Investigation into Diphosphine Oxides as Ligands in Diorganotin(IV) Adducts. Part 1. Synthesis and Spectroscopic Characterization of 1,2-Bis(diphenylphosphoryl)ethane Tin Complexes and *X*-Ray Structure of [1,2-Bis(diphenylphosphoryl)ethane]di-n-butyldichlorotin(IV) †

Philip G. Harrison and Nelson W. Sharpe
Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD
Corrado Pelizzi, Giancarlo Pelizzi,* and Pieralberto Tarasconi
Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Via M. D'Azeglio 85, 43100 Parma, Italy

---

1,2-Bis(diphenylphosphoryl)ethane (dppoe) forms complexes with diorganotin(IV) chlorides of the type SnR_2Cl_2(dppoe) (R = Pr^n, Bu^n, or Ph), the i.r. and tin-119 Mössbauer spectra of which have been recorded. The crystal structure of $SnBu^n{}_2Cl_2$(dppoe) has been determined from single-crystal *X*-ray data collected by counter methods and refined by full-matrix least-squares techniques to R = 0.0461 for 2 430 observed reflections. Crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions a = 11.775(5), b = 15.987(7), c = 11.006(5) Å, α = 102.12(5), β = 114.55(6), γ = 101.69(5)°, and Z = 2. Tin is bonded to two Cl^- ions, to two C atoms and to two O atoms, to one more loosely than the other. The weaker co-ordination of one of the two O=P groups is also reflected in distortions of the geometry of the co-ordination polyhedron. The structure is polymeric in that the dppoe ligand forms bridges between adjacent tin atoms. Tin-119 Mössbauer spectra have been recorded for the three SnR_2Cl_2(dppoe) complexes in the temperature range 77—150 K, and for the complex $(SnPh_3Cl)_2$(dppoe) at 77 K. Quadrupole-splitting data for the former are consistent with a *trans*-SnC_2X_4 arrangement about the tin atom in each case. Recoil-free fraction temperature coefficients, a, have also been determined for the three SnR_2Cl_2 complexes; root-mean-square amplitudes of vibration, $\langle x \rangle$, and absolute recoil-free fractions, f, have been estimated at various temperatures for $SnBu^n{}_2Cl_2$(dppoe).

As part of our study of the chemical and structural properties of organotin(IV) compounds, we have investigated the reactions of triorganotin and diorganotin derivatives with oxides of diphosphines, whose co-ordinating properties have still been relatively little explored,[1–6] in order to elucidate the effect of the nature and size of the organic and inorganic ligands on the molecular structure of the complex and on the tin–ligand interactions.

We have previously reported the synthesis and the *X*-ray structural results of adducts of triphenyltin chloride and triphenyltin nitrate with 1,2-bis(diphenylphosphoryl)ethane (dppoe) and *cis*-1,2-bis(diphenylphosphoryl)ethylene (dppoet),[7–9] and we now describe the preparation and the characterization by i.r. and tin-119 Mössbauer techniques of three new adducts of formula SnR_2Cl_2(dppoe) (R = Pr^n, Bu^n, or Ph), the *X*-ray diffraction analysis of $SnBu^n{}_2Cl_2$(dppoe), together with the tin-119 Mössbauer spectrum of $(SnPh_3Cl)_2$(dppoe).

Experimental

Preparations.—Solvents were dried and distilled before use. 1,2-Bis(diphenylphosphino)ethane (dppe) and organotin chlorides were commercially available and were used without further purification.

1,2-Bis(diphenylphosphoryl)ethane was obtained by adding an excess of H_2O_2 (31.5%) to a toluene (or benzene) solution of dppe and refluxing the reaction mixture for 1 h.[10] The preparation of $(SnPh_3Cl)_2$(dppoe) has been reported previously.[8]

Diorganotin(IV) adducts were prepared as follows. R_2SnCl_2 dissolved in acetone was added to a toluene solution of dppoe (1 : 1 molar ratio) and allowed to stir at room temperature for 1 h. After several hours, by slow evaporation of the solvent, a white crystalline product was isolated. The compounds can be obtained also by exposing to air for some days the organotin derivative and dppe in acetone solution. On the basis of the analytical data the diorganotin complexes show similar stoicheiometry with a tin : phosphorus ligand molar ratio of 1 : 1, which is independent of the amounts of the reagents. This stoicheiometry differs from that shown by the triphenyltin derivative, in which the phosphorus ligand bridges two $SnPh_3Cl$ groups.

Table 1. Analytical data (%)

		C	H
$SnPh_2Cl_2$(dppoe)	Found	59.15	4.15
	Calc.	58.95	4.55
$SnPr^n{}_2Cl_2$(dppoe)	Found	54.6	5.55
	Calc.	54.4	5.4
$SnBu^n{}_2Cl_2$(dppoe)	Found	49.5*	5.8
	Calc.	55.6	5.75

* Probably due to impurities.

