Crystal and Molecular Structure of Dimeric Dimethyltin Nitrate Hydroxide [Di-μ-hydroxo-bis(dimethylnitratotin)]

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Crystals of the title compound are triclinic, space group $B\bar{1}$, $a = 6\cdot53(2)$, $b = 8\cdot73(2)$, $c = 11\cdot20(3)$ Å, $\alpha = 86\cdot5(3)$, $\beta = 89\cdot2(4)$, $\gamma = 88\cdot3(3)^\circ$, $Z = 2$. The structure was determined from photographic data by Patterson and Fourier methods and refined by full-matrix least-squares to R 0·113 for 844 unique observed reflections. The structure consists of centrosymmetric hydroxo-bridged dimers, with $(SnO)_2$ rings, five-co-ordinate tin, and unidentate nitrate ligands. Except for the methyl groups, all the atoms in each dimeric molecule are approximately coplanar.

DIMETHYLTIN dinitrate,[1] methyltin trinitrate,[2] and tin tetranitrate[3] have recently been shown to possess asymmetric bidentate nitrate ligands, and tin co-ordination numbers of 6, 7, and 8 respectively. On the other hand the nitrate group in trimethyltin nitrate monohydrate[4] is unidentate, and the approximately trigonal bipyramidal co-ordination of tin involves axial $O(NO_2)$ and $O(H_2)$ substituents. Di-μ-hydroxo-bis(dimethylnitratotin) was first prepared by Yasuda and Okawara,[5] who assigned four possible structures on the basis of i.r. spectra and physical properties. All these structures involved six-co-ordinate tin and bridging nitrate and hydroxide groups. In view of the possible structural similarity with the dialkyltin halide alkoxides, $R_2Sn(OR')X$, we have determined the crystal structure of $Me_2Sn(OH)NO_3$. The structure reported here is different from those suggested by Yasuda and Okawara, but is consistent with the alkoxide-bridged dimeric structures suggested by Chapman *et al.* for the dialkyltin halide alkoxides.[6]

EXPERIMENTAL

The title compound was prepared by the reaction[5] of dimethyltin oxide with nitric acid, followed by evaporation to dryness. Approximately needle-shaped crystals (from methanol) were sealed into Lindemann glass capillary tubes. Preliminary investigations showed that decomposition became significant after *ca.* 40 h irradiation in the *X*-ray beam, so exposure times were minimised. Intensities were estimated visually from equi-inclimation Weissenberg photographs (layers 0—5*kl*) using nickel-filtered Cu-K_α radiation and a total exposure time of 34 h. Intensity data obtained about other oscillation axes were not of good enough quality to use in the structure refinement, so it was necessary to refine the inter-layer scale factors (with the consequence that little physical significance should be attached to the value of U_{11} for Sn). Lorentz, polarisation, and absorption corrections were applied. Unit-cell dimensions were obtained by least-squares analysis of 61 α_1—α_2 splittings on the 0—5*kl* and *h*0*l* Weissenberg photographs.[7]

RESULTS

Crystal Data.—$C_4H_{14}N_2O_8Sn_2$, $M = 455\cdot6$, Triclinic, $a = 6\cdot53(2)$, $b = 8\cdot73(2)$, $c = 11\cdot20(3)$ Å, $\alpha = 86\cdot5(3)$, $\beta = 89\cdot2(4)$, $\gamma = 88\cdot3(3)^\circ$, $U = 637\cdot2$ Å^3, $Z = 2$, $D_c = 2\cdot37$, $F(000) = 432$. Cu-K_α radiation, $\lambda = 1\cdot5418$ Å, $\mu(\text{Cu-}K_\alpha) = 327$ cm^{-1}. This unit cell (which is *B* face centred) was chosen in preference to a primitive cell because it gives interaxial angles close to 90°.† Space group $B1$ or $B\bar{1}$, the latter confirmed by successful refinement of the structure. All atoms occupy four-fold general positions; the structure determination revealed the presence of dimers, which are required by space-group symmetry to lie across centres of inversion.

