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A TETRANUCLEAR COMPLEX OF TIN: CRYSTAL STRUCTURE OF $\{[(n-C_4H_9)_2SnOOCCL_3]_2O\}_2$ AND RELATED PROPERTIES IN SOLUTION

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Summary

The structure of the title compound has been determined by X-ray analysis. Tetranuclear dimers with a planar, central, four-membered Sn_2O_2 ring are present in the solid. The compound crystallizes in space group $P\bar{1}$ with a 12.202(8), b 12.785(8), c 12.535(8) Å, α 101.97(3), β 111.49(3), γ 108.73(3)°, and $Z = 1$. The structure was refined to R 6.7%. The coordination modes in the solid are discussed and related to the IR spectra in the solid and in solution.

Introduction

The structures of some disubstituted distannoxanes, $[R_2SnX]_2O$ ($X =$ anion) in the solid state have been determined [1–4]. In particular, dimeric ladder-type structures were established for $[Me_2SnOSiMe_3]_2O$ [1] and $[Me_2SnNCS]_2O$ [4]. The dimeric forms are generally not maintained in solution in organic solvents [1,5,6] at room temperature, where the equilibrium dimer \rightleftharpoons monomer seems to exist. Recently many distannoxanes containing carboxylate groups of the type $[R_2SnOOCR']_2O$ or $(R'COO)R_2Sn-O-SnR_2(OH)$ ($R = CH_2-CH=CH_2$ [5], $n-C_4H_9$ [6], $CH_2=CH$ [7] and $R' = H, CH_3, CH_2Cl, CHCl_2, CCl_3, CF_3$ and $CPh_3, SiPh_3, GePh_3$ [8]) have been prepared in our laboratory. From the infrared pattern of these compounds, particularly in the region of the asymmetric COO stretching frequencies [3,6], it was possible to recognize that alternative bonding possibilities exist for the potentially bidentate carboxylate ligands; in the solid bridging groups seem to be present, whereas in chloroform an ester-

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TABLE 1
MOLECULAR WEIGHTS OF TETRABUTYL-1,3-TRICHLOROACETOXY-DISTANNOXANE (37°C)

Solvent	Concn. (mg/ml)	Mol.wt. found	i^c
CCl ₄	7.10	1665	2.05
	3.55	1601	1.98
	1.77	1734	2.15
	0.88	1672	2.07
		1665 ^b	2.05
CHCl ₃ ^a	12.71	1148	1.42
	6.35	1105	1.37
	3.18	1052	1.30
	1.59	1005	1.24
		988 ^b	1.12

^a See ref. 6. ^b Extrapolated value, concn. \rightarrow 0. ^c i = mol.wt.found/mol.wt.calcd. (806.37).

like coordinating form also exists. Since such data are not sufficient to establish precisely the nature of the bonding in these complexes and since structural data are unavailable, apart from preliminary results on [Me₂SnOOCCH₃]₂O [9], a detailed X-ray analysis was carried out on [Bu₂SnOOCCL₃]₂O and the results are discussed along with the spectral data for the solid and its solutions.

Experimental

Preparation of the compound

Commercially available dibutylallyltin was used without further purification in preparing the tetrabutyl-1,3-trichloroacetoxydistannoxane as previously reported [6]. The compound was further purified by recrystallization from a CHCl₃/n-hexane mixture. All products and solvents were of reagent grade.

Molecular weights

Molecular weights were determined in CCl₄ with a Mechrolab Model 302B vapour phase osmometer. The data are listed in Table 1 together with those previously reported for chloroform solutions [6]. The i -values show that in carbon tetrachloride the dimer is effectively present exclusively whereas in chloroform the equilibrium dimer \rightleftharpoons monomer exists.

Infrared spectra

Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer with KBr optics. The spectra in solid and in solution for the tetrabutyl-1,3-trichloroacetoxydistannoxane in the region of the COO asymmetric stretching vibrations are shown in Fig. 1 and 2. They are found at 1685 and 1650 cm⁻¹ for the solid and for the carbon tetrachloride solution (cf. Fig. 1 and 2 (a)(b)(c) and (d)). In chloroform solution (cf. Fig. 2 (e)(f)(g) and (h)) the band centered at 1650 cm⁻¹ does not change its position; on the other hand, that at 1685 cm⁻¹ disappears whereas a new one centered at 1715 cm⁻¹ appears.