Measurements.—Elemental C, H, and N analyses (Table 1) were made on Perkin-Elmer model 240 automatic equipment. The quantitative determination for tin was obtained by atomic absorption spectroscopy on a Perkin-Elmer model 303 instrument.

The i.r. spectra were recorded on a Perkin-Elmer model 283B spectrophotometer in the 4 000—200 cm^{-1} region using KBr discs.

The Mössbauer spectrometer has been described previously; [11] samples were finely ground, to eliminate preferential orientation effects, prior to loading in the variable-temperature cryostat (Oxford Instruments Ltd.). Spectra were recorded at various temperatures in the range 77—150 K,

---

† *Supplementary data available* (No. SUP 23542, 19 pp.): Mössbauer spectral data, observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 2. Fractional atomic co-ordinates for non-hydrogen atoms ($\times 10^5$ for Sn, $\times 10^4$ for other atoms) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sn	34 674(5)	28 175(3)	15 584(4)
Cl(1)	3 965(2)	1 562(1)	2 449(2)
Cl(2)	5 841(2)	3 706(2)	2 866(2)
P(1)	−406(2)	1 185(2)	−618(2)
P(2)	3 178(2)	4 816(2)	161(2)
O(1)	926(6)	1 874(4)	110(6)
O(2)	3 160(5)	4 094(4)	825(5)
C(1)	2 877(7)	3 411(5)	3 018(7)
C(2)	2 372(8)	2 801(6)	3 692(8)
C(3)	2 040(10)	3 320(7)	4 778(10)
C(4)	1 608(14)	2 726(9)	5 500(13)
C(5)	3 237(8)	2 277(5)	−485(7)
C(6)	3 300(14)	1 365(7)	−894(10)
C(7)	2 994(12)	985(9)	−2 448(10)
C(8)	1 553(12)	528(10)	−3 352(12)
C(9)	−1 379(11)	1 116(9)	−2 424(10)
C(10)	−909(11)	1 810(9)	−2 856(11)
C(11)	−1 658(14)	1 804(9)	−4 239(14)
C(12)	−2 843(13)	1 126(11)	−5 147(11)
C(13)	−3 281(12)	432(9)	−4 725(11)
C(14)	−2 554(11)	456(7)	−3 354(9)
C(15)	−1 338(9)	1 443(7)	271(8)
C(16)	−981(9)	2 323(7)	1 144(9)
C(17)	−1 704(12)	2 536(8)	1 815(10)
C(18)	−2 777(12)	1 900(9)	1 630(10)
C(19)	−3 158(11)	1 034(9)	760(12)
C(20)	−2 441(11)	809(8)	73(10)
C(21)	−412(7)	37(6)	−759(8)
C(22)	1 567(7)	4 647(5)	−1 220(7)
C(23)	1 310(10)	4 891(8)	−2 384(10)
C(24)	33(12)	4 771(9)	−3 358(12)
C(25)	−987(10)	4 397(8)	−3 215(11)
C(26)	−773(9)	4 114(8)	−2 063(11)
C(27)	532(9)	4 249(7)	−1 055(10)
C(28)	3 665(6)	5 905(6)	1 425(7)
C(29)	4 017(7)	5 970(6)	2 813(7)
C(30)	4 322(7)	6 807(8)	3 786(8)
C(31)	4 277(8)	7 542(8)	3 377(10)
C(32)	3 949(8)	7 485(7)	1 993(10)
C(33)	3 629(8)	6 674(6)	1 012(9)
C(34)	4 283(6)	4 901(5)	−588(7)

accumulating a minimum of 10^6 counts per channel, and subsequently fitted to Lorentzian lineshapes by usual least-squares methods. Data for the three SnR_2Cl_2(dppoe) compounds have been deposited in SUP No. 23542.

X-Ray Data Collection, and Determination and Refinement of the Crystal Structure of $SnBu^n{}_2Cl_2$(dppoe).—A small single crystal mounted on a glass fibre was used for *X*-ray work. Preliminary Weissenberg photographs and a systematic search in reciprocal space using a single-crystal Siemens AED diffractometer showed that crystals display triclinic symmetry and that the space group is $P1$ or $P\bar{1}$. Successful solution of the structure proved the space group to be $P\bar{1}$. The unit-cell dimensions were obtained by a least-squares fit to the 2θ angles of 27 strong reflections chosen from widely different regions of reciprocal space and automatically centred.

Crystal data. $C_{34}H_{42}Cl_2O_2P_2Sn$, $M = 734.25$, $a = 11.775(5)$, $b = 15.987(7)$, $c = 11.006(5)$ Å, $\alpha = 102.12(5)$, $\beta = 114.55(6)$, $\gamma = 101.69(5)°$, $U = 1\,742(1)$ Å^3, $Z = 2$, $D_c = 1.400$ g cm^{-3}, $F(000) = 752$, μ(Cu-K_α) = 85.21 cm^{-1}.