Structure Solution and Refinement.—The tin atom co-ordinates were obtained by interpretation of the Patterson function, and the remaining atoms were located from difference electron-density syntheses. The structure was refined by full-matrix least squares, with an anisotropic temperature factor for tin and isotropic temperature factors for the other atoms. In the final stages of refinement a total of 44 parameters were varied simultaneously, including the Zachariasen secondary extinction coefficient, which refined[8] to the value $10^5 Q_0 r^* = 66(16)$ cm^{-1}. Complex neutral-atom scattering factors[9,10] were employed for all atoms. The weighting scheme was $w = 1/(3\cdot98 + |F_o| + 0\cdot00879|F_o|^2)$. The refinement converged at R' 0·122 (where $R' = \Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}|F_o|$), for a total of 844 unique observed reflections; the corresponding unweighted index R was 0·113. The strongest peak in the final difference Fourier was *ca.* 1·8 eÅ^{-3}. An analysis of variance is presented in Table 1, and the results of the final least-squares cycle in Table 2. Bond lengths and angles are in Table 3; no corrections have been applied for molecular thermal motion. Shortest non-bonded distances are in Table 4. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20902 (6 pp., 1 microfiche).‡ Figure 1 shows one dimeric molecule, and Figure 2 illustrates the packing of the molecules.

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† The Dirichet cell ($a = 6\cdot44$, $b = 6\cdot52$, $c = 8\cdot73$ Å, $\alpha = 86\cdot1$, $\beta = 87\cdot8$, $\gamma = 60\cdot5^\circ$) is obtained from the original cell by the matrix transformation (by rows): −0·5, 0, 0·5; 0·5, 0, 0·5; 0, 1, 0. The Delaunay cell ($a = 6\cdot44$, $b = 6\cdot53$, $c = 8\cdot73$ Å, $\alpha = 91\cdot7$, $\beta = 92\cdot2$, $\gamma = 119\cdot6^\circ$) is obtained by the transformation: 0·5, 0, −0·5; −1, 0, 0; 0, 1, 0.

‡ See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full size copies).

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TABLE 1

Analysis of variance

(*a*) As a function of the parity of the indices

	ggg	*gug*	*ugu*	*uuu*	All
N	204	202	224	214	844
V	340	357	357	332	347

(*b*) As a function of sin θ

Sin θ	0·00—0·40	0·40—0·51	0·51—0·59	0·59—0·64	0·64—0·71	0·71—0·75	0·75—0·81	0·81—0·87	0·87—0·93	0·93—0·99
N	89	89	80	81	94	73	87	92	86	73
V	473	381	394	430	352	280	275	296	213	273

(*c*) As a function of F_o

$(F_o/F_{max})^{\frac{1}{2}}$	0·00—0·18	0·18—0·22	0·22—0·26	0·26—0·29	0·29—0·33	0·33—0·38	0·38—0·43	0·43—0·49	0·49—0·58	0·58—1·00
N	89	84	99	75	77	96	72	99	73	80
V	264	264	281	321	337	314	356	418	451	426

(*d*) As a function of Weissenberg layer

h	0	1	2	3	4	5
N	110	168	160	159	136	111
V	335	383	326	331	384	301

N is the number of reflections in the group; *V* is the root mean square deviation (×10²) of a reflection of unit weight on absolute scale of *F*.