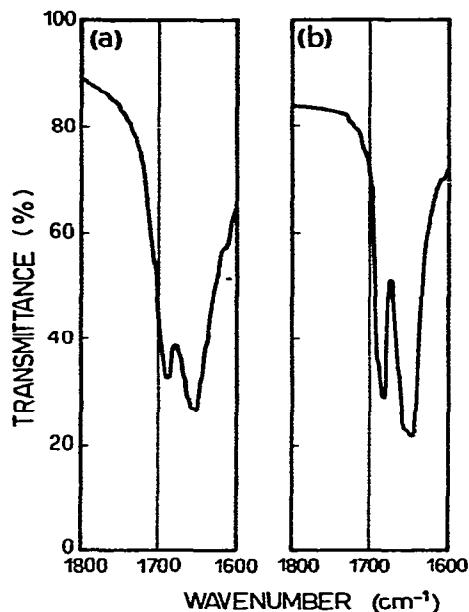


Fig. 1. (a) IR spectrum of the $\nu_a(\text{COO})$ region of tetrabutyl-1,3-trichloroacetoxydistannoxane in Nujol mull. (b) IR spectrum of the $\nu_a(\text{COO})$ region of tetrabutyl-1,3-trichloroacetoxydistannoxane in KBr disk.

Crystal data

$\{[(\text{C}_4\text{H}_9)_2\text{SnOCCCl}_3]_2\text{O}\}_2$, $\text{C}_{40}\text{H}_{72}\text{O}_{10}\text{Cl}_{12}\text{Sn}_4$; mol.wt. 1613. Triclinic; space group $P\bar{1}$, a 12.202(8), b 12.785(8), c 12.535(8) Å, α 101.97(3), β 111.49(3), γ 108.73(3) $^\circ$; V 1602 Å 3 ; Z 1; D_m 1.68; D_x 1.67 g cm $^{-3}$; $\mu(\text{Mo-K}\alpha) \times 24.1$ cm $^{-1}$.

Intensity data

Preliminary Weissenberg and precession photographs showed C_i Laue symmetry and the space group $P\bar{1}$ was confirmed by the structure analysis. The lattice parameters and the intensities were measured at room temperature on an automatic four-circle Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo- K_α radiation (λ 0.7107 Å). With a crystal of approximate dimensions 0.20 \times 0.15 \times 0.15 mm, 6052 independent reflections were scanned in the $\theta - 2\theta$ mode with $\theta \leq 25^\circ$. The net intensities, I , were given by: $I = \{[(C - 2(B_1 + B_2))]A\}/S$, where C = scan count, B_1 and B_2 are the two background counts, A is the attenuator factor, and S is a measure of the scan speed. Structure magnitudes were derived from I by the use of the Lorentz and polarization factors. Reflections with $I \leq 2\sigma(I)$ were considered unobserved and were discarded; a total of 1924 observed reflections was used in the calculation. A first crystal deteriorated rapidly under irradiation and the measurements were repeated with a second crystal of better quality. This crystal slowly deteriorated and at half way the measurement was stopped and then restarted with a new graphite monochromator which was giving higher primary intensity. No absorption correction was applied.

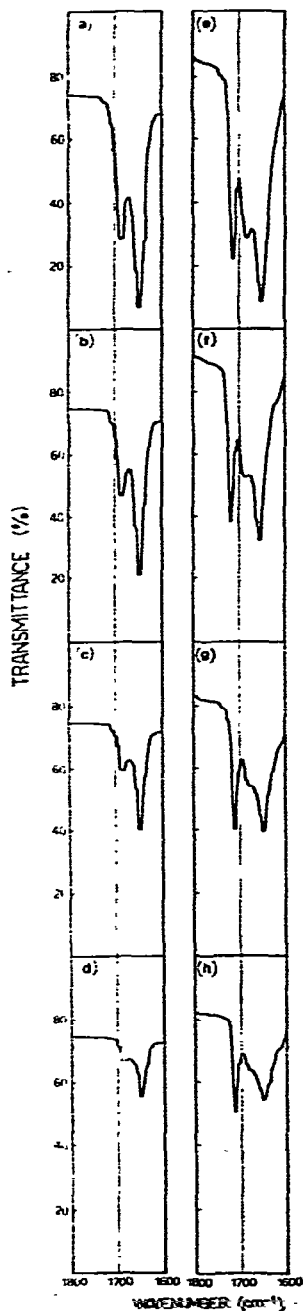


Fig. 2. IR spectrum in CCl_4 of the $\nu_{\text{C=O}}$ region of tetrabutyl-1,3-trichloroacetoxydistannoxane: (a) 14.2 mg/ml; (b) 7.1 mg/ml; (c) 3.55 mg/ml; (d) 1.77 mg/ml.
 IR spectrum in CHCl_3 of the $\nu_{\text{C=O}}$ region of tetrabutyl-1,3-trichloroacetoxydistannoxane: (e) 12.7 mg/ml; (f) 6.35 mg/ml; (g) 3.17 mg/ml; (h) 1.58 mg/ml; optics KBr, 0.5 mm.

Determination of the structure

Scattering factors for neutral atoms were taken from ref. 10. The tin scattering factor was corrected for anomalous dispersion with constant average values $\Delta f' = -0.81$ and $\Delta f'' = 1.73$ for the real and imaginary components [11]. The structure was determined by the heavy-atom method. The relative positions of the tin atoms were obtained from a sharpened Patterson function. A Fourier synthesis phased by the tin atoms revealed the skeleton of the structure, but several subsequent difference-Fourier maps were necessary to locate the aliphatic chains exactly because of the poor resolution of the peaks of some terminal carbon atoms, which are probably freely oscillating in relatively large holes in the packing. This is consistent with the fact that the thermal vibrations of these peripheral atoms are larger than the average vibrations of carbon atoms in the rest of the molecule.

