Crystal Structure of Tin(II) Maleate Monohydrate

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The structure of the title compound has been determined by the heavy-atom method from 822 diffractometer reflections and refined by full-matrix least-squares methods to R 0.030. Crystals are orthorhombic, space group $P2_1ab$, a = 7.35(1), b = 16.84(2), c = 5.32(1) Å, Z = 4. The tin atoms are in distorted square-pyramidal sites. Each maleate ion is bonded through three oxygen atoms to three different tin atoms (Sn–O 2.176, 2.196, 2.440 Å), and each tin atom is also bonded to a water molecule (Sn–O 2.312 Å).

ONLY two tin(II) complex carboxylate structures are known, $KSn[HCO_2]_3$ (ref. 1) and $Na_2Sn[C_2O_4]_2$.[2] $KSn[HCO_2]_3$ has a distorted trigonal-pyramidal tin(II) environment,[1] while in $Na_2Sn[C_2O_4]_2$ it is distorted square-pyramidal:[2] both these structures contain discrete complex anions and isolated cations.

There has been no crystal structure determination of a

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[1] A. Jelen and O. Linquist, *Acta Chem. Scand.*, 1969, **23**, 3071.

[2] J. D. Donaldson, M. T. Donoghue, and C. H. Smith, *Acta Cryst.*, 1976, **B32**, 2098.

simple 1 : 1 tin(II) carboxylate. We now report the structure of tin(II) maleate monohydrate.

EXPERIMENTAL

Tin maleate monohydrate was prepared [3] by dissolving blue-black SnO (0.6 mol) in boiling aqueous 40% w/v maleic acid (50 mol). The hot cloudy solution was filtered, and on cooling white crystals separated (Found: C, 19.0; H, 1.6; O, 30.6; Sn, 47.4. $C_4H_4O_5Sn$ requires C, 19.1; H, 1.6; O, 31.9; Sn, 47.4%).

Crystal Data.—$C_4H_4O_5Sn$, $M = 251$, Orthorhombic, $a = 7.35(1)$, $b = 16.84(2)$, $c = 5.32(1)$ Å, $U = 659$ Å^3, $D_m = 2.52$, $Z = 4$, $D_c = 2.53$, $F(000) = 472$. Space group $P2_1ab$ (C_{2v}^5, No. 29, in a non-standard setting) or $Pmab$ (D_{2h}^{11}, No. 57, in a non-standard setting) from systematic absences: $hk0$ when $h \neq 2n$ and $h0l$ when $l \neq 2n$. $P2_1ab$ was confirmed by the subsequent successful refinement. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 36 cm^{-1}. Single-crystal precession and Weissenberg photographs and diffractometer data.

Structure Determination.—Intensity data were collected about the c axis (layers $hk0$—5) with a Stoe two-circle computer-controlled 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° on the lower levels, counting for 1s at 0.01° intervals. For reflections on the second 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 $0.1 < \sin\theta/\lambda \leqslant 0.65$, 822 independent reflections having $I > 2.5\sigma(I)$ were obtained and considered observed. Data were corrected for Lorentz and polarization factors but not for absorption.

The structure was solved by conventional Patterson–Fourier techniques. Scattering factors used were those for neutral atoms,[4] with corrections for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$) [5] applied to those for tin. Initial refinement by full-matrix least-squares methods was with layer scale-factors refined separately, and all atoms vibrating isotropically. Refinement was continued with the layer scale-factors held constant and with the introduction of anisotropic thermal parameters, for all 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 four hydrogen atoms of the structure were easily located *ca.* 1 Å from their respective carbon and oxygen atoms. The water molecule was refined as a rigid group with O–H fixed at 1.0 Å, H · · · H fixed at 1.58 Å, and the hydrogen-atom temperature factors held at U 0.05. The remaining two hydrogen atoms were not refined and their positional parameters are listed in Table 1. In the final stages of refinement the weighting scheme $w = [\sigma^2(F_o) + (0.07\,|F_o|)^2]^{-1}$ 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 0.030, and R' $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ was 0.042. All calculations were carried out on the ICL 1906A at the University of Birmingham Computer Centre using SHELX-76.[6] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21914 (6 pp., 1 microfiche),* final positional parameters and temperature factors, with their estimated standard deviations, in Table 1, and interatomic distances and angles in Table 2.

