Synthesis and characterisation of dialkyltin 2,3-bis(diphenylphosphino)maleic acid adducts

Richard J. Bowen *,a,b, Judy Caddy b, Manuel A. Fernandes a, Marcus Layh a,*, Messai A. Mamo a, Reinout Meijboom c

a Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, Wits 2050, Johannesburg, South Africa
b Project AuTEK, Mintek, Private Bag X 3015, Randburg 2125, South Africa
c Department of Chemistry, University of the Free State, P.O. Box 339, Bloemfontein 9300, South Africa

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Abstract

The novel dialkyltin 2,3-bis(diphenylphosphino)maleic acid adducts (R₂Sn)(O,O⁻-dpmaa) [1a, R = Me; 1b, R = Bu; dpmaa = bis(diphenylphosphino)maleic acid] were synthesised from dpmaa and R₂SnCl₂ or Bu₂SnO. They were fully characterised by elemental analysis, IR- and multinuclear NMR-spectroscopies as well as X-ray crystallography [in the case of 1a as its Ph₂P(O)(CH₂)₂P(O)Ph₂ adduct]. Both were found to be cyclic trimers in the solid state that dissolve in the case of 1b into an equilibrium mixture of oligomers.

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Keywords: Dialkytin carboxylates; Cyclic trimer; 2,3-Bis(diphenylphosphino)maleic acid adducts; X-ray

1. Introduction

The self-assembly of organic ligands coordinated to metal ions or organometallic substances has been extensively studied [1]. The increasing interest in the field is mainly due to the potential relevance of such complexes to catalysis [2]. Another important objective is the synthesis of new, highly water soluble metal complexes useful in biological systems. Organo-tin compounds show a spectrum of biological effects and have been studied as fungicides, bactericides, acaricides and wood-preservatives [3]. Organo-tin compounds have also been studied as anti-tumour drugs and were reported to exhibit lower toxicity than the related platinum drugs [4]. Although the first testing of organotin compounds as anti-tumour agents was carried out in 1929, the application of organotin compounds did not attract much attention until the late 1980s [4].

Diorganotin(IV) complexes of adenine and glycyglycine were reported by Barbieri et al. [5]. Testing on these compounds revealed that the complex species is transported into the tumour cells. Saxena and Tandon [6] indicated that the presence of highly electronegative groups in diorganotin complexes could greatly enhance their activity. The organic group R in diorganotin compounds R₂SnX₂ determines the potential anti-tumour activity [7]. One of the most promising groups in substituted salicylic acids with diorganotin oxides appeared to be di-n-butyltin [7].

The solid-state structures of trialkyltin(IV) carboxylates can be either monomeric [8], oligo- and polymeric [9] or cyclooligomeric [10], whereby the oligo- and polymeric structures are formed through intermolecular Sn–O–C=O–Sn bonds. Since these bonds are relatively weak, a discrete molecular structure can be expected in solution. Because of interest in the creation of oligo- and polymeric structures with strong binding interactions between the repeating units, we became interested in the chemistry of diorganotin(IV) derivatives of dicarboxylic acids, and the literature search shows that the first complexes of this type were prepared more than 50 years ago [11]. Since then, various diorganotin(IV) moieties, mainly dimethyl and di-n-butyltin(IV), have been combined with the most common
dicarboxylic acids, such as oxalic [12], malonic [13], succinic [13], adipic [13], maleic [14], phthalic [15,16], and terephthalic acid [16]. The resulting complexes were used as PVC stabilisers [17], catalysts for transesterification reactions [18], catalysts for polyurethane polymerisations [18], and in RTV silicone curing reactions [19]. A series of diorganotin(IV) derivatives of dicarboxylic acids have been tested also as anti-tumour agents [20]. However, a conclusive characterisation of diorganotin(IV) derivatives of dicarboxylic acids with respect to their structures in solution is not trivial, since they are frequently insoluble due to their polymeric or oligomeric nature, and for the case that they are soluble, they are often involved in dynamic equilibria with fast ligand exchange reactions [21].