Refinement of the parameters was carried out by full-matrix least-squares calculations. The function minimized was $\Sigma(k|F_o| - |F_c|)^2$ and unit weights were assigned to all reflections used. Refinement with individual isotropic temperature factors was followed by refinement with individual anisotropic temperature factors for all atoms except the chains carbon atoms. In the last cycle the average ratio parameter shift/standard deviation was 0.2. The final *R* value was 6.7%. A final difference map showed no relevant residual electron density, and the hydrogen atoms were not located. Calculations were performed on a CDC 6600 computer using the "X-Ray" program system [12].

Final positional and anisotropic thermal parameters obtained from the least-squares refinements are given in Table 2, and bond lengths and angles in Tables 3 and 4.

Discussion

The molecular structure of the complex is shown in Fig. 3 together with the atom numbering scheme used. The structure reflects the well-known property of the association of organotin units by oxygen bridges and consists of dimeric molecules with crystallographically imposed $\bar{1}$ symmetry.

Linking of the distannoxane oxygen atoms of dibutyl-bis(trichloroacetoxy)-distannoxane to the tin atoms of the centrosymmetric units forms tetranuclear dimers with a planar, central, four membered Sn_2O_2 ring. The tin atoms of the same asymmetric unit, Sn(1) and Sn(2), are also linked by a carboxylate bridge; the other chloroacetate group acts as a monodentate ligand being coordinated only through an oxygen atom to Sn(2). The tin atoms are in a distorted trigonal bipyramidal coordination with oxygen atoms at the apices and one oxygen and two (chain) carbon atoms in the basal plane. This environment is shown in greater detail in Figs. 4 and 5 in which selected distances and angles are reported. Angular distortions in the basal planes seem to be only an effect on the adjustment of bond angles according to the electronegativity of the attached groups. In fact the butyl groups subtend angles of 143° and 137° in the two units, while the mean butyl-tin-oxygen angles are 110° .

Deviations from linearity in the axial angles (166° and 170°) are due to the fact that O(1') and O(4) are slightly displaced from the ideal positions. In particular O(4) is shifted toward the neighbouring Sn(1'), with which it makes a

(continued on p. 50)

TABLE 2
FRACTIONAL ATOMIC CO-ORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^3$), a, b

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	356(2)	759(2)	1408(2)	83(2)	49(1)	49(1)	27(1)	36(1)	19(1)
Sn(2)	533(2)	-2175(2)	750(2)	100(2)	50(1)	58(1)	37(1)	40(1)	28(1)
Cl(1)	1213(13)	-1390(8)	5115(8)	274(15)	116(8)	92(7)	39(9)	98(8)	57(6)
Cl(2)	2141(14)	1071(9)	5733(8)	316(16)	127(8)	78(6)	115(10)	74(8)	30(6)
Cl(3)	3616(12)	-85(13)	5233(10)	131(10)	295(17)	116(8)	109(11)	23(7)	59(10)
Cl(4)	-945(11)	-3409(8)	-3911(7)	213(11)	134(8)	69(6)	95(8)	68(7)	50(5)
Cl(5)	-628(12)	-5480(7)	-3740(8)	229(12)	73(6)	105(7)	55(7)	89(8)	13(5)
Cl(6)	1615(11)	-3269(8)	-2733(9)	164(10)	127(8)	146(8)	64(7)	108(8)	54(6)
O(1)	285(16)	-752(11)	416(12)	83(2)	36(6)	76(10)	21(8)	54(9)	24(8)
O(2)	1086(22)	337(20)	3109(17)	151(21)	125(19)	72(13)	67(17)	54(14)	35(13)
O(3)	1228(22)	-1372(17)	2733(17)	183(22)	75(13)	84(15)	82(15)	55(14)	48(11)
O(4)	50(19)	-2680(13)	-1243(16)	144(18)	43(10)	113(14)	58(11)	93(14)	43(10)
O(5)	217(22)	-4342(15)	-1175(16)	169(21)	71(12)	75(12)	63(13)	69(14)	29(10)
C(1)	1355(29)	-474(26)	3425(31)	79(22)	71(18)	189(27)	54(17)	51(20)	71(20)
C(2)	2033(29)	-209(22)	4838(19)	166(27)	88(19)	49(13)	78(19)	46(16)	49(14)
C(3)	68(27)	-3656(27)	-1579(25)	79(22)	96(22)	71(19)	27(18)	24(17)	59(18)
C(4)	28(32)	-3923(22)	-2948(22)	145(30)	71(18)	61(16)	45(19)	53(19)	28(14)
	x	y	z	U	x	y	z	U	
C(5)	-1145(30)	-3515(26)	502(27)	77(8)	C(13)	-1398(36)	356(32)	1511(32)	104(10)
C(6)	-1545(36)	-3382(32)	1459(32)	114(11)	C(14)	-2421(72)	-800(83)	916(63)	229(27)
C(7)	-2844(44)	-421(38)	1161(40)	138(15)	C(15)	-3610(68)	-843(60)	1036(57)	195(24)
C(8)	-3172(49)	-4246(44)	2223(46)	169(18)	C(16)	-4880(95)	-1783(80)	-23(89)	329(47)
C(9)	2513(38)	-1869(34)	1313(34)	114(12)	C(17)	2314(36)	2097(30)	2208(31)	101(10)
C(10)	2796(49)	-2734(44)	2082(44)	179(18)	C(18)	3421(62)	1750(53)	2616(53)	139(20)
C(11)	3902(59)	-2991(52)	2261(52)	347(20)	C(19)	4764(62)	2892(55)	3239(54)	166(22)
C(12)	3731(50)	-3683(45)	2845(45)	168(18)	C(20)	5751(59)	2432(51)	3531(52)	232(21)

