Crystal Structure of Polymeric Tris(trimethyltin) Chromate Hydroxide

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Crystals of the title compound are orthorhombic, space group *Pbca*, *a* = 20·85(2), *b* = 11·55(2), *c* = 16·58(2) Å (at *ca.* −30 °C), *Z* = 8. The structure was determined at *ca.* −30 °C from diffractometer data by direct methods and refined by full-matrix least-squares to *R* 0·045 for 488 unique observed reflexions. The structure consists of a complicated network polymer. There are three crystallographically independent and approximately planar trimethyltin groups, and in each case, approximately trigonal bipyramidal co-ordination of the tin atom is completed by two axial oxygen atoms. Each oxygen atom in the chromate group is also bonded to tin, and the hydroxide group bridges two trimethyltin groups and is probably hydrogen bonded to one of the chromate oxygens. The two tin atoms linked by the hydroxide group have similar co-ordination geometries, with short Sn–O(H) [2·14(3) and 2·17(4) Å] and long Sn–O(Cr) [2·48(5) and 2·51(4) Å]. The two oxygen atoms responsible for the long Sn–O bonds make the shortest two Cr–O bond lengths [1·61(4) and 1·56(4) Å]. Other bond lengths and angles are: Sn–O, 2·16(4) and 2·29(4); Cr–O, 1·78(4) and 1·70(4); mean Sn–C, 2·13 Å; mean C–Sn–C, 119; mean O–Sn–O, 176; mean Cr–O–Sn, 144; and Sn–O–Sn, 136(2)°.

TRIMETHYLTIN chromate was first prepared by Clark and Goel,[1] who suggested a structure having planar trimethyltin groups and chromate groups of T_d symmetry on the basis of the i.r. spectrum. Both features are consistent with a polymeric structure in which all four chromate oxygens are co-ordinated to tin, although from the i.r. spectrum, it was not possible to distinguish between an ionic and a co-ordinated structure. For trimethyltin perchlorate[2,3] and related compounds, the i.r. spectra were consistent with structures in which the co-ordination of tin was trigonal bipyramidal, with axial oxygen atoms and equatorial methyl groups. As part of our study of the structures of organotin derivatives we have determined the structure of a crystal which we thought was trimethyltin chromate, but which turned out to be a partial hydrolysis product.

EXPERIMENTAL

Trimethyltin chromate was prepared[1] by the reaction of trimethyltin chloride with silver chromate in dry methanol. Precipitated silver chloride was immediately filtered off, and solvent removed under vacuum at room temperature. The yellow solid obtained was identified as $(Me_3Sn)_2CrO_4$ on the basis of its i.r. spectrum and elemental analysis (Found: C, 16·1; H, 3·7. Calc. for $C_6H_{18}O_4CrSn_2$: C, 16·2; H, 4·0%). It proved very difficult to obtain crystals suitable for *X*-ray diffraction. Eventually a few needle-shaped yellow crystals were obtained by adding diethyl ether to an acetone solution and storing at *ca.*

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[1] H. C. Clark and R. G. Goel, *Inorg. Chem.*, 1965, **4**, 1428.

[2] R. Okawara, B. J. Hathaway, and D. E. Webster, *Proc. Chem. Soc.*, 1963, 13.

[3] H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, 1963, **2**, 740.

−10 °C for 2 weeks. The crystals were sealed into Lindemann glass capillary tubes. Preliminary *X*-ray photographs indicated appreciable thermal motion of the atoms and some decomposition of the crystals in the *X*-ray beam, so the intensity data were collected at *ca.* −30 °C.

TABLE 1

Analysis of variance

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

	ggg	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	133	59	63	23	69	36	71	34	488
V	1102	1120	1247	1222	1251	1651	813	922	1154

(*b*) As a function of sin θ

sin θ	0·00—0·12	—0·15	—0·18	—0·19	—0·21	—0·23	—0·25	—0·28	—0·31	—0·44
N	51	50	65	32	59	48	41	58	47	37
V	1392	997	1051	835	963	869	986	1478	1009	1658

(*c*) As a function of F_o

$(F_o/F_{max})^{\frac{1}{2}}$	0·00—0·38	—0·42	—0·44	—0·48	—0·50	—0·52	—0·55	—0·59	—0·67	—1·00
N	53	57	36	66	45	43	51	41	49	47
V	1223	1224	1319	1039	1020	1560	1265	992	841	957

(*d*) As a function of the equi-inclination layer number

k	0	1	2	3	4	5	6	7	8
N	54	81	109	64	78	26	38	20	18
V	1043	1102	1141	884	1049	1207	1729	1048	1520

N is the number of reflexions in the group; *V* is the root-mean-square deviation (× 10²) of a reflexion of unit weight on a absolute scale of *F* [$V = 100(M\Sigma w\Delta^2/N\Sigma w)^{\frac{1}{2}}$ where *M* is the total number of reflexions].