TABLE 2

Fractional co-ordinates (×10⁴) and isotropic temperature factors (Å² × 10³)

	x/a	*y/b*	*z/c*	*U*
Sn	6623(2)	3232(2)	8001(1)	*
N	2556(37)	1694(28)	8441(20)	80(5)
O(1)	3110(31)	3059(21)	8068(15)	73(4)
O(2)	3966(35)	695(26)	8706(20)	100(6)
O(3)	772(33)	1443(25)	8565(17)	88(5)
O(4)	9326(29)	4596(22)	7610(16)	84(5)
C(1)	6994(48)	3079(35)	9886(26)	84(7)
C(2)	6907(57)	1826(44)	6512(33)	114(11)

* Anisotropic temperature factors (Å² × 10³), in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn	82(4)	46(1)	78(1)	1(1)	−1(1)	−6(1)

TABLE 3

Molecular geometry

(*a*) Bond lengths (Å)

Sn–C(1)	2·12(4)	N–O(1)	1·30(3)
Sn–C(2)	2·13(4)	N–O(2)	1·27(3)
Sn–O(1)	2·30(3)	N–O(3)	1·20(3)
Sn–O(4)	2·18(3)		
Sn–O(4′)	2·06(3)		

(*b*) Bond angles (°)

O(1)–Sn–O(4)	149·3(1·5)	Sn–O(1)–N	111·5(1·7)
O(1)–Sn–O(4′)	77·9(1·5)	Sn–O(4)–Sn′	108·6(1·1)
O(4)–Sn–O(4′)	71·4(1·4)		
O(1)–Sn–C(1)	95·4(1·0)	O(2)–N–O(1)	117·7(2·7)
O(1)–Sn–C(2)	92·6(1·3)	O(3)–N–O(1)	119·3(2·5)
C(1)–Sn–O(4′)	111·5(1·1)	O(3)–N–O(2)	123·0(2·8)
C(2)–Sn–O(4′)	108·6(1·2)		
C(1)–Sn–O(4)	95·5(1·1)		
C(2)–Sn–O(4)	97·3(1·4)		
C(2)–Sn–C(1)	139·9(1·4)		

TABLE 4

Non-bonded distances <3·8 Å

(*a*) Within the asymmetric unit

Sn ··· N	3·03	O(1) ··· C(1)	3·28
Sn ··· O(2)	2·92	O(1) ··· C(2)	3·21
		O(2) ··· O(3)	2·17
N ··· C(1)	3·61	O(2) ··· C(1)	3·26
N ··· C(2)	3·55	O(2) ··· C(2)	3·22
		O(4) ··· C(1)	3·19
O(1) ··· O(2)	2·20	O(4) ··· C(2)	3·24
O(1) ··· O(3)	2·15		

TABLE 4 (*Continued*)

(*b*) Others

$N^{I}\cdots O(4)$	3·34	$O(2^{III})\cdots O(2)$	3·62
$O(1^{I})\cdots O(4)$	2·81	$O(2^{III})\cdots O(3)$	3·24
$O(3^{I})\cdots Sn$	3·14	$O(3^{III})\cdots C(2)$	3·40
$O(3^{I})\cdots O(4)$	3·02	$O(2^{IV})\cdots C(2)$	3·44
$O(3^{I})\cdots C(1)$	3·20	$N^{V}\cdots C(2)$	3·47
$O(3^{I})\cdots C(2)$	3·43	$O(2^{V})\cdots C(2)$	3·58
$Sn^{II}\cdots Sn$	3·44	$O(3^{V})\cdots C(2)$	3·43
$O(1^{II})\cdots O(4)$	2·75	$O(4^{V})\cdots C(1)$	3·78
$O(4^{II})\cdots O(4)$	2·48	$C(1^{VI})\cdots O(1)$	3·65
$O(4^{II})\cdots C(1)$	3·46	$C(1^{VI})\cdots O(4)$	3·78
$O(4^{II})\cdots C(2)$	3·40	$O(1^{VII})\cdots O(1)$	3·62
$N^{III}\cdots N$	3·74	$O(2^{IX})\cdots O(2)$	3·36
$N^{III}\cdots O(2)$	3·45	$O(2^{IX})\cdots C(1)$	3·63
$N^{III}\cdots O(3)$	3·77		