a The estimated standard deviations, given in parentheses, refer to the last significant place. b The thermal parameters U_{ij} (\AA^2) are in the form $\exp[-2\pi^2(\sum_{i,j} h_i h_j U_{ij})]$

TABLE 3

OBSERVED BOND DISTANCES (Å), WITH ESTIMATED STANDARD DEVIATIONS^a

Atoms	Bond distance (Å)	Atoms	Bond distance (Å)
Sn(1)—O(1)	2.03(2)	Sn(2)—O(1)	2.05(2)
Sn(1)—O(1 ^f)	2.12(2)	Sn(2)—O(3)	2.20(2)
Sn(1)—O(2)	2.32(2)	Sn(2)—O(4)	2.22(2)
Sn(1)—O(4 ^f)	2.68(2)	Sn(2)—C(5)	2.11(3)
Sn(1)—C(13)	2.08(5)	Sn(2)—C(9)	2.07(5)
Sn(1)—C(17)	2.13(3)		
C(1)—O(2)	1.24(5)	C(3)—O(4)	1.26(4)
C(1)—O(3)	1.20(4)	C(3)—O(5)	1.20(4)
C(1)—C(2)	1.57(4)	C(3)—C(4)	1.55(5)
C(2)—Cl(1)	1.71(3)	C(4)—Cl(4)	1.76(3)
C(2)—Cl(2)	1.72(4)	C(4)—Cl(5)	1.78(3)
C(2)—Cl(3)	1.74(4)	C(4)—Cl(6)	1.74(4)
C(5)—C(6)	1.45(6)	C(13)—C(14)	1.41(7)
C(6)—C(7)	1.55(6)	C(14)—C(15)	1.50(13)
C(7)—C(8)	1.52(9)	C(15)—C(16)	1.50(9)
C(9)—C(10)	1.64(8)	C(17)—C(18)	1.50(9)
C(10)—C(11)	1.48(10)	C(18)—C(19)	1.57(8)
C(11)—C(12)	1.42(10)	C(19)—C(20)	1.47(11)

^a Superscripts are in footnote to Table 5.