Intensity data were collected for the hemisphere $\pm h$, $\pm k$, $+l$ within the range $6.0 < 2\theta < 130.0°$, by use of Ni-filtered Cu-K_α radiation ($\lambda = 1.541\,78$ Å). Attenuator filters were inserted whenever the counting rate exceeded 9 000 counts s^{-1}. Out of the 3 072 independent data measured, 2 430 had intensities $I \geqslant 2\sigma(I)$ and were therefore considered observed and used for structure analysis. Two standard reflections (7$\bar{2}$3 and $\bar{2}$15) were measured after every 50 reflections as a monitor for possible misalignment and/or deterioration of the crystal and showed no unusual trends during the course of data collection. The data were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by a combination of direct methods and the heavy-atom technique. The positions of the tin and the chlorine atoms were obtained by direct methods (SHELX 76 [12]), while those of the remaining non-hydrogen atoms were determined by additional Fourier-difference calculations. Two cycles of full-matrix least-squares refinement, with isotropic models for all atoms, gave convergence at a conventional *R* index of 0.086, while with the introduction of anisotropic thermal parameters, three more cycles of refinement lowered the index to 0.056. All the atoms were refined freely. Since the least-squares program could not deal with more than 306 variables simultaneously, refinement of the carbon atoms was carried out in two blocks, with the phenyl carbons included in the first block and the butyl carbons in the second. All the hydrogen atoms were placed in calculated positions: those belonging to the methyl groups were given a common temperature factor ($U = 0.20$ Å^2) and were refined as rigid groups; the other hydrogens were assigned individual isotropic temperature factors and allowed to ride on the corresponding carbon atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$; unit weights were used initially, and in the final stages of refinement a weighting scheme of the form $w = 0.1793/[\sigma^2(F_o) + 0.0163\,F_o{}^2]$ was employed. The final residuals were $R = 0.0461$ and $R' = 0.0490$. The largest peak in the final difference map was 0.46 e Å^{-3} and was a ripple 1.12 Å from tin. Scattering factors for neutral atoms were taken from ref. 13; both real and imaginary components for anomalous dispersion were included [14] for all non-hydrogen atoms. All the computations were performed, using the SHELX 76 system of programs,[12] on the Cyber 76 Computer of Consorzio per la gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale.

The final atomic co-ordinates are presented in Table 2. Selected bond distances and angles are in Table 3.

Results and Discussion

X-Ray Structure of $SnBu^n{}_2Cl_2$(dppoe).—The principal features of the structure are displayed in Figures 1 and 2. As shown by the results of the *X*-ray analysis, it consists of polymeric $CH_2(Ph)_2PO(Bu^n)_2Sn(Cl)_2OP(Ph)_2CH_2$ units, in which the tin atoms bind to two chloride ions, to two butyl carbon atoms, and to two oxygen atoms [more loosely to one, O(1), than the other]. As regards the co-ordination polyhedron, if only the five nearest neighbours are considered, the tin environment can be viewed as a highly distorted tetragonal pyramid with Cl(2) at the apex. If O(1) is also regarded as being part of the metal environment, the molecular geometry may be thought of as consisting of an irregular octahedral array. In the latter case, the most striking deviation of the

Table 3. Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses

Sn–Cl(1)	2.483(2)	P(1)–O(1)	1.483(6)	P(2)–C(28)	1.792(9)	C(2)–C(3)	1.54(2)
Sn–Cl(2)	2.468(3)	P(2)–O(2)	1.491(7)	P(2)–C(34)	1.805(9)	C(3)–C(4)	1.50(2)
Sn–O(1)	2.640(7)	P(1)–C(9)	1.800(11)	C(21)–C(21$^{\mathrm{I}}$)	1.590(12)	C(5)–C(6)	1.46(1)
Sn–O(2)	2.386(7)	P(1)–C(15)	1.799(12)	C(34)–C(34$^{\mathrm{II}}$)	1.556(8)	C(6)–C(7)	1.54(2)
Sn–C(1)	2.126(9)	P(1)–C(21)	1.807(10)	C(1)–C(2)	1.51(1)	C(7)–C(8)	1.48(2)
Sn–C(5)	2.112(8)	P(2)–C(22)	1.790(7)				