Monodentate and bidentate phosphines are amongst the most common ligands in coordination chemistry. During our ongoing investigations in the coordination chemistry of metal-phosphine complexes [22], we became interested in the coordination behaviour of 2,3-bis(diphenylphosphino)maleic acid. Combination of the dialkyltin moiety with 2,3-bis(diphenylphosphino)maleic acid would give potentially new ligands for the synthesis of hetero-bimetallic compounds. Here, we report on our results in the solution- and solid-state study of dimethyltin(IV)- and di-n-butyltin(IV)-2,3-bis(diphenylphosphino)maleic acid adducts, which both form trinuclear macrocyclic structures in the solid state. The here presented adducts form the first examples of tin carboxylates containing two phosphine functionalities.

2. Results and discussion

2.1. Synthesis

The tin complexes 1 were synthesised from the reaction of 2,3-bis(diphenylphosphino)maleic acid (dpmaa) and one equivalent of R₂SnCl₂ in the presence of two equivalents of base (KOH or NEt₃) in benzene at room temperature (Scheme 1(i)). Complex 1b was alternatively obtained from the equilibrium reaction of dpmaa and Bu₂SnO by azeotropic removal of water (Scheme 1(ii)). Both compounds were yellow solids, moderately stable in moist air and soluble in polar organic solvents, but insoluble in hydrocarbons.

Complex formation and Sn–O bond formation in the products was evident in the IR spectrum from the absence of an ν(OH) absorption band at around 3500 cm⁻¹ and the appearance of strong ν(CH) bands in the alkyl region (2900–3100 cm⁻¹) attributed to the alkyl groups of the tin moiety. The differences (Δν, Table 1) between antisymmetric and symmetric carboxylate stretching frequencies have previously been used to deduce the bonding mode of metal carboxylates [23]. Large Δν values were related to an unidentate bonding mode (Δν > 200–260 cm⁻¹; cf. Δν for dpmaa in Table 1) and a small Δν (Δν < 200 cm⁻¹) to a bidentate chelating or bridging bonding mode [23]. Between the two extremes exists a bonding mode that is commonly referred to as anisobidentate where one metal oxygen contact is significantly shorter than the other. This region is not very well defined and was more recently shown to extend considerably beyond Δν = 260 cm⁻¹ [24].

The tin complexes 1 were found to have both in the solid state as well as in solution Δν values around 260 cm⁻¹ which is therefore consistent with an anisobidentate coordination of the tin atoms.

Complex formation was also confirmed in the ¹H NMR spectrum of 1 by the absence of the OH signal at around δ 3 and the presence of signals of expected intensity in the alkyl region of the spectrum.

The chemical shift values in the ³¹P NMR spectrum of the complexes were not surprisingly similar to that of the free ligand (Table 1) indicating that tin coordination to the carboxylate had only a negligible effect on the electronic environment of the phosphorus atoms. The butyl-derivative 1b, however, showed unexpectedly two distinct signals at δ –8.5 and δ –10.1. Repeated recrystallisation of 1b and powder-XRD analysis confirmed the purity of 1b and the absence of free dpmaa. Dilution experiments of a saturated solution of 1b in CDCl₃ that was stepwise diluted, revealed that the ratio of the two peaks changed.
from 6:1 (saturated solution) to about 0.8:1. Variable temperature analysis showed further that the signal at $\delta$ = 8.5 resolved into three broad signals at $\delta$ = 7.4, $\delta$ = 9.0 and $\delta$ = 15.1 at 213 K (coalescence temperature 233 K), while the signal at $\delta$ = 10.1 remained essentially unaffected. In a tentative interpretation of these results the signal at $\delta$ = 8.5 was assigned to a trimeric species ($1b$ was found to be a trimer in the solid state, see below) whose different phosphorus environments or different conformers (cf. the existence of different polymorphs in the solid state) were partially resolved at lower temperature. The signal at $\delta$ = 10.1 is consistent with a second species, possibly a monomer, in equilibrium with the trimer (equilibrium was established fast as there was no visible time dependence in the ratio of the intensities of the two signals at room temperature when a sample of $1b$ was measured immediately after preparation and then again after a period of 15 h), whose $^{31}$P NMR spectrum was not influenced by temperature and whose formation from the trimer, in agreement with the dilution experiments, should be favoured at lower total concentration of $1b$. The presence of several oligomers in solutions of tin carboxylates has been described previously [13,25].