TABLE 4

OBSERVED BOND ANGLES (°), WITH ESTIMATED STANDARD DEVIATIONS

Atoms	Bond angles (°)	Atoms	Bond angles (°)
O(1)—Sn(1)—C(13)	109(1)	O(1)—Sn(2)—C(5)	111(1)
O(1)—Sn(1)—C(17)	107(1)	O(1)—Sn(2)—C(9)	111(1)
C(13)—Sn(1)—C(17)	143(2)	C(5)—Sn(2)—C(9)	137(2)
O(1)—Sn(1)—O(1 ^f)	75(1)	O(1)—Sn(2)—O(3)	92(1)
O(1)—Sn(1)—O(2)	90(1)	O(1)—Sn(2)—O(4)	79(1)
O(2)—Sn(1)—C(13)	85(1)	C(5)—Sn(2)—O(3)	91(1)
O(2)—Sn(1)—C(17)	85(1)	C(5)—Sn(2)—O(4)	96(1)
O(1 ^f)—Sn(1)—C(13)	100(1)	C(9)—Sn(2)—O(3)	84(1)
O(1 ^f)—Sn(1)—C(17)	98(1)	C(9)—Sn(2)—C(4)	94(1)
O(1 ^f)—Sn(1)—O(2)	166(1)	O(3)—Sn(2)—O(4)	170(1)
O(2)—Sn(1)—O(4 ^f)	126(1)	Sn(1)—O(1)—Sn(1 ^f)	105(1)
O(4 ^f)—Sn(1)—O(1 ^f)	68(1)	Sn(1)—O(1)—Sn(2)	136(1)
O(4 ^f)—Sn(1)—C(13)	78(1)	Sn(1 ^f)—O(1)—Sn(2)	119(1)
O(4 ^f)—Sn(1)—C(17)	79(1)	Sn(1 ^f)—O(4)—Sn(2)	94(1)
Sn(1)—O(2)—C(1)	134(2)	Sn(2)—O(4)—C(3)	112(2)
Sn(2)—O(3)—C(1)	136(2)	O(4)—C(3)—O(5)	129(3)
O(2)—C(1)—O(3)	130(4)	O(4)—C(3)—C(4)	115(3)
O(2)—C(1)—C(2)	112(3)	O(5)—C(3)—C(4)	116(3)
O(3)—C(1)—C(2)	117(3)	C(3)—C(4)—Cl(4)	113(3)
C(1)—C(2)—Cl(1)	109(2)	C(3)—C(4)—Cl(5)	111(2)
C(1)—C(2)—Cl(2)	114(3)	C(3)—C(4)—Cl(6)	109(2)
C(1)—C(2)—Cl(3)	107(3)	Cl(4)—C(4)—Cl(5)	107(1)
Cl(1)—C(2)—Cl(2)	109(2)	Cl(4)—C(4)—Cl(6)	109(2)
Cl(2)—C(2)—Cl(3)	109(2)	Cl(5)—C(4)—Cl(6)	108(2)
Cl(2)—C(2)—Cl(3)	108(1)	Sn(2)—C(5)—C(6)	120(2)
Sn(1)—C(13)—C(14)	122(6)	C(5)—C(6)—C(7)	115(3)
C(13)—C(14)—C(15)	112(6)	C(6)—C(7)—C(8)	112(3)
C(14)—C(15)—C(16)	114(7)	Sn(2)—C(9)—C(10)	106(3)
Sn(1)—C(17)—C(18)	119(8)	C(9)—C(10)—C(11)	116(5)
C(17)—C(18)—C(19)	109(8)	C(10)—C(11)—C(12)	104(6)
C(16)—C(19)—C(20)	104(6)		

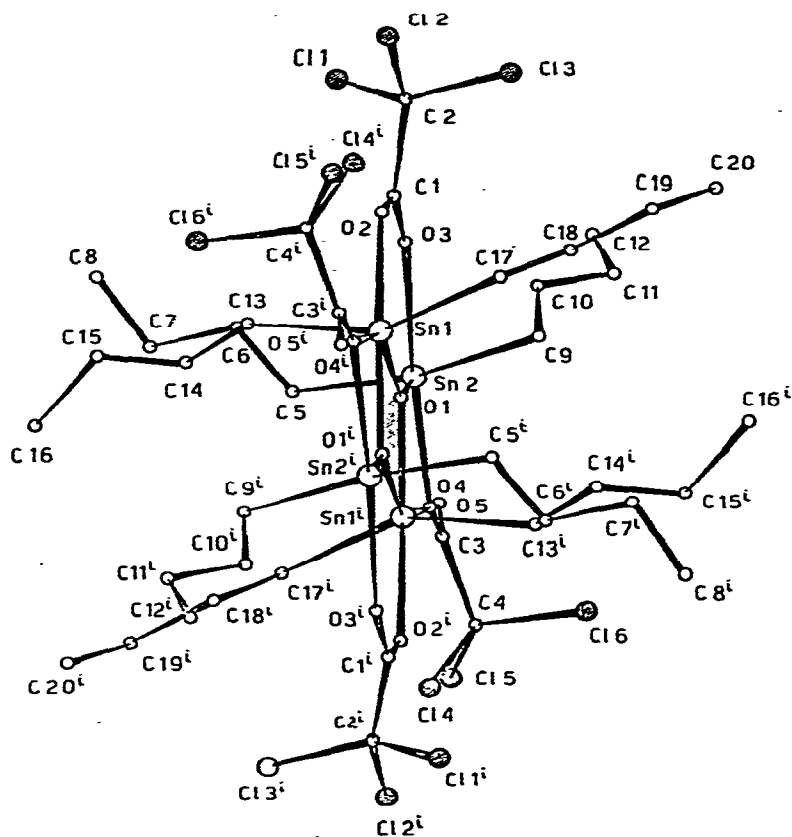


Fig. 3. Projection of the molecule along [010].

relatively short contact distance of 2.69 Å, which raises the question whether this oxygen is chemically interacting with tin. An argument for this is that the large distortion in the trigonal bipyramidal arrangement around Sn(1), and therefore Sn(1ⁱ), allows the carboxylate oxygen of the monodentate ligands to occupy a relatively large hole in the coordination sphere of the tin atom.

On the other hand the relatively great bulk of the aliphatic residues actually prevents O(4) from approaching closer to Sn(1ⁱ) (see Table 5 for contact distances). However, if O(4) is assumed to be bonded, then Sn(1ⁱ) and the symmetry related Sn(1) must be considered six-coordinated in a distorted octahedral arrangement. A similar long Sn—O distance (2.68 Å) was found in the trigonal bipyramidal structure of dichlorodimethyltin(IV) 1/1 salicylaldehyde adduct [13], in which the aldehydic oxygen of the monodentate ligand forms the second axial bond.

