Di-μ_3-oxo-bis-(μ-dichloro)-bis[μ-dimethyltin(IV)]-bis-[chlorodimethyltin(IV)]; a Decomposition Product of Dimethylchlorotin(IV) Ethylxanthate

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As part of a general study covering the chemistry of metal haloxanthate complexes [1–6] we prepared dimethylchlorotin(IV) ethylxanthate by addition of potassium ethylxanthate to a dichloromethane solution containing dimethyltin(IV) dichloride. The tin-119 NMR spectrum of the filtrate after removal of potassium chloride showed a single resonance (δ^{119}Sn −123) consistent with the formation of dimethylchlorotin(IV) ethylxanthate. A tin −119 resonance is observed in an identical position for a solution containing equimolar quantities of dimethyltin(IV) dichloride and dimethyl bis(ethylxanthato)tin(IV). Fractional crystallisation of either solution gives two products one of which analyses for $(CH_3)_4Sn_2Cl_2O$ and the other which analyses for $(CH_3)_2Sn(Cl)(S_2COC_2H_5)$. The latter compound has infrared absorptions ν_{CO} 1260 cm^{-1} ν_{CS} 1000, 1028 cm^{-1} consistent with its formulation as $(CH_3)_2Sn(Cl)(S_2COC_2H_5)$. In order to characterize $Me_4Sn_2Cl_2O$ a single crystal X-ray structural determination was undertaken which showed the compound to be the dimeric species $[Me_4Sn_2Cl_2O]_2$, identical with the structure previously reported for the compound obtained from the reaction between dimethyl tin(IV) dichloride and 2-amino-benzthiazole [7].

Intensity data were collected on an Enraf-Nonius CAD-4F, four circle, single crystal, automatic diffractometer. A crystal of approx. dimensions 0.38 × 0.33 × 0.11 mm was used. Accurate cell dimensions were obtained from the setting angles of 25 reflections, using MoKα radiation (0.71069 Å). A total of 3410 reflections were measured, in the range $2° \leqslant 2\theta \leqslant 53°$; of these 2530 were unique and 2096 were considered observed, $I \geqslant 2\sigma(I)$. The data were then corrected for Lorentz, polarization and absorption effects.

Crystal Data

$C_4H_{12}Cl_2OSn_2$, M = 384.43, monoclinic, a = 7.281(1), b = 18.532(2), c = 8.7218(8) Å, β = 109.82(1)°, U = 1107.1 Å^3, Dm = 2.27 Mgm^{-3}, Z = 4, Dc = 2.306 Mgm^{-3}, $F(000)$ = 712, space group $P2_1/c$ (No. 14), MoKα (graphite monochromatic) radiation 0.71069 Å, μ = 4.592 mm^{-1}.

TABLE I. Atomic Coordinates of $[Me_4Sn_2Cl_2O]_2$, Standard Deviations in Parentheses.

Atom	x/a	y/b	z/c
Sn(1)	0.06482(6)	0.33707(2)	0.65916(4)
Sn(2)	0.01407(6)	0.46319(2)	0.33177(4)
Cl(1)	0.0370(4)	0.3880(1)	0.9090(2)
Cl(2)	0.0974(4)	0.3207(1)	0.3515(2)
O	0.0324(7)	0.4382(2)	0.5641(4)
C(1)	−0.2690(11)	0.4457(4)	0.1646(9)
C(2)	0.2924(10)	0.4798(5)	0.3093(8)
C(3)	0.3655(11)	0.3121(5)	0.7516(9)
C(4)	−0.2109(11)	0.2866(4)	0.5625(9)

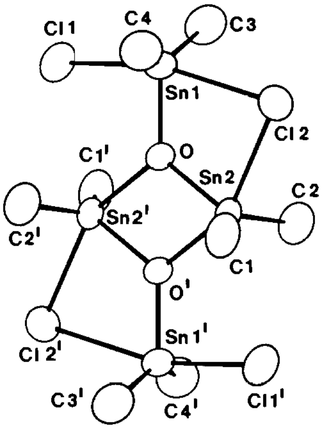

Fig. 1. Diagram of $[Me_4Sn_2Cl_2O]_2$, showing numbering scheme. Primed atoms are related by the centre of symmetry (0, ½, ½) to the coordinates in Table I.