The $^{31}$P NMR spectrum of the methyl derivative $1a$ at room temperature showed, in contrast, only a single line at $\delta$ = 8.7 similar to the postulated trimeric species of $1b$ and a dent in the baseline at $\delta$ = 11.3. Cooling of the sample resulted in significant line broadening (64 Hz) at 223 K but gave no further evidence of the existence of more than one species in solution.

The $^{119}$Sn NMR spectra of $1a$ and $1b$ showed a single broad signal (Table 1) on the lower side or just outside the region ($\delta$ = 90 to 190) [21] associated with five coordinated tin and similar to those of related compounds such as [1,2-(Bu$_2$SnO$_2$C)$_2$C$_6$H$_4$]$_n$ ($\delta$ = 139) or [1,3-(Bu$_2$SnO$_2$C)$_2$C$_6$H$_4$]$_n$ ($\delta$ = 161) [25]. This is consistent with the previously described anisobidentate coordination (coordination number 5 as average between 4 and 6) of the carboxylic acid group found in the IR spectrum and the molecular structure of $1b$ in the solid state (see below). $^{119}$Sn NMR-spectroscopic shift values above $\delta$ = 90 or below $\delta$ = 190 were found to indicate tin complexes with coordination number 4 or 6, respectively [21]. The negligible influence of the solvent on the $^{119}$Sn NMR spectrum of the complexes in a non-polar as compared to a polar solvent (Table 1) indicated that the average coordination number of the complexes was independent of the solvent. A shift of $\delta$ 30 ppm and more to higher field strength in the $^{119}$Sn NMR spectrum of four and five coordinate tin compounds as a result of a change from a non-polar to a polar NMR solvent has been attributed to an increase in coordination number of the tin complexes in polar solvents [21]. Variable temperature experiments showed that the $^{119}$Sn NMR spectrum of $1b$ resolved in agreement with the complex behaviour discussed for the $^{31}$P NMR spectrum into three broad signals at $\delta$ = 96.6, -104.2 and -196.3.

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta\nu$ (solid) (cm$^{-1}$)</th>
<th>$\Delta\nu$ (CHCl$_3$) (cm$^{-1}$)</th>
<th>$\delta$ ($^{31}$P, CDCl$_3$)</th>
<th>$\delta$ ($^{119}$Sn, CDCl$_3$)</th>
<th>$\delta$ ($^{119}$Sn, DMso)</th>
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</thead>
<tbody>
<tr>
<td>dpmaa</td>
<td>509</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$1a$</td>
<td>264</td>
<td>257</td>
<td>–11.7</td>
<td>–104.2</td>
<td>–116.5</td>
</tr>
<tr>
<td>$1b$</td>
<td>253</td>
<td>258</td>
<td>–8.7</td>
<td>–93.3</td>
<td>–116.5</td>
</tr>
</tbody>
</table>

* Not observed: signal presumably very broad as evident from $^{31}$P NMR spectrum.

2.3. Crystallographic studies

A considerable number of diorganotin(IV) carboxylates has been crystallographically characterised in the last two decades and several structural types have been identified [26]. These included (i) monomeric structures [27] with a six-coordinate tin atom and chelating carboxylate groups, (ii) polymeric structures [24,25,27b,28] with bridging carboxylate groups, (iii) dimeric structures [29] similar to the monomeric type but with an additional interaction between tin atoms and oxygen atoms of adjacent monomers, and (iv) more recently a cyclic trimer [25].