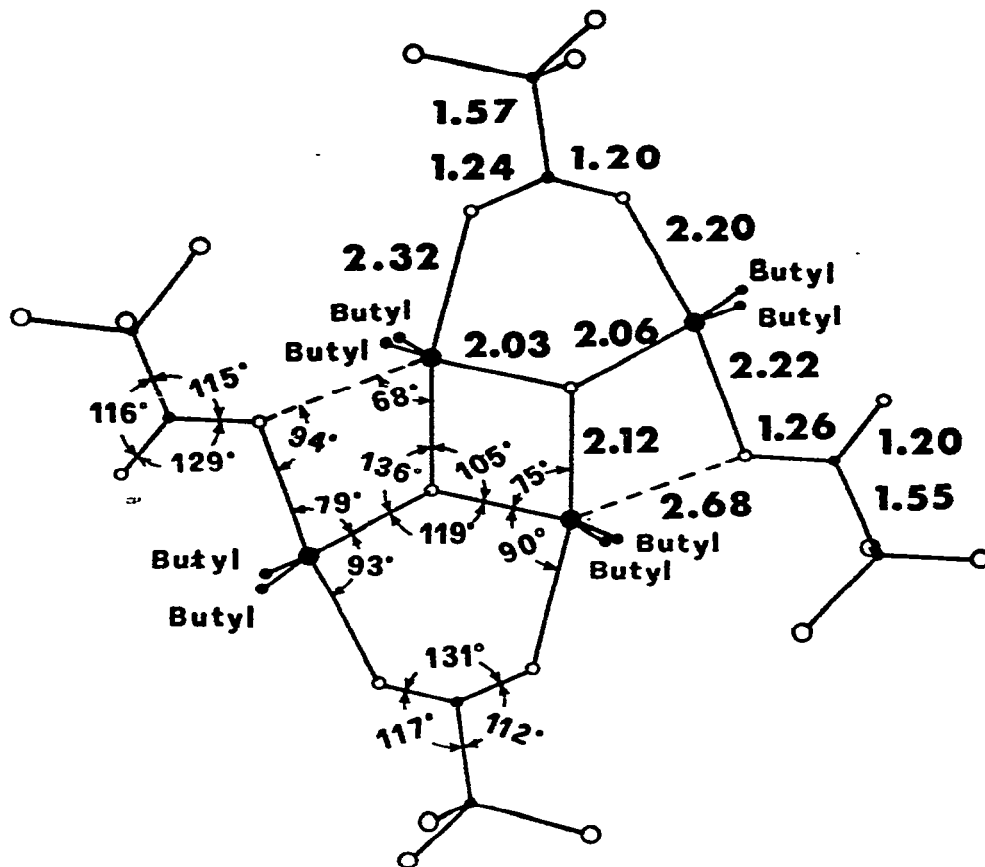


Fig. 4. Coordination modes in $\{[(n-C_4H_9)_2SnOCCCCl_3]_2O\}_2$.