Cl(1)–Sn–Cl(2)	90.1(1)	O(1)–Sn–C(5)	78.5(3)	C(9)–P(1)–C(21)	103.4(5)
Cl(1)–Sn–O(1)	90.7(2)	O(2)–Sn–C(1)	81.8(3)	O(2)–P(2)–C(22)	111.2(4)
Cl(1)–Sn–O(2)	175.6(2)	O(2)–Sn–C(5)	83.3(2)	O(2)–P(2)–C(28)	110.9(3)
Cl(1)–Sn–C(1)	98.2(2)	C(1)–Sn–C(5)	154.3(3)	O(2)–P(2)–C(34)	114.2(4)
Cl(1)–Sn–C(5)	98.2(3)	Sn–O(1)–P(1)	167.8(4)	C(22)–P(2)–C(28)	105.9(4)
Cl(2)–Sn–O(1)	178.8(2)	Sn–O(2)–P(2)	163.9(4)	C(28)–P(2)–C(34)	106.8(4)
Cl(2)–Sn–O(2)	85.6(2)	O(1)–P(1)–C(9)	113.5(5)	C(22)–P(2)–C(34)	107.3(4)
Cl(2)–Sn–C(1)	99.2(2)	O(1)–P(1)–C(15)	110.6(4)	Sn–C(1)–C(2)	116.8(6)
Cl(2)–Sn–C(5)	100.5(3)	O(1)–P(1)–C(21)	114.8(5)	Sn–C(5)–C(6)	117.7(6)
O(1)–Sn–O(2)	93.6(2)	C(9)–P(1)–C(15)	106.3(6)	P(1)–C(21)–C(21$^{\mathrm{I}}$)	110.8(6)
O(1)–Sn–C(1)	81.7(3)	C(15)–P(1)–C(21)	107.6(5)	P(2)–C(34)–C(34$^{\mathrm{II}}$)	109.5(5)

Roman numeral superscripts indicate the transformations I $\bar{x}, \bar{y}, \bar{z}$; II $1 - x, 1 - y, \bar{z}$.

bond angles at tin from the theoretical values concerns the C–Sn–C angle, which is 154.3(3)° rather than 180°. Such a marked distortion from linearity could be attributed to steric effects involving the chlorine atoms which are bulkier and more strongly bonded to tin than the oxygen atoms. In confirmation of this hypothesis, the two carbon atoms point at the diagonal of the O–Sn–O fragment, as shown by the values of the C–Sn–O angles (78.5—83.3°) which are systematically narrower than the C–Sn–Cl angles (98.2—100.5°). The two oxygen and the two chlorine atoms are practically coplanar, lying within 0.03 Å of the mean least-squares plane.

The two Sn–Cl bond distances, 2.483(2) and 2.468(3) Å, are comparable with those found in other six-co-ordinate diorganotin(IV) adducts having two *cis* chlorines, which are in the range 2.43—2.53 Å.[15-18]

The two Sn–O bond distances are notably different at 2.386(7) and 2.640(7) Å, but no reason was found to justify this. The shorter one, involving O(2), is similar to those found in $(SnPh_3Cl)_2$(dppoe)[8] [2.357(3) Å] and in $SnPh_3Cl$(dppoet)[9] [2.346(6) Å] and somewhat longer than that found in $[SnPh_3(NO_3)]_2$(dppoe)[7] [2.238(5) Å], while the Sn–O(1) distance of 2.640(7) Å is fairly long and rather unusual for this kind of bond. Nevertheless, there are a few cases in which similar Sn–O bonds have already reported: *e.g.* 2.558(10) Å in the six-co-ordinate complex $[Ni(salen)SnMe_2Cl_2]$ [salen = *NN'*-ethylenebis(salicylideneiminate)],[16] 2.591(6) Å in the five-co-ordinate $[(CF_3SO_2)N(SnMe_3)S(Me)N(SO_2CF_3)]$,[19] and 2.680(13) Å in the five-co-ordinate $SnMe_2Cl_2{\cdot}C_7H_6O_2$.[20] Despite the Sn–O inequivalences, the geometry and the dimensions of the two dppoe moieties are very similar, with both the Sn–O–P fragments bent with angles of 167.8(4)° at O(1) and 163.9(4)° at O(2), and with the two P–O bonds, 1.483(6) and 1.491(7) Å, equal within experimental errors, and in good agreement with the sum of the double-bond covalent radii. Moreover, in both the $-PPh_2$ moieties, the phosphorus atoms are not displaced by any significant amount (max. 0.10 Å) from the corresponding phenyl planes, and the aromatic rings are nearly perpendicular to each other, the dihedral angles being 106.7 and 98.1°. The tetrahedral co-ordination around the P atoms cannot be considered as quite regular, particularly because of the bond angles, which deviate considerably from the ideal tetrahedral angles, ranging from 103.4(5) to 114.8(5)°. The phenyl rings are perfectly planar and there are no significant departures from the expected structural parameters as indicated by the C–C bond distances, which are 1.32—1.41 Å, and by the C–C–C angles, which are 118—122°, with average values of 1.38(2) Å and 120(1)°, respectively. Perhaps surprisingly, both the C–C ethane bonds are significantly lengthened from that found in the monoclinic modification of solid ethane[21] [1.532(2) Å], as well as from that observed in structurally known dppoe compounds {*e.g.* 1.522(8) Å in $CuCl_2{\cdot}$dppoe;[1] 1.522(16) and 1.536(17) Å in $CoCl_2{\cdot}$dppoe;[22] 1.52(1) Å in $[SnPh_3(NO_3)]_2$(dppoe);[7] 1.523(8) Å in $(SnPh_3Cl)_2$(dppoe)[8]}.