TABLE 1

Atomic positional and thermal (× 10^3) parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn	$\frac{1}{4}$	0.596 09(2)	0.639 66(6)	23.9(2)	20.0(2)	21.5(5)	3.6(1)	−2.7(3)	0.5(2)
O(1)	0.258 2(10)	0.473 2(2)	0.777 6(7)	28(2)	22(1)	25.5(8)	3(1)	−10(3)	4(3)
O(2)	0.530 1(8)	0.534 9(3)	0.487(1)	50(3)	32(2)	41(1)	7(2)	25(2)	8(2)
O(3)	0.422(1)	0.613 0(4)	0.969(1)	51(3)	19(2)	35(1)	−3(2)	−5(3)	−6(2)
O(4)	0.402 5(9)	0.740 2(4)	0.853 2(8)	45(3)	25(2)	35(1)	5(1)	−6(2)	2(2)
O(5)	0.016(1)	0.610 3(5)	0.927(1)	62(5)	35(3)	48(2)	4(3)	25(4)	5(3)
C(1)	0.645 2(9)	0.567 5(4)	0.351 0(9)	19(2)	25(3)	22(1)	2(2)	0(2)	2(2)
C(2)	0.662(1)	0.656 7(4)	0.360(1)	28(3)	25(3)	26(1)	−5(2)	4(2)	−9(3)
C(3)	0.583 3(9)	0.708 6(3)	0.209(1)	28(2)	23(2)	26(1)	−6(2)	0(2)	−1(2)
C(4)	0.460 3(8)	0.686 5(3)	−0.005(1)	24(2)	25(2)	25(1)	−5(1)	1(2)	−4(2)
H(1)	0.911(1)	0.647(1)	−0.099(1)	0.05 *					
H(2)	0.965(1)	0.566(1)	−0.029(1)	0.05 *					
H(3) †	0.747	0.676	0.498						
H(4) †	0.619	0.764	0.244						

* Isotropic, not refined. † Parameters not included in refinement. In the non-standard setting of the space group the equivalent positions are: x, y, z; $\frac{1}{2} + x, \bar{y}, \bar{z}$; $\frac{1}{2} + x, \frac{1}{2} - y, z$; $x, \frac{1}{2} + y, \bar{z}$.

DISCUSSION

The structure of tin(II) maleate monohydrate (Figure 1) consists of a three-dimensional network wherein each maleate group is bonded to three different tin(II) atoms *via* three of its oxygen atoms [O(1)—(3)] at 2.196(3), 2.440(6), and 2.176(7) Å. In addition to this, O(1) and O(4) of each maleate group is hydrogen bonded to H(2) and H(1) of different water molecules of crystallization, at 2.13(1) and 1.92(1) Å. The network is completed by a bond between each tin(II) atom and the oxygen of a water molecule at 2.312(9) Å.

Each tin(II) atom is at the apex of a distorted square pyramid, the basal plane of which is made up of four oxygen atoms, three from each of three different maleate groups and the fourth from a water molecule of crystallization. Two of the bonds are short (2.176 and 2.196 Å) and two are slightly longer (2.312 and 2.440 Å), with long and short bonds arranged alternately around the basal plane. The apex of the pyramid is occupied by a stereochemically active lone pair of electrons, and the next-

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[3] E. J. Filmore, Ph.D. Thesis, London, 1972.

[4] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[5] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[6] G. M. Sheldrick, 'Program for Crystal Structure Determination,' University of Cambridge, 1975.

nearest non-bonding Sn–O distances are 2.817 and 2.904 Å. Figure 2 shows the tin(II) environment.

This square-pyramidal arrangement around tin has also been found in the recently determined structure of $Na_2Sn[C_2O_4]_2$.[2] In this compound the tin(II) atom is surrounded by four oxygen atoms from two chelating oxalate groups. There are two short bonds (2.246 Å) and two slightly longer distances (2.357 Å), giving tin the distorted square-pyramidal environment. Again the apex is occupied by a stereochemically active lone-pair, which prevents close approach to the tin from this direction, and the next-nearest non-bonding Sn–O distance is 2.910 Å. This distorted square-pyramidal co-ordination of tin is found in a few other tin(II) compounds (discussed more fully in ref. 2) and the only compound where a regular square-pyramidal tin(II) environment has been reported is in tetragonal SnO,[7] a structure which has previously been rationalized in terms of *s*-electron density being donated from the lone pair into conduction bands, thus reducing the distorting effect of the lone pair.[8] The more common environment found for tin(II) 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. Again, these longer contacts arise because close approach to the tin is prevented by the lone-pair orbital in this direction. Tin(II) compounds with this type of environment are listed in ref. 2.

TABLE 2

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

(*a*) Distances			
Sn–O(1$^{\rm I}$)	2.196(3)	O(2) · · · O(3$^{\rm II}$)	2.987(8)
Sn–O(2)	2.440(6)	O(2) · · · H(2$^{\rm I}$)	3.38(1)
Sn–O(2$^{\rm I}$)	2.817(5)	O(2) · · · O(5$^{\rm IV}$)	3.293(9)
Sn–O(3$^{\rm II}$)	2.176(7)	O(2) · · · H(2$^{\rm IV}$)	3.01(1)
Sn–O(4$^{\rm II}$)	2.904(6)	O(3)–C(4)	1.278(8)
Sn–O(5$^{\rm III}$)	2.312(9)	O(3) · · · O(4)	2.233(8)
Sn · · · C(1)	3.321(6)	O(3) · · · O(5$^{\rm X}$)	3.00(1)
Sn · · · C(1$^{\rm I}$)	2.860(7)	O(3) · · · O(1$^{\rm IV}$)	2.831(8)
Sn · · · C(4$^{\rm II}$)	2.878(6)	O(3) · · · H(2$^{\rm IV}$)	3.04(1)
O(1)–C(1)	1.275(8)	O(4)–C(4)	1.253(8)
O(1) · · · O(2)	2.194(8)	O(4) · · · O(5$^{\rm VI}$)	2.68(1)
O(1) · · · O(5)	2.84(1)	O(4)–H(1$^{\rm VI}$)	1.92(1)
O(1) · · · H(1)	2.88(1)	O(4) · · · H(2$^{\rm VI}$)	3.36(1)
O(1)–H(2)	2.13(1)	C(1)–C(2)	1.51(1)
O(1) · · · O(2$^{\rm V}$)	2.731(8)	C(2)–C(3)	1.323(9)
O(1) · · · O(3$^{\rm IX}$)	2.831(8)	C(2)–H(3)	1.02(1)
O(1) · · · O(5$^{\rm IV}$)	3.02(1)	C(3)–C(4)	1.499(9)
O(1) · · · H(2$^{\rm IV}$)	2.85(1)	C(3)–H(4)	0.98(1)
O(2)–C(1)	1.242(8)	O(5)–H(1)	1.00
O(2) · · · O(3)	3.158(8)	O(5)–H(2)	1.00
(*b*) Angles			
O(1$^{\rm I}$)–Sn–O(2)	72.0(2)	Sn$^{\rm VII}$–O(3)–C(4)	110.2(5)
O(1$^{\rm I}$)–Sn–O(2$^{\rm I}$)	50.1(2)	Sn$^{\rm VII}$–O(4)–H(1$^{\rm VI}$)	153.2(4)
O(1$^{\rm I}$)–Sn–O(3$^{\rm II}$)	80.7(2)	Sn$^{\rm VII}$–O(4)–C(4)	76.3(4)
O(1$^{\rm I}$)–Sn–O(4$^{\rm II}$)	130.2(2)	C(4)–O(4)–H(1$^{\rm VI}$)	128.6(5)
O(1$^{\rm I}$)–Sn–O(5$^{\rm III}$)	84.1(3)	Sn$^{\rm VIII}$–O(5)–H(1)	123.1(7)
O(2)–Sn–O(2$^{\rm I}$)	94.2(2)	Sn$^{\rm VIII}$–O(5)–H(2)	114.3(9)
O(2)–Sn–O(3$^{\rm II}$)	80.4(2)	O(1)–C(1)–O(2)	121.3(7)
O(2)–Sn–O(4$^{\rm II}$)	99.0(2)	O(1)–C(1)–C(2)	119.8(6)
O(2)–Sn–O(5$^{\rm III}$)	152.9(2)	O(2)–C(1)–C(2)	118.7(6)
O(2$^{\rm I}$)–Sn–O(3$^{\rm II}$)	128.9(2)	C(1)–C(2)–C(3)	127.0(6)
O(2$^{\rm I}$)–Sn–O(4$^{\rm II}$)	165.8(2)	C(1)–C(2)–H(3)	113.3(6)
O(2$^{\rm I}$)–Sn–O(5$^{\rm III}$)	79.2(2)	C(3)–C(2)–H(3)	119.8(7)
O(3$^{\rm II}$)–Sn–O(4$^{\rm II}$)	49.7(2)	C(2)–C(3)–C(4)	124.2(5)
O(3$^{\rm II}$)–Sn–O(5$^{\rm III}$)	83.4(3)	C(2)–C(3)–H(4)	113.0(6)
O(4$^{\rm II}$)–Sn–O(5$^{\rm III}$)	86.7(2)	C(4)–C(3)–H(4)	122.7(6)
C(1)–O(1)–H(2)	129.5(4)	C(3)–C(4)–O(3)	117.3(6)
C(1)–O(1)–Sn$^{\rm V}$	108.0(4)	C(3)–C(4)–O(4)	118.9(5)
H(2)–O(1)–Sn$^{\rm V}$	121.4(3)	O(3)–C(4)–O(4)	123.8(6)
Sn–O(2)–C(1)	125.6(4)	O(5)–H(1)–O(4$^{\rm XI}$)	131(1)
Sn–O(2)–Sn$^{\rm V}$	153.4(2)	O(5)–H(2)–O(1)	138.1(9)
C(1)–O(2)–Sn$^{\rm V}$	79.3(4)		