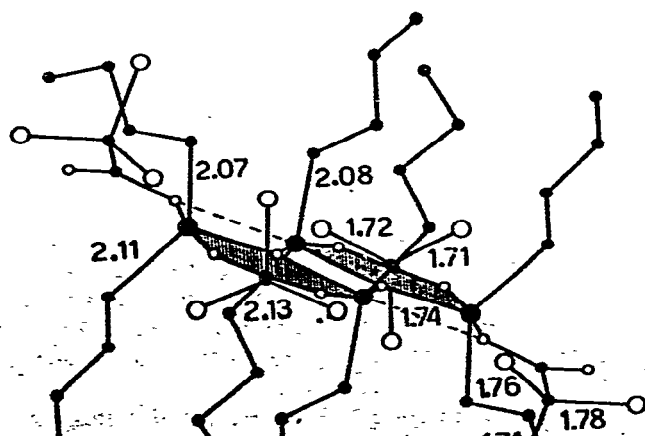


TABLE 5
CONTACT DISTANCES (Å), WITH ESTIMATED STANDARD DEVIATIONS

(a) Intramolecular contacts		(b) Intermolecular contacts	
Sn(1)---Sn(1 ⁱ)	3.287(3)	Cl(1)---Cl(4 ^{iv})	3.79(2)
Sn(1)---Sn(2 ⁱ)	3.602(4)	Cl(1)---Cl(5 ^{vi})	3.71(2)
Sn(1)---Sn(2)	3.786(4)	Cl(1)---Cl(6 ^{iv})	3.97(2)
Sn(1)---Cl(4 ⁱ)	3.76(1)	Cl(3)---Cl(3 ^v)	3.60(2)
Cl(1)---Cl(2)	2.79(2)	Cl(5)---Cl(6 ^{viii})	3.93(2)
Cl(1)---Cl(3)	2.81(2)	Cl(2)---C(8 ^{vi})	3.82(5)
Cl(2)---Cl(3)	2.79(2)	Cl(2)---C(15 ^{vi})	3.90(7)
Cl(4)---Cl(5)	2.84(2)	Cl(3)---C(11 ^v)	3.81(5)
Cl(4)---Cl(6)	2.85(2)	Cl(3)---C(20 ^v)	3.84(7)
Cl(5)---Cl(6)	2.85(2)	Cl(5)---C(20 ^{iv})	3.99(5)
O(1)---O(1 ⁱ)	2.54(2)	Cl(5)---C(16 ^{vii})	3.86(8)
O(2)---O(3)	2.21(4)	Cl(6)---C(20 ^{vi})	3.61(8)
O(4)---O(5)	2.21(3)		
O(1)---O(2)	3.09(3)		
O(1)---O(3)	3.08(3)		
O(1)---O(4)	2.72(2)		
O(2)---C(13)	2.98(5)		
O(2)---C(17)	3.02(5)		
O(3)---C(5)	3.08(3)		
O(3)---C(9)	2.87(5)		
O(4)---C(5)	3.22(5)		
O(4)---C(9)	3.15(4)		
O(4)---C(13 ⁱ)	3.04(4)		
O(4)---C(17 ⁱ)	3.08(5)		

^a Superscript denote the following equivalent positions relative to the reference molecule at x, y, z : $i -x, -y, -z$; $ii 1+x, 1+y, 1+z$; $iii 1+x, y, z$; $iv x, y, 1+z$; $v 1-x, -y, 1-z$; $vi -x, -y, 1-z$; $vii -x, -1-y, -z$; $viii -x, -1-y, -1-z$.

The distannoxane oxygen O(1) makes two chemically equivalent bonds (2.03 and 2.06 Å) with Sn(1) and Sn(2) and a slightly longer bond with Sn(1ⁱ) (2.12 Å). Very similar tin—oxygen bond distances (2.04 and 2.10 Å) in the Sn₂O₂ ring are found in the above mentioned compound and in $\{[(CH_3)_2SnNCS]_2O\}_2$ [4] (1.99 and 2.15 Å).

The two independent tin—oxygen (ligand) bonds Sn(2)—O(3) and Sn(2)—O(4) are *trans* to each other and their lengths agree well (2.20 and 2.22 Å), but they are significantly shorter than the Sn(1)—O(2) bond (2.32 Å). Corresponding bond lengths of 2.25(2) Å were found in $[(C_6H_5)_2SnOOCCH_3]_2$ [15], in which two five-coordinated tin atoms are bridged by the acetate groups, but significant differences between the Sn—O bond lengths were observed in the polymeric trimethyltin(IV) acetate and trimethyltin(IV) trifluoroacetate [16] where the tin atoms are linked by carboxylate bridges. It was proposed that the difference in the character of the Sn—O bonds is due to the difference between the carbonyl and carboxyl bond lengths, but in this case the relative weakness of the Sn(1)—O(2) bond could also be related to the fact that O(1) is *trans* to the very strong Sn(1)—O(1ⁱ) bond (2.12 Å).

In both the chelated and in the monodentate ligand the C—O bond distances are non-equivalent. The C(1)—O(3) and C(3)—O(5) bonds (1.20 Å) have a marked double bond character and the distances are in good agreement with the C=O length of the aliphatic ketones, whereas C(1)—O(2) and C(3)—O(4) are longer (mean 1.25 Å).

TABLE 6
LEAST SQUARES PLANES

(a) Coefficients for least-squares planes $PI + QJ + RK = S$ in orthogonal angstrom space ^a

Plane		P	Q	R	S
I	Sn(1), O(1), Sn(1 ^f), O(1 ^f)	0.868	0.496	0.022	0.0
II	Sn(1), Sn(2), O(1), O(2), O(3)	0.877	0.481	0.008	-0.026
III	O(2), O(3), C(1), C(2)	0.871	0.477	-0.120	-0.496
IV	O(4), O(5), C(3), C(4)	0.832	0.490	0.258	-0.114
V	Sn(1), O(1), C(13), C(17)	0.136	-0.261	0.956	1.046
VI	Sn(2), O(1), C(5), C(9)	-0.285	0.428	0.858	0.202

(b) Distances of atoms from planes (Å) ^b

I	II	III	IV	V	VI
*Sn(2) -0.08	Sn(1) -0.01	O(2) 0.01	O(4) 0.01	Sn(1) -0.09	Sn(2) -0.02
*Sn(2 ^f) 0.08	Sn(2) -0.03	O(3) 0.01	O(5) 0.01	O(1) 0.02	O(1) 0.0
	O(1) 0.03	C(1) -0.02	C(3) -0.03	C(13) 0.04	C(5) 0.01
	O(2) -0.01	C(2) 0.0	C(4) 0.01	C(17) 0.03	C(9) 0.01
	O(3) 0.02				
	*C(1) 0.04				
	*C(2) 0.26				