Intensities were determined on a Stoe Stadi-2 two-circle diffractometer (layers *h*0—8*l* inclusive), with Mo-K_α radiation and a graphite-crystal monochrometer. A Stoe low-temperature attachment was used to generate a cold nitrogen stream which was directed at the crystal along the oscillation axis direction. Heated mylar screens were used to minimise condensation. Data were collected in an approximately ' constant count ' mode; where a prescan indicated that the count could not be achieved within a specified time, the reflexion was ignored. A stationary background–ω scan–stationary background technique was employed, with variable reflexion width, and with the background measurement time proportional to the step measurement time. A total of **1415** reflexions were measured, from 4 octants hkl, $hk\bar{l}$, $\bar{h}kl$, and $\bar{h}k\bar{l}$, of which **205** were rejected because the net count was $<3\sigma$ based on counting statistics, because of background imbalance, or because of peak centring errors. Averaging equivalent reflexions led to 488 unique observed reflexions. Although the data were placed on a common scale by use of repeated measurements of standard (zero-layer) reflexions, it was found that refinement of the inter-layer scale factors led to a significant improvement in the final stages of structure refinement. Lorentz, polarisation, and absorption corrections were applied. Unit-cell dimensions were obtained from diffractometer ω and μ angle measurements at *ca.* −30 °C.

RESULTS

Crystal Data.—$C_9H_{28}CrO_5Sn_3$, $M = 624{\cdot}4$, Orthorhombic, $a = 20{\cdot}85(2)$, $b = 11{\cdot}55(2)$, $c = 16{\cdot}58(2)$ Å, $U = 3991$ Å³, $Z = 8$, $D_c = 2{\cdot}08$. $F(000) = 2368$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 42·8 cm⁻¹. Space group *Pbca* from systematic absences: 0*kl* with *k* odd, *h*0*l* with *l* odd, and *hk*0 with *h* odd. All atoms occupy the eight-fold general positions of the set $\pm(x, y, z;\ \tfrac{1}{2} + x, \tfrac{1}{2} - y, -z;\ -x, \tfrac{1}{2} + y, \tfrac{1}{2} - z;\ \tfrac{1}{2} - x, -y, \tfrac{1}{2} + z)$. The asymmetric unit consists of one formula unit.

Structure Solution and Refinement.—Attempts to interpret the Patterson function assuming that the crystal was trimethyltin chromate were not entirely successful, so multisolution Σ_2 refinement was employed instead to locate the heavy atoms. The asymmetric unit of the resulting *E* map contained only three strong- and one medium-intensity peaks. Successive difference electron-density syntheses calculated on the assumption that these were three tin and one chromium atom revealed the remaining atoms and the chemical identity of the crystal.

TABLE 2

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

	x/*a*	*y*/*b*	*z*/*c*	*U*
Sn(1)	4776(1)	5344(4)	2443(3)	*
Sn(2)	2492(2)	9784(4)	3509(2)	*
Sn(3)	1467(3)	11 359(4)	5231(2)	*
Cr	3943(4)	8036(7)	2521(8)	*
O(1)	3962(17)	8028(34)	1580(25)	69(13)
O(2)	3248(18)	8415(36)	2861(23)	64(13)
O(3)	4061(15)	6578(34)	2832(20)	48(12)
O(4)	4523(16)	8904(32)	2911(22)	52(12)
O(5)	1828(13)	10 986(27)	4031(20)	28(9)
C(1)	4197(23)	4576(54)	1535(34)	55(17)
C(2)	4714(20)	4662(47)	3601(27)	35(14)
C(3)	5494(21)	6528(45)	2209(27)	31(16)
C(4)	2544(21)	10 625(45)	2372(32)	41(16)
C(5)	1877(22)	8183(48)	3578(31)	42(17)
C(6)	3235(18)	10 037(43)	4380(27)	27(13)
C(7)	655(19)	12 493(47)	4803(28)	31(13)
C(8)	1335(30)	9618(67)	5546(36)	89(22)
C(9)	2294(25)	12 231(59)	5640(35)	68(21)