Roman numerals, as superscripts, refer to atoms in the following equivalent positions:

I	$-\frac{1}{2} + x, 1 - y, 1 - z$	VII	$x, y, -1 + z$
II	$x, y, 1 + z$	VIII	$1 + x, y, -1 + z$
III	$-1 + x, y, 1 + z$	IX	$\frac{1}{2} + x, 1 - y, -z$
IV	$-\frac{1}{2} + x, 1 - y, -z$	X	$-1 + x, y, z$
V	$\frac{1}{2} + x, 1 - y, 1 - z$	XI	$\frac{1}{2} + x, \frac{3}{2} - y, z$
VI	$-\frac{1}{2} + x, \frac{3}{2} - y, z$		

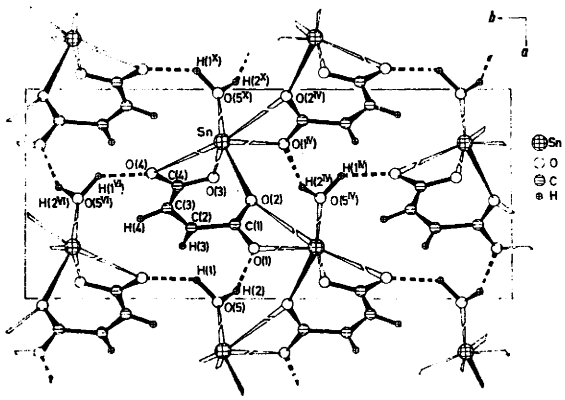

FIGURE 1 Projection of the structure down [001]. Open bonds, with single breaks, represent contacts to or from atoms which lie at 1 ± *z* to those shown. Dashed bonds represent hydrogen-bonding contacts. For symmetry code see footnote to Table 2

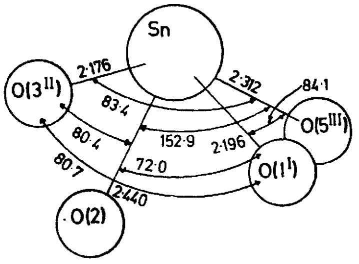

FIGURE 2 The tin(II) bonding environment [distances (Å), angles (°)]; for symmetry code see footnote to Table 2

The geometry of the maleate group is shown in Figure 1, and the bond lengths of the carbon skeleton agree well with those found for the maleate ion in potassium hydrogen maleate,[9] and those of cadmium(II)[10] and copper(II)[11] hydrated maleates. The carbon–oxygen bond lengths are also similar to those in the potassium compound and the angles are similar to those in both the potassium compound and those in maleic acid itself.[12,13] The bond

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lengths and angles around the hydrogen atoms on C(2) and C(**3**) are close to expected values. The tin(II) environment, in the present structure, is very different to the more symmetrical environments found for the cadmium(II) [10] and copper(II) [11] hydrated maleates, because of the distorting effect of the stereochemically active lone pair of non-bonding electrons on tin(II).

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