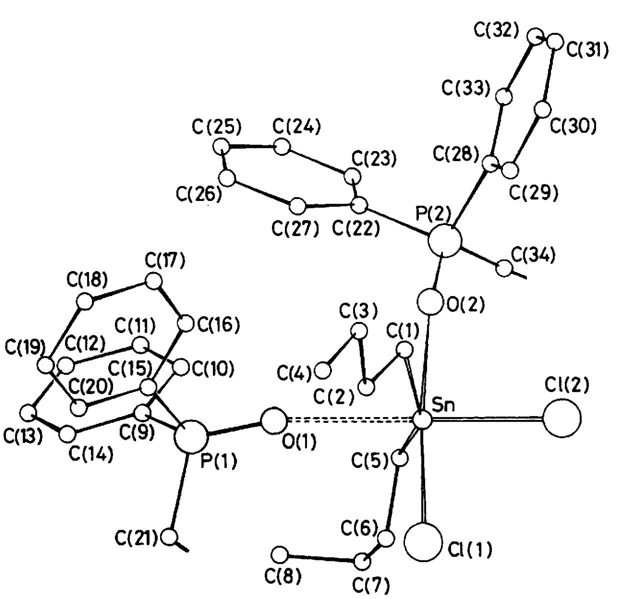

Figure 1. Perspective drawing illustrating the molecular structure with the atom numbering scheme. Hydrogen atoms have been omitted for clarity

The co-ordinating behaviour of the dppoe ligand in the present compound resembles that found in the closely related tin adducts $(SnPh_3Cl)_2$(dppoe) and $[SnPh_3(NO_3)]_2$(dppoe) with the difference that these compounds have a dinuclear structure with the phosphorus ligand functioning as a bridge, through its oxygen atoms, between two tin atoms related by a crystallographic centre of symmetry, while here the whole

Table 4. Selected i.r. bands (cm^{-1}) and relative assignments

Compound	ν(P=O)	Phenyl ring	ν(P–C)	ν(Sn–O)	ν(Sn–C)	ν(Sn–Cl)
dppoe	1 188vs	1 120s	450m			
	1 175vs	1 105 (sh)	410m			
		1 090 (sh)				
		1 070 (sh)				
$(SnPh_3Cl)_2(dppoe)$	1 180s	1 120s	450m	375mw	250 (sh)	
	1 155vs	1 100s	415m			
		1 075ms				
$SnPr^n{}_2Cl_2(dppoe)$	1 200 (sh)	1 125s	425m	385m	530vs	320w
	1 190 (sh)	1 095s			510s	300w
	1 160vs					
$SnBu^n{}_2Cl_2(dppoe)$	1 195 (sh)	1 120s	440m	405m	530vs	270 (sh)
	1 160vs	1 085s		390 (sh)	505s	
		1 070m (sh)				
$SnPh_2Cl_2(dppoe)$	1 190m	1 120s	458ms	385m	285ms	260s
	1 150vs	1 095s				
		1 070 (sh)				