(c) Angles between the planes

I-II	1.3°	I-VI	89.1°
I-III	8.2°	III-IV	21.9°
I-IV	13.7°	V-VI	48.0°
I-V	89.4°		

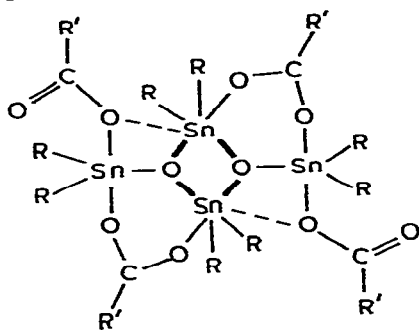
^a The orthogonal angstrom space is defined as three orthogonal vectors, *I*, *J* and *K*, one angstrom in magnitude with *I* parallel to *a*, *J* parallel to *b*^{*}, and *K* perpendicular to *a* in the plane of *a* and *c*. ^b Atoms marked with an asterisk are not included in calculating the plane.

The tin-carbon distances (mean value 2.10 Å) and the other distances and angles in the molecule appear to be normal. Some carbon-carbon bond distances in the chains are probably not really significant because of the relatively greater uncertainty in the position for this part of the molecule.

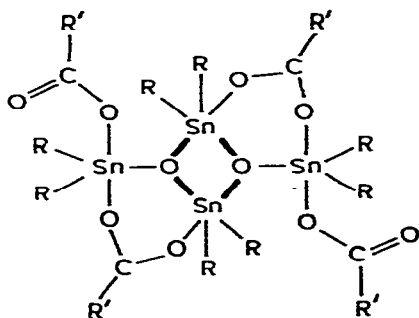
The central part of the structure is essentially planar, the two acetate groups being inclined at angle of 8.2 and 13.7 degrees with respect to the Sn₂O₂ ring (see Table 6). The mean planes determined by the equatorial atoms in both coordination polyhedrons (planes V and VI of Table 6) are strictly orthogonal with respect to the same central ring.

Previous IR studies in the solid state have shown that two asymmetric carbonyl absorptions are present, one near 1560 cm⁻¹ which was attributed to a bridging carboxylate group, the other near 1630 cm⁻¹ corresponding to a non-bridging group. On the other hand, IR spectra of a series of compounds [n-Bu₂-SnX]₂O (X = CH₂ClCOO, CHCl₂COO, CCl₃COO) in chloroform solutions [6], where these compounds exist in a dimer-monomer equilibrium, have shown that in dilute solutions a band at 1715 cm⁻¹ arises from a stretching vibration of an ester-like carboxylic group. From the behaviour of tetrabutyl-1,3-trichloroacetoxdistannoxane in solution it appears that it is a dimer in a non polar solvent like carbon tetrachloride (cf. Table 1). Comparison of the IR spectra suggests that the same molecular structure is maintained in the solid and in CCl₄ solution. In fact in the COO asymmetric stretching region (cf. Fig. 1 and Fig. 2 (a)(b)(c) and (d)), only two bands are present: (i) one near 1685 cm⁻¹ must be attributed

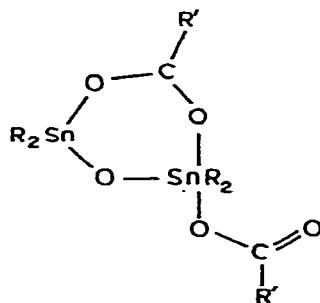
to the monodentate chloroacetate group, with the oxygen atom shared between two tin atoms, and (ii) one near 1650 cm^{-1} which arises from the chelate carboxylate group (see Fig. 4). These arguments are supported by the IR pattern in the more polar solvent chloroform (cf. Fig. 2 (e)(f)(g) and (h)) in which the monomers are along with the dimers (cf. Table 1). In this solvent the weak $\text{Sn}(1^i)\cdots\text{O}(4)$ bond is preferentially broken, whereas the chelate ligands seem to remain unaffected. This behaviour is shown in Fig. 2 (e)(f)(g) and (h), which show that, at varying concentrations, no change is observed in the position of the band centered at 1650 cm^{-1} , whereas that at 1685 cm^{-1} disappears on dilution and a strong band appears at 1715 cm^{-1} . The last band relates to the stretching vibrations of an ester-like carboxylic group. It seems likely that in CCl_4 a dimeric ladder-type structure such as I is present whereas in CHCl_3 , species like II and III are present.



(I)



(II)



(III)

In the dimeric species I, in which two carboxylate groups are acting as bridging bidentate ligands and the other two as bridged monodentate ligands, the tin atoms are in different environments and might be distinguishable: tin atoms seem to have coordination modes six and five in I, five in II and five and four in III.

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