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

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	26(2)	50(3)	42(3)	11(3)	0(3)	5(2)
Sn(2)	30(2)	42(3)	29(2)	4(3)	−2(2)	1(3)
Sn(3)	38(2)	53(3)	23(2)	−6(3)	5(2)	−6(3)
Cr	35(4)	33(6)	29(5)	−7(7)	7(6)	1(5)

No attempt was made to locate the hydrogen atoms. The structure was refined by full-matrix least squares, with a weighting scheme $w = (109{\cdot}29 + |F_o| + 0{\cdot}00269\ F_o^2)^{-1}$. Complex neutral-atom scattering factors were employed for all atoms.[4,5] An attempt to refine an isotropic secondary extinction parameter did not result in a significant improvement, so extinction was ignored. In the final

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[4] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

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

TABLE 3

Molecular geometry

(*a*) Bond lengths (Å)

Sn(1)–O(3)	2·16(4)	Sn(1)–C(1)	2·10(6)
Sn(1)–O(4)	2·29(4)	Sn(1)–C(2)	2·08(5)
Sn(2)–O(2)	2·48(5)	Sn(1)–C(3)	2·06(5)
Sn(2)–O(5)	2·14(3)	Sn(2)–C(4)	2·12(6)
Sn(3)–O(5)	2·17(4)	Sn(2)–C(5)	2·25(6)
Sn(3)–O(1)	2·51(4)	Sn(2)–C(6)	2·14(5)
		Sn(3)–C(7)	2·25(5)
Cr–O(1)	1·56(4)	Sn(3)–C(8)	2·10(8)
Cr–O(2)	1·61(4)	Sn(3)–C(9)	2·11(6)
Cr–O(3)	1·78(4)		
Cr–O(4)	1·70(4)		

(*b*) Bond angles (°)

C(2)–Sn(1)–C(1)	117(2)	C(1)–Sn(1)–O(3)	95(2)
C(3)–Sn(1)–C(1)	124(2)	C(2)–Sn(1)–O(3)	86(2)
C(3)–Sn(1)–C(2)	118(2)	C(3)–Sn(1)–O(3)	97(2)
C(5)–Sn(2)–C(4)	117(2)	C(1)–Sn(1)–O(4)	83(2)
C(6)–Sn(2)–C(4)	120(2)	C(2)–Sn(1)–O(4)	90(2)
C(6)–Sn(2)–C(5)	119(2)	C(3)–Sn(1)–O(4)	88(2)
C(8)–Sn(3)–C(7)	122(2)	C(4)–Sn(2)–O(2)	83(2)
C(9)–Sn(3)–C(7)	116(2)	C(4)–Sn(2)–O(5)	95(2)
C(9)–Sn(3)–C(8)	119(3)	C(5)–Sn(2)–O(2)	82(2)
		C(5)–Sn(2)–O(5)	98(2)
O(2)–Cr–O(1)	112(2)	C(6)–Sn(2)–O(2)	85(2)
O(3)–Cr–O(1)	106(2)	C(6)–Sn(2)–O(5)	96(2)
O(3)–Cr–O(2)	106(2)	C(7)–Sn(3)–O(5)	95(2)
O(4)–Cr–O(1)	111(2)	C(8)–Sn(3)–O(5)	95(2)
O(4)–Cr–O(2)	110(2)	C(9)–Sn(3)–O(5)	96(2)
O(4)–Cr–O(3)	110(2)	C(7)–Sn(3)–O(1)	81(2)
		C(8)–Sn(3)–O(1)	90(2)
Cr–O(1)–Sn(3)	152(2)	C(9)–Sn(3)–O(1)	82(2)
Cr–O(2)–Sn(2)	153(2)		
Cr–O(3)–Sn(1)	129(2)	O(5)–Sn(2)–O(2)	178(1)
Cr–O(4)–Sn(1)	142(2)	O(3)–Sn(1)–O(4)	175(1)
		O(1)–Sn(3)–O(5)	175(1)
Sn(3)–O(5)–Sn(2)	136(2)		