Roman numeral superscripts refer to the following equivalent positions:

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

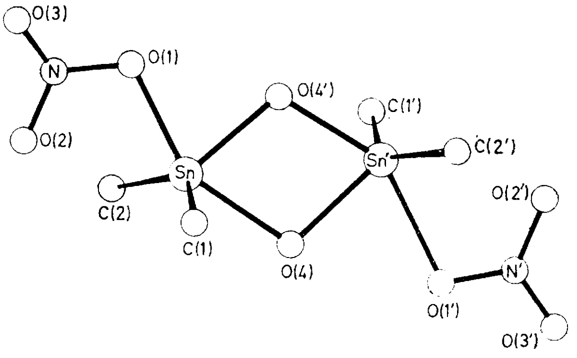

FIGURE 1 View of one dimeric molecule

DISCUSSION

The structure consists of $[Me_2Sn(OH)(NO_3)]_2$ molecules, with $(SnO)_2$ rings, five-co-ordinate tin, and unidentate nitrate ligands. The Sn–ONO_2 bond [2·30(3) Å] is appreciably longer than the Sn–O bonds involving the bridging hydroxide groups [2·18(3) and 2·06(3) Å], possibly indicating some ionic character. The co-ordination of the tin atom can be described as very distorted trigonal bipyramidal, with the methyl groups

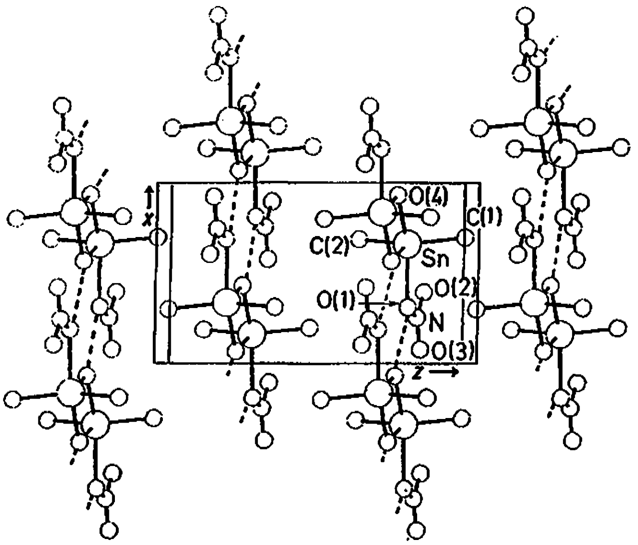

FIGURE 2 The structure in projection down the Y axis with the asymmetric unit labelled. Probable hydrogen bonds are indicated by dashed lines

and shorter Sn–O(H) bond equatorial. As in the other methyltin nitrates [1-4] the longest N–O bond is to the oxygen atom bonded to tin. No attempt was made to locate the hydrogen atoms from the diffraction data, but the short intermolecular distance O(1) $\cdots$ O(4′) 2·81 Å may well involve an O–H $\cdots$ O hydrogen bond, in which case the molecules are joined by pairs of hydrogen bonds to form infinite chains along the X axis, which is the crystal needle axis. All the atoms in one dimeric molecule, except the methyl groups, lie approximately in the plane defined by: $0{\cdot}106x + 2{\cdot}948y + 10{\cdot}753z = 9{\cdot}619$ Å, where x, y, and z are fractional co-ordinates; the mean deviation is 0·014 Å. The probable hydrogen bonds also lie approximately in this plane.

Although the structure found is unlike any of those suggested by Yasuda and Okawara,[5] it does not appear to be inconsistent with the i.r. spectrum reported by them (and confirmed by us); there is a possible ambiguity in the assignment of the Sn–C stretching modes, and the insolubility in non-polar solvents may be the result of intermolecular hydrogen bonding rather than nitrate bridging.

Calculations were performed by use of the Cambridge University IBM 370/165 computer and programs by G. M. S.

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