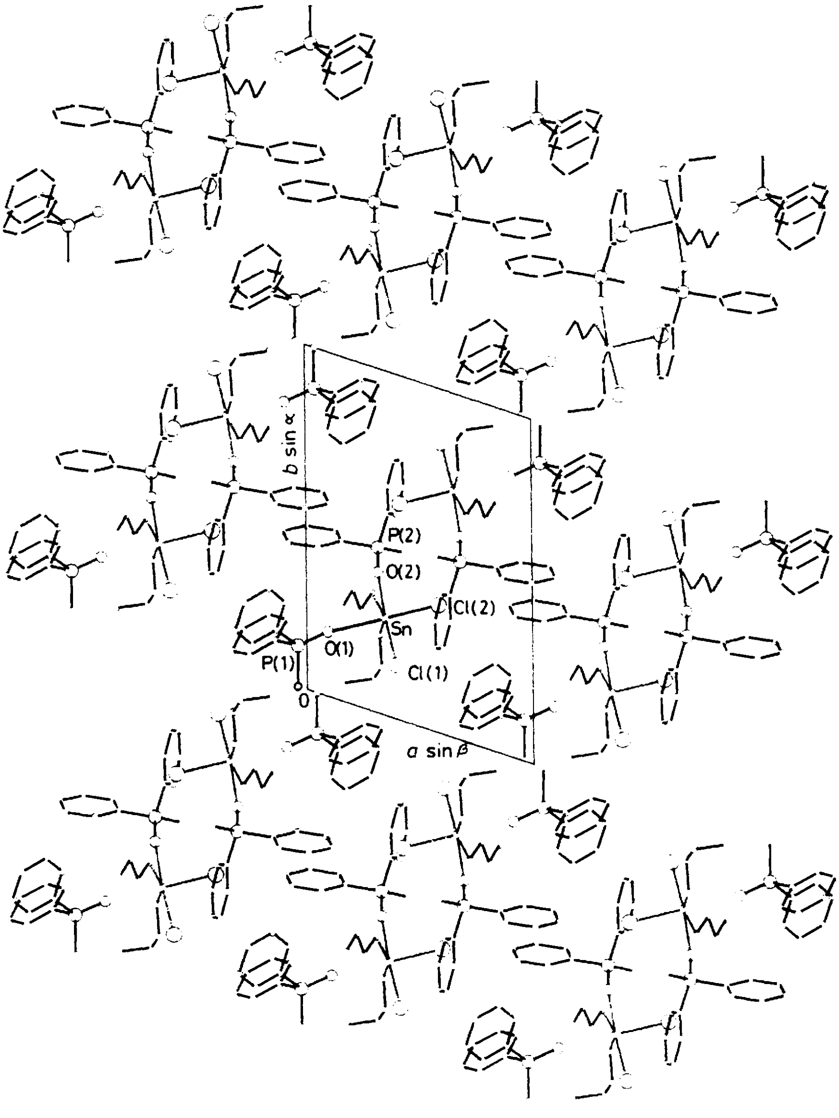

Figure 2. Projection of the structure showing the molecular packing

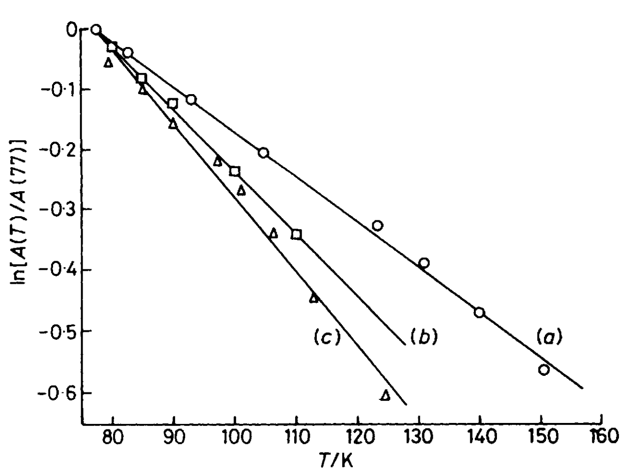

Figure 3. Plots of ln *A*(*T*) *versus* *T* for (*a*) $SnPr^n_2Cl_2(dppoe)$, (*b*) $SnPh_2Cl_2(dppoe)$, and (*c*) $SnBu^n_2Cl_2(dppoe)$. Equations of least-squares computed straight lines are as follows: $SnPr^n_2Cl_2(dppoe)$, $\ln[A(T)/A(77)] = -0.758 \times 10^{-2}\,T + 0.589$; $SnPh_2Cl_2(dppoe)$, $\ln[A(T)/A(77)] = -1.041 \times 10^{-2}\,T + 0.805$; $SnBu^n_2Cl_2(dppoe)$, $\ln[A(T)/A(77)] = -1.231 \times 10^{-2}\,T + 0.952$

crystal structure is polymeric, exactly as found previously in $CuCl_2{\cdot}dppoe$ [1] and $CoCl_2{\cdot}dppoe$.[22]

The two butyl chains show a different conformation. The values of +177.3(7) and −177.0(9)° for the torsion angles about C(1)–C(2) and C(2)–C(3), respectively, indicate that the chain C(1)–C(2)–C(3)–C(4), present in the extended form, adopts an anti-periplanar conformation, unlike the C(5)–C(6)–C(7)–C(8) chain which shows a non-planar molecular backbone, with C(8) 1.40 Å out of the plane of the three other carbon atoms. This different behaviour must be undoubtedly attributable to packing constraints: the conformation adopted by the second chain [torsion angles about C(5)–C(6) and C(6)–C(7) are +174.6(8) and −88.2(13)° respectively] is so as to minimize non-bonded interactions, in fact an abnormally short intermolecular C(8) ··· C(12) contact of 2.50 Å would exist if this chain was in its extended form.

None of the intermolecular distances in the structure is shorter than 3.50 Å. Consequently, the molecules are held together by van der Waals forces, the closest approaches being C(26) ··· C(29) ($\bar{x}$, $1 - y$, $\bar{z}$) = 3.52(1) Å and C(2) ··· C(30) ($1 - x$, $1 - y$, $1 - z$) = 3.54(1) Å.

Infrared Spectra.—The vibrational bands in the 4 000—200 cm^{-1} region are very similar for all the diorganotin(IV) adducts, in agreement with a presumably analogous stereochemistry. The more significant absorptions concern the diphosphine molecule, the P=O group stretching modes being in particular affected by the co-ordination.

A comparison of the main vibrational absorptions of the three complexes with those of the free dppoe and of the complex $(SnPh_3Cl)_2(dppoe)$ is reported in Table 4.

The significant negative shift of the ν(P=O) bands, which is observed in the spectra of all the complexes with respect to that of the free ligand, agrees fairly well with the co-ordination of the phosphoryl oxygen atom to tin as well as with the values reported previously for other co-ordinated phosphine oxides.[5,8,23,24] There is no evidence for two sorts of P=O frequencies, as the two Sn–O distances could imply.

Vibrational bands involving the tin atoms occur in the far-i.r. region and are presented in Table 4 together with their relative assignments. The stretching modes of Sn–C, Sn–Cl, and Sn–O bonds have been attributed on the basis of known literature data [25–28] and our earlier results [7,8,29,30] on complexes containing the Sn–O–P system. The assignment of the ν(Sn–O) band in particular is not always certain, because of the presence of other absorptions in the same spectral region and the large range of values reported for this stretching mode, related to the nature of the oxygen ligand.[31]

Table 5. Root-mean-square amplitudes of vibration, ⟨*x*⟩, and absolute recoil-free fraction values, *f*, for $SnBu^n_2Cl_2(dppoe)$

T/K	⟨*x*⟩/Å	*f*
77.3	0.146	0.0438
79.5	0.147	0.415
85.0	0.148	0.398
89.9	0.150	0.375
97.1	0.151	0.352
101.0	0.152	0.334
106.3	0.154	0.313
112.7	0.156	0.280
124.6	0.160	0.240
290	0.198	0.0032

*Tin-*119 *Mössbauer Spectra.*—Spectra have been recorded for the three $SnR_2Cl_2(dppoe)$ complexes in the temperature range 77—150 K, and for $(SnPh_3Cl)_2(dppoe)$ at 77 K. The value of the quadrupole splitting for the latter complex (2.92 mm s^{-1}) is within the range expected [32] for a *trans*-SnR_3X_2 geometry around the tin atom as determined in an earlier *X*-ray study.[8] Likewise, in the case of the $SnR_2Cl_2(dppoe)$ complexes, values of $\gtrsim 4$ mm s^{-1} are indicative of a *trans*-SnR_2X_4 arrangement about tin. This observation is also corroborated for the butyltin complex by the *X*-ray analysis, although the framework is severely distorted from regular octahedral co-ordination [CSnC = 154.3(3)°]. That the quadrupole splittings for the propyltin and phenyltin homologues are, respectively, higher and lower than for the butyltin complex suggests varying degrees of distortion in the three complexes.

We have previously [33] shown that the temperature coefficient, *a*, of the recoil-free fraction, *f*, defined in equation (1)

$$a = \frac{df(T)}{dT} = \frac{d}{dT} \cdot \exp\left[\frac{-6E_R T}{K\theta^2_D}\right] \qquad (1)$$

in the high-temperature limit of the Debye model is a useful guide to the lattice structure of tin compounds. Thus, in compounds possessing a structure comprising non-interacting molecules, *a* has a value of *ca.* -1.8×10^{-2} K^{-1}. However, the presence of intermolecular bonding interactions serves to increase the value of *a*. Weak association of adjacent molecules by hydrogen bonds as in $SnMe_3(O_3SPh){\cdot}H_2O$ reduces *a* slightly to -1.7×10^{-2} K^{-1}, whereas the values for $SnMe_3(O_2CC_5H_4N\text{-}2){\cdot}H_2O$ and $SnMe_2(ONHCOMe)_2$, which both have complex hydrogen-bonding networks, are -1.27×10^{-2} and -0.92×10^{-2} K^{-1}, respectively. The strongly bridged one-dimensional chain structure of $SnMe_3(ONC_6H_{10})$ has a value of *a* of -0.97×10^{-2} K^{-1}. Values of *a* are most conveniently derived from plots of ln *A*(*T*) *versus* *T*, where *A*(*T*) is the area of the resonance absorption, and is directly proportional to *f*(*T*) in the thin-absorber approximation. Plots of ln *A*(*T*) *versus* *T* for the three $SnR_2X_2(dppoe)$ complexes are illustrated in Figure 3, and least-squares computed values of the temperature coefficients, *a*, for the linear portion of the plots have been determined to be -0.758×10^{-2}, -1.231×10^{-2}, and -1.041×10^{-2} K^{-1} for R = Pr^n, Bu^n, and Ph respectively. These values lie in the range associated with strongly associated lattices, in accord with the known one-dimensional chain structure of the butyltin complex. The higher values for the propyltin and phenyltin complexes are indicative of similar, but more tightly bonded chain structures.