TABLE 4

Non-bonded distances <3·8 Å

(*a*) Within asymmetric unit

Sn(1) · · · Cr	3·56
Cr · · · C(3)	3·71
O(1) · · · O(2)	2·63
O(1) · · · O(3)	2·67
O(1) · · · O(4)	2·70
O(2) · · · O(3)	2·72
O(2) · · · O(4)	2·72
O(3) · · · O(4)	2·86
O(1) · · · C(3)	3·78
O(2) · · · C(4)	3·05
O(2) · · · C(5)	3·11
O(2) · · · C(6)	3·14
O(3) · · · C(1)	3·15
O(3) · · · C(2)	2·89
O(3) · · · C(3)	3·16
O(4) · · · C(3)	3·60
O(5) · · · C(4)	3·16
O(5) · · · C(5)	3·32
O(5) · · · C(6)	3·18
O(5) · · · C(7)	3·26
O(5) · · · C(8)	3·14
O(5) · · · C(9)	3·18
C(1) · · · C(2)	3·56
C(1) · · · C(3)	3·68
C(2) · · · C(3)	3·55
C(4) · · · C(5)	3·72
C(4) · · · C(6)	3·69
C(5) · · · C(6)	3·79
C(7) · · · C(9)	3·70
C(8) · · · C(9)	3·62

(*b*) Others

$O(2^{I}) \cdots O(5)$	3·41
$O(3^{I}) \cdots O(5)$	2·80
$O(2^{I}) \cdots C(4)$	3·71
$O(3^{I}) \cdots C(4)$	3·60
$O(3^{I}) \cdots C(7)$	3·48
$O(4^{I}) \cdots C(7)$	3·55
$C(2^{I}) \cdots C(5)$	3·73
$O(5^{II}) \cdots C(2)$	3·63
$O(5^{II}) \cdots C(5)$	3·78
$C(4^{II}) \cdots C(5)$	3·77
$C(2^{III}) \cdots C(8)$	3·76
$C(3^{IV}) \cdots C(5)$	3·70
$O(1^{V}) \cdots C(7)$	3·11
$O(1^{V}) \cdots C(8)$	3·27
$O(1^{V}) \cdots C(9)$	3·06
$Sn(1^{VI}) \cdots Cr$	3·77
$O(1^{VII}) \cdots C(2)$	3·36
$O(4^{VII}) \cdots C(1)$	2·92
$O(4^{VII}) \cdots C(2)$	3·10
$O(4^{VII}) \cdots C(3)$	3·04

Roman numeral superscripts refer to the following equivalent positions:

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

cycles of refinement a total of 101 parameters were varied independently, with anisotropic temperature factors for the tin and chromium atoms, and isotropic temperature factors for the remaining atoms. Since it was also necessary to refine the 8 inter-layer scale factors, the values of U_{22} are not reliable. The final value of R' was 0·048 (where $R' = \Sigma w^{\frac{1}{2}}|F_o| - F_c|/\Sigma w^{\frac{1}{2}}|F_o|$), with a corresponding unweighted index R of 0·045. All peaks in the final difference electron-density synthesis were $<0·4$ eÅ^{-3}, compared with an electron-density maximum of 5·9 eÅ^{-3} for the weakest carbon atom. An analysis of variance is presented in Table 1; atomic co-ordinates and anisotropic temperature factors from the final least-squares cycle are in Table 2; the resulting bond lengths and angles are in Table 3. Shortest non-bonded distances are in Table 4. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20903 (4 pp., 1 microfiche).*

DISCUSSION

The three crystallographically independent and approximately planar trimethyltin groups are linked by the chromate and hydroxide groups to form a complicated network polymer. There are $-Me_3Sn(1)-O(3)-CrO_2-O(4)-Me_3Sn(1')-O(3')-Cr'O_2-O(4')-$ chains in the *Y* axis direction (Figure 1), and $-O(1)-CrO_2-O(2)-Me_3Sn(2)-O(5)H-Me_3Sn(3)-O(1')-Cr'O_2-O(2')-$ chains along the *Z* axis (Figure 2). Each oxygen atom in the chromate moiety is also bonded to a tin atom, and the hydroxide group bridges two trimethyltin groups. The co-ordination of each tin atom is approximately trigonal bipyramidal, with three equatorial methyl groups and two axial oxygen atoms. The two tin atoms linked by the hydroxide group have similar co-ordination geometries, with short Sn–O(H) [2·14(3) and 2·17(4) Å] and long Sn–O(Cr) [2·48(5) and 2·51(4) Å]. In each case the three methyl carbon atoms are bent away from the shorter Sn–O bond [mean C–Sn(2,3)–O(H) 96(1), mean C–Sn(2,3)–O(Cr) 84(2)°], so that the co-ordination geometry may be considered to be intermediate between trigonal bipyramidal (OC_3O) and