The repeated recrystallisation of $1b$ in diethyl ether gave several batches of the dibutyltin-derivative, two of which were characterised by X-ray crystallography and found to represent two different polymorphs of $1b$. While numerous attempts to obtain crystals of $1a$ suitable for X-ray diffraction from solvents such as Et$_2$O, CH$_2$Cl$_2$ or CHCl$_3$ were unsuccessful, co-crystals $1a$: [Ph$_3$P(O)(CH$_2$)$_2$P(O)Ph$_2$]$_{1/6}$ of $1a$ and Ph$_3$P(O)(CH$_2$)$_2$P(O)Ph$_2$ were obtained from diethyl ether (or a mixture of Et$_2$O and CH$_2$Cl$_2$) solution by slow evaporation of the solvent. All three structures are cyclic trimers [in the case of $1a$ bridged by Ph$_3$P(O)(CH$_2$)$_2$P(O)Ph$_2$] and crystallise with one or in the case of $1a$: [Ph$_3$P(O)(CH$_2$)$_2$P(O)Ph$_2$]$_{1/6}$ three molecules of diethyl ether per trimer. The molecular structures of $1a$ and $1b$ are illustrated in Figs. 1 and 2, respectively. Selected bond distances and angles are listed in Table 2.

The backbone of all three structures is a trimeric 21-membered macrocycle that is formed as a result of dpmaa binding to the tin atoms in a bridging anisobidentate bonding mode. The coordination geometry of the tin atoms (except Sn1c of $1a$) may be described as highly distorted octahedral or bicapped tetrahedral with the coordinative bound carboxyl oxygen atoms O2a, O4a, O2b, O4b, O2c and O4c capping the faces. The Sn–O bond distances to the latter are much longer [ranging from 2.350(3)–2.846(3) Å] than to the covalently bound oxygen.
atoms [ranging from 2.070(3)–2.166(3) Å]. The ‘normal’
tetrahedral angles around the tin atoms are in the range
of 100.3(2)° to 111.8(2)°, while the remaining two sets of
angles show the effect of the capping resulting in much
more acute [79.3(1)–86.4(1)°] and obtuse angles [129.4(1)–
146.5(2)°]. The octahedral view of the geometry is evident
from the planarity of the SnO₄ fragment (largest deviation
from planarity ranging from 0.018 to 0.081 Å in 1b but
1.0 Å in 1a) and the large C–Sn–C angles. The covalent
Sn–C and Sn–O distances show little variation and are sim-
ilar to those described in the literature [24–29]. The coordi-
native Sn–O distances (Table 2) show much larger
variations which is in agreement with the wide range of val-
ues (2.46–3.11 Å) reported for that type of bond in trialkyl-
and dialkyltin carboxylates [26–30]. The difference in Sn–O
bond distances is also reflected in the disparity of the two
associated CO distances of the carboxylate groups, one
representing a C–O single [1.283(4)–1.307(5) Å] and one a
C=O double bond [1.209(5)–1.260(5) Å].

In the case of 1a two trimers are bridged via the O atoms
of a Ph₂P(O)(CH₂)₃P(O)Ph₂ molecule that has an inversion
centre in the wide range of values (2.46–3.11 Å) reported for that type of bond in trialkyl-
and dialkyltin carboxylates [26–30]. The difference in Sn–O
bond distances is also reflected in the disparity of the two
associated CO distances of the carboxylate groups, one
representing a C–O single [1.283(4)–1.307(5) Å] and one a
C=O double bond [1.209(5)–1.260(5) Å].

A comparison of the two polymorphs of 1b reveals the
main difference to be the different contact distances for
Sn1a–O2a (2.848 versus 2.574 Å) and Sn1c–O2c (2.413 ver-
sus 2.549 Å) and a different arrangement of the phenyl
groups of the phosphine ligands (Fig. 2). This is evident
from an overlap of the two polymorphs that shows a root
mean square (RMS) difference of 0.29 Å for the backbone
of the molecule excluding butyl and phenyl groups other
then α- and ipso-C atoms (Fig. 3) as compared to a RMS
value of 2.78 Å for the whole molecule.

The molecular structure of the related trimeric dibutyl-
tin(IV) isophthalate [1,3-(Bu₂SnO₂C)₂C₆H₄] [25] differs
from that of 1a and 1b in the ring size (24-membered)
and the near-planarity of the ring. This creates a cavity
in the isophthalate derivate that is occupied by a butyl
group of a neighbouring trimer. Adjacent trimers are fur-
ther connected to long chains by an interaction between
the tin atoms in one trimer with a carbonyl group of an
adjacent trimer hereby increasing the coordination num-
ber around tin to seven (cf. 1a). The macