	174(2)	−72(3)	204(3)	93(12)	O(251)	149(1)	398(2)	5(2)	48(9)
O(152)	75(2)	−154(3)	181(3)	103(14)	O(252)	241(2)	424(3)	−73(4)	117(17)
C(151)	122(4)	−138(6)	241(6)	132(28)	C(251)	216(3)	286(4)	−12(5)	70(18)
C(152)	143(4)	−209(6)	306(7)	159(32)	C(252)	247(3)	201(3)	36(4)	71(16)
N(1)	132(2)	438(2)	317(2)	31(8)	N(2)	614(2)	350(3)	226(4)	77(14)
C(11)	105(2)	537(3)	316(4)	71(13)	C(21)	643(3)	447(5)	224(5)	112(25)
C(12)	131(3)	402(4)	406(5)	89(18)	C(22)	601(3)	319(4)	326(5)	99(20)
C(13)	200(3)	432(3)	279(4)	71(17)	C(23)	555(4)	329(5)	162(6)	146(29)
C(14)	84(3)	387(4)	258(4)	73(16)	C(24)	668(5)	296(6)	197(7)	171(37)

* In the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

DISCUSSION

The structure contains two independent $[Sn(O_2CMe)_5]^-$ and $[NMe_4]^+$ ions, packed without any unusual interactions. The two anions are essentially identical (Figure) with seven-co-ordinate tin atoms in pentagonal-bipyrimidal geometry. This co-ordination is not unknown for tin,[4] but (1) seems to be the only example with all ligands identical although they do not bond identically. The observed arrangement, with the bidentate acetate groups in the equatorial plane, is obviously the most satisfactory. Similarly, of the possible seven-co-ordinate geometries, the pentagonal bipyramid is well adapted to the combination of two bidentate ligands of small 'bite', combined with three unidentate ligands.[5]

The in-plane O · · · O contacts (mean 2.75 Å in molecule 1) are just long enough to impose no steric strain, but are

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

[2] N. W. Alcock, in 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970, p. 271.

[3] Technical Report TR 192, Computer Science Center, University of Maryland, 1972. Scattering factors were from 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[4] See, for example, D. V. Naik and W. R. Scheidt, *Inorg. Chem.*, 1973, **12**, 273.

[5] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1975, 2611 and refs. therein.

TABLE 2

Bond lengths (Å) and angles (°) with standard deviations in parentheses. Corresponding values for molecules 1 and 2 are collected together, labelled according to the atoms of molecule 1

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
(*a*) Bidentate					
Sn(1)–O(111)	2.23(3)	2.24(3)	Sn(1)–O(111)–C(111)	89(3)	94(3)
Sn(1)–O(112)	2.12(3)	2.17(3)	Sn(1)–O(112)–C(112)	96(3)	90(3)
Sn(1)–O(121)	2.22(3)	[2.18(6)]	Sn(1)–O(121)–C(121)	94(2)	[93(5)]
Sn(1)–O(122)	2.30(3)	[2.26(8)]	Sn(1)–O(122)–C(122)	90(3)	[102(6)]
(*b*) Unidentate axial					
Sn(1)–O(131)	2.01(3)	2.00(3)	Sn(1)–O(131)–C(131)	139(3)	125(3)
Sn(1)–O(141)	2.10(3)	2.07(3)	Sn(1)–O(141)–C(141)	132(3)	135(4)
(*c*) Unidentate equatorial					
Sn(1)–O(151)	1.88(4)	2.03(3)	Sn(1)–O(151)–C(151)	134(4)	122(3)
(*d*) O · · · O Contact distances					
O(111) · · · O(112)	2.12(4)	2.17(4)	O(111)–Sn(1)–O(112)	58(1)	59(1)
O(121) · · · O(122)	2.19(4)	[1.76(9)]	O(121)–Sn(1)–O(122)	58(1)	[47(2)]
O(112) · · · O(122)	2.77(4)	[2.77(8)]			
O(111) · · · O(151)	2.83(5)	2.90(4)			
O(121) · · · O(151)	2.65(5)	[3.00(7)]			
O(131) · · · O(111)	3.18(4)	3.00(4)			
O(131) · · · O(112)	2.96(4)	2.92(4)			
O(131) · · · O(121)	2.82(4)	[2.96(7)]			
O(131) · · · O(122)	2.90(4)	[2.85(8)]			
O(131) · · · O(151)	2.91(5)	3.12(4)			
O(141) · · · O(111)	3.19(4)	2.85(4)			
O(141) · · · O(112)	3.07(4)	3.00(4)			
O(141) · · · O(121)	2.94(4)	[3.09(7)]			
O(141) · · · O(122)	3.01(5)	[3.20(8)]			
O(141) · · · O(151)	2.70(5)	2.72(4)			
(*e*) Light-atom distances (averaged); individual standard deviations are 0.04—0.07					
(*i*) Bidentate acetates [(11), (12), (21), with (22) excluded]					
O(1,2)–C(1)	1.26		O(1)–C(1)–O(2)	117.8	
C(1)–C(2)	1.51		O(1,2)–C(1)–C(2)	121.1	
(*ii*) Unidentate axial acetates [(13, (14), (23), (24)]					
O(1)–C(1)	1.27		O(1)–C(1)–O(2)	117.0	
O(2)–C(2)	1.31		O(1)–C(1)–C(2)	124.7	
C(1)–C(2)	1.50		O(2)–C(1)–C(2)	117.0	
(*iii*) Unidentate equatorial acetates [(15), (25)]					
O(1)–C(1)	1.42		O(1)–C(1)–O(2)	119.7	
O(2)–C(1)	1.22		O(1)–C(1)–C(2)	122.4	
C(1)–C(2)	1.51		O(2)–C(1)–C(2)	112.6	
(*iv*) Tetramethylammonium ions					
N–C	1.48		C–N–C	109.4	