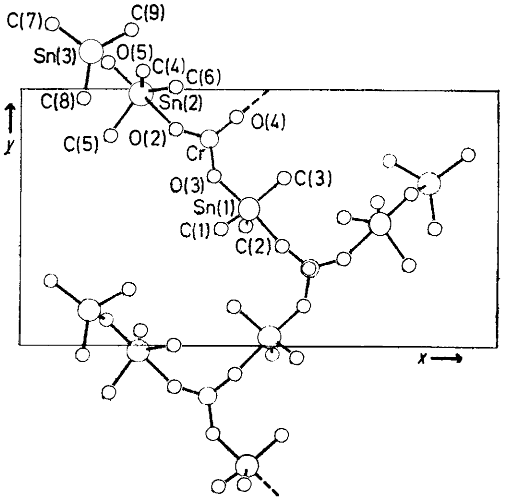

FIGURE 1 Projection of part of the structure perpendicular to *Z*, showing the chains in the *Y* axis direction

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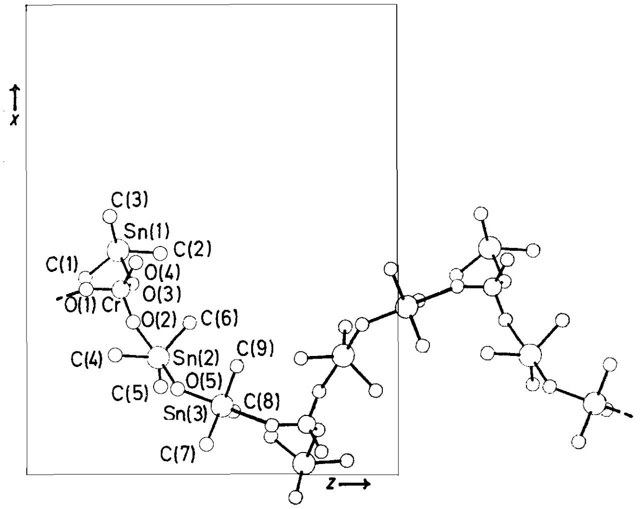

FIGURE 2 Projection of part of the structure perpendicular to Y, showing the chains in the Z axis direction

tetrahedral (OC_3), the long Sn–O bond being omitted from the tetrahedron. A similar intermediate tin co-ordination number arises in trimethyltin isothiocyanate (NC_3 or NC_3S).[6] The co-ordination of the remaining tin atom is less distorted from trigonal bipyramidal, though here again the carbon atoms of the methyl groups tend to be bent away from the shorter Sn–O bond [Sn(1)–O(3) 2·16(4), Sn(1)–O(4) 2·29(4) Å; mean C–Sn(1)–O(3) 93(3)°, mean C–Sn(1)–O(4) 87(3)°]. There is a complete inverse correlation between Cr–O and Sn–O bond lengths to the same oxygen atom, the shortest Cr–O distance corresponding to the longest Sn–O distance. The mean Sn–O–Cr angle is 144°, but there are considerable variations, with the smallest angle corresponding to the longest Cr–O bond. The mean Sn–C distance has the unexceptionable value of 2·13(4) Å; the mean O–Sn–O angle is 176(1) and the mean C–Sn–C angle is 119(2)°.

It is interesting to compare the structure with that of Me_3SnNCO,Me_3SnOH,[7] which is a partial hydrolysis product of trimethyltin isocyanate. The $-Me_3Sn-O(H)-Me_3Sn-$ units in the two structures have almost identical dimensions (isocyanate given first): mean Sn–O 2·15(5), 2·16(3) Å; Sn–O–Sn 138(3), 136(2); mean C–Sn–O(H) 95(2), 96(1)°. In both structures there is probably a hydrogen bond involving the O(H) group and another oxygen atom [2·84(8) in the isocyanate; O(3) · · · O(5′) 2·80(4) Å in the chromate].

The two pairs of Cr–O distances straddle the values found for ionic chromates {*e.g.* mean Cr–O 1·658(4) Å in $[NH_4]_2CrO_4$},[8] but are close to those for the two pairs of Cr–O distances in $(Ph_3Si)_2CrO_4$ [mean 1·54(2) and 1·74(4) Å].[9] The O–Cr–O angles do not differ significantly from the tetrahedral value. The structure reported here for the chromate hydroxide is consistent with the suggested structure for trimethyltin chromate,[1] in which there is trigonal bipyramidal (OC_3O) co-ordination of tin and all four chromate oxygen atoms are bonded to tin.

Calculations were performed by use of the Cambridge University IBM 370/165 computer and programs by G. M. S., and the structural diagrams were produced by use of the program PLUTO by Dr. S. Motherwell. We thank the S.R.C. for providing the diffractometer.

[3/1860 *Received, 7th September,* 1973]

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