The coordinates of all non-hydrogen atoms were obtained by Patterson and Fourier methods. Refinement was achieved using a least squares refinement procedure, employing anisotropic thermal parameters, and a weighting scheme of $w = (\sigma^2(F) + 0.00015F^2)^{-1}$; the refinement converging with R 0.032 and Rw 0.033. The final difference map showed peaks of height 0.6 e Å^{-3} or less. Some of these were at positions expected of hydrogen atoms, however as not all hydrogen atoms could be located, none was included in the refinement.

Calculations for the structure determination and refinement were performed using the SHELX-76 program system [8]; the scattering factors used were those incorporated in the program. The final atomic coordinates, given in Table I, are those of atoms of the same asymmetric unit, whereas those of Harrison *et al.* [7] appear to be of different asymmetric units. Listings of the final calculated and observed structure factors, anisotropic temperature factors, bond angles, intermolecular contacts, and

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TABLE II. Bond Lengths (A) for $[Me_4Sn_2Cl_2O]_2$, Standard Deviations in Parentheses.

Atoms	Separation	Atoms	Separations
Sn(1)–Cl(1)	2.445(2)	Sn(2)–Cl(2)	2.702(2)
Sn(1)–Cl(2)	2.789(2)	Sn(2)–O	2.038(4)
Sn(1)–O	2.031(4)	Sn(2)–$O^{I\ a}$	2.118(4)
Sn(1)–C(3)	2.112(8)	Sn(2)–C(1)	2.107(8)
Sn(1)–C(4)	2.114(8)	Sn(2)–C(2)	2.124(7)
Sn(1)–$Cl(2^{II})^b$	3.339(2)	Sn(2)–$Cl(1^I)^a$	3.409(2)
Sn(2)·····$Sn(2^I)^a$	3.3049(5)	Sn(2)····Sn(1)	3.7508(5)
O·········O^I	2.522(2)	Sn(2)····$Sn(1^I)^a$	3.6107(5)

[a] I = (–x, 1 – y, 1 – z). [b] II = (x, ½ – y, ½ + z).

the equations of the mean planes have been deposited with the editors. There are some anomalies with the planes data given in ref. [7]. Bond lengths are given in Table II.

Our final result of *R* 0.033 is lower than the value of *R* 0.087, obtained by Harrison *et al.* [7]. We believe that this is substantially due to the present work correcting the intensity data for absorption effects, which was not done by the previous authors. This however has little effect on the structural details (Fig. 1). The geometry around Sn(1) is a distorted *cis*-R_2SnXYZ trigonal bipyramid, with an additional intermolecular interaction with a chlorine atom ($Cl(2^{II})$ 3.339(2) Å) which bisects the C(3)–Sn–C(4) angle. This increases the coordination to 6, and results in a polymer in the solid state. The environment around Sn(2) can be described as a grossly distorted *cis*-R_2SnXYZ trigonal bipyramid, with an additional intramolecular interaction with $Cl(1^I)$ (3.409(2) Å), producing a distorted octahedral coordination.

It is notable that the four chlorine atoms, four tin atoms and the two oxygen atoms in the molecule are planar, the greatest deviation being Sn(2) 0.0676(4) Å.

Finally, there is an important point of interpretation with which we differ with the previous authors and this concerns the nature of the Sn to Cl(2) interaction which has been suggested to be ionic [7]. We believe that the Sn to Cl(2) interatomic distances [Sn(1)–Cl(2) 2.702(2) and Sn(2)–Cl(2) 2.789(2) Å] are those that would be expected for the covalent bridged species Sn–Cl–Sn which shows an elongation of *ca.* 0.35 Å relative to the Sn–Cl (terminal) bond length [2.445(2) Å]. This is comparable to observations made for similar systems such as $[[(C_6H_{11})_2P\text{–}C(S)\text{–}NHPh]ClHgCl]_2$ where the Hg–Cl(terminal) and Hg–Cl(bridging) distances are 2.35 and 2.70 Å [9].

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