considerably shorter than the axial–equatorial contacts (mean 2.97 Å in molecule 1). There are some second-order distortions that presumably improve the molecular packing. Thus acetates (21) and (22) are tipped 7 and 5° away from the equatorial plane; of the axial acetate groups, all except (14) are twisted, so that the tin atoms are well away from the acetate plane, but the individual deviations and the dihedral angles between these acetates and the equatorial planes show no systematic trends. In contrast, although acetates (15) and (25) are rotated by different amounts from the equator (63 and 42°), both their tin atoms are quite close to the acetate planes.

TABLE 3

Equations of mean planes in orthogonal co-ordinates (Å). Deviations (Å) of atoms from the planes are given in square brackets. All the acetate groups are planar to within experimental error

(*a*) Molecule 1

Plane: Sn(1), O(111), O(112), O(121), O(122), O(151)

$$0.5635X + 0.5770Y + 0.5912Z = 2.99$$

[Sn(1) −0.03, O(111) −0.03, O(112) 0.01, O(121) −0.06, O(122) 0.05, O(151) 0.06]

Acetate	Dihedral angle (°) to acetate plane	Deviation (Å) of Sn from acetate plane
(11)	1.8	0.06
(12)	2.9	0.05
(13)	80.1	0.58
(14)	86.9	0.08
(15)	62.9	0.15

TABLE 3 (*Continued*)

(*b*) Molecule 2

Plane: Sn(2), O(211), O(212), O(221), O(222), O(251)

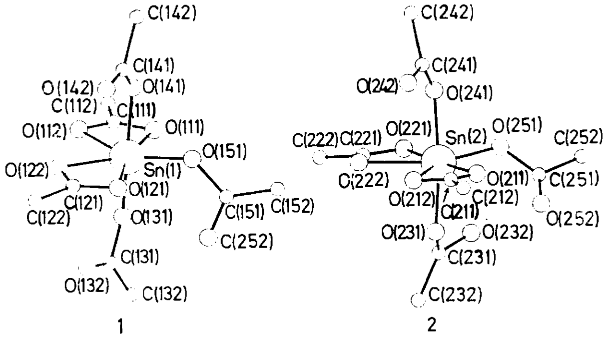
$$0.7512X - 0.6440Y - 0.1446Z = 8.66$$

[Sn(2) 0.06, O(211) −0.06, O(212) 0.04, O(221) 0.00, O(222) 0.01, O(251) −0.05]

Acetate	Dihedral angle (°) to acetate plane	Deviations (Å) of Sn
(21)	6.5	0.27
(22)	4.5	0.10
(23)	65.0	0.72
(24)	79.7	0.38
(25)	42.2	0.07

There is a substantial difference between the bond distances Sn–O(bidentate) (mean 2.21 Å) and Sn–

O(unidentate) (mean 2.02 Å), but there seems to be no significant asymmetry in the pairs of distances in the bidentate acetates (in contrast to methyltin trinitrate [6]). The Sn–O distances in the only other seven-co-ordinate tin carboxylate, tin(IV) ethylenediaminetetra-acetate, fall between the two sets of values (mean 2.09 Å).[7] Some differences would be expected between the dimensions of the bi- and uni-dentate acetate groups, but these are not well marked, no doubt because of the relatively low accuracy with which the light atoms are located.



Structure of the $[Sn(O_2CMe)_5]^-$ anions 1 and 2

Consideration of the general question of why this compound shows seven- rather than eight- or six-co-ordination is deferred to Part 4.

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[6] G. S. Brownlee, A. Walker, S. C. Nyburg, and J. T. Szymanski, *Chem. Comm.*, 1971, 1073.

[7] F. P. van Remoortere, J. J. Flynn, and F. P. Boer, *Inorg. Chem.*, 1971, **10**, 2313.