Employing the ambient temperature crystallographic temperature factors, u_{ij}, as a datum point, values of the root-mean-square amplitudes of vibration, $\langle x \rangle$, and of the absolute recoil-free fraction, f, at various temperatures may also be determined using the relationship (2), where λ is the wave-

$$f(T) = \exp[-\langle x(T)^2 \rangle / \lambda^2] \qquad (2)$$

length of the Mössbauer transition, divided by 2π. These data are listed in Table 5. The value of $\langle x \rangle$ falls from 0.198 Å at 290 K to 0.146 Å at 77 K, corresponding to values of f of 0.0032 and 0.0438, respectively.

Acknowledgements

This investigation was supported by an International Grant of the National Research Council (Rome). We also thank the University of Parma for financial support of the *X*-ray work.

References

1 M. Mathew and G. J. Palenik, *Inorg. Chim. Acta*, 1971, **5**, 573.

2 S. Z. Goldberg and K. N. Raymond, *Inorg. Chem.*, 1973, **12**, 2923.

3 J. S. Field, P. J. Wheatley, and S. Bhaduri, *J. Chem. Soc., Dalton Trans.*, 1974, 74.

4 A. E. Kalinin, V. G. Andrianov, and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 1976, **17**, 153.

5 V. G. Kumar Das, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1241.

6 C. R. White and M. D. Joesten, *J. Inorg. Nucl. Chem.*, 1976, **38**, 2173.

7 M. Nardelli, C. Pelizzi, and G. Pelizzi, *Inorg. Chim. Acta*, 1979, **33**, 181.

8 C. Pelizzi and G. Pelizzi, *J. Organomet. Chem.*, 1980, **202**, 411.

9 C. Pelizzi and G. Pelizzi, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 451.

10 W. E. Slinkard and D. W. Meek, *J. Chem. Soc., Dalton Trans.*, 1973, 1024.

11 P. F. R. Ewings, P. G. Harrison, A. Morris, and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1976, 1602.

12 G. M. Sheldrick, SHELX 76 program for crystal structure determination, University of Cambridge, 1976.

13 'International Tables for *X*-ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99—101.

14 Ref. 13, pp. 149—150.

15 N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc. A*, 1970, 1257.

16 M. Calligaris, L. Randaccio, R. Barbieri, and L. Pellerito, *J. Organomet. Chem.*, 1974, **76**, C56.

17 P. G. Harrison, T. J. King, and J. A. Richards, *J. Chem. Soc., Dalton Trans.*, 1974, 1723.

18 L. Coghi, M. Nardelli, C. Pelizzi, and G. Pelizzi, *Gazz. Chim. Ital.*, 1975, **105**, 1187.

19 J. W. Bats, H. Fuess, M. Diehl, and H. W. Roesky, *Inorg. Chem.*, 1978, **17**, 3031.

20 D. Cunningham, J. Douek, M. J. Frazer, M. McPartlin, and J. D. Matthews, *J. Organomet. Chem.*, 1975, **90**, C23.

21 G. J. H. Van Nes and A. Vos, *Acta Crystallogr., Sect. B*, 1978, **34**, 1947.

22 G. R. Clark and G. J. Palenik, *Cryst. Struct. Commun.*, 1979, **8**, 261.

23 S. S. Sandhu and S. S. Sandhu, *J. Inorg. Nucl. Chem.*, 1969, **31**, 1363.

24 E. I. Sinyavskaya and Z. A. Shcheka, *Russ. J. Inorg. Chem.*, 1976, **21**, 1330.

25 P. Taimsalu and J. L. Wood, *Spectrochim. Acta*, 1964, **20**, 1043.

26 A. J. Crowe and P. J. Smith, *Inorg. Chim. Acta*, 1976, **19**, L7.

27 M. E. Bishop, C. D. Schaeffer, and J. J. Zuckerman, *Spectrochim. Acta, Part A*, 1976, **32**, 1519.

28 W. D. Honnick, M. C. Hughes, C. D. Schaeffer, jun., and J. J. Zuckerman, *Inorg. Chem.*, 1976, **15**, 1391.

29 M. Nardelli, C. Pelizzi, and G. Pelizzi, *J. Organomet. Chem.*, 1976, **112**, 263.

30 M. Nardelli, C. Pelizzi, G. Pelizzi, and P. Tarasconi, *Inorg. Chim. Acta*, 1978, **30**, 179.

31 T. Tanaka, *Organomet. Chem. Rev.*, 1970, **5**, 1.

32 G. M. Bancroft, V. G. Kumar Das, T. K. Sham, and M. G. Clark, *J. Chem. Soc., Dalton Trans.*, 1976, 643.

33 P. G. Harrison, R. C. Phillips, and E. W. Thornton, *J. Chem. Soc., Chem. Commun.*, 1977, 603.

Received 9th *July* 1982; *Paper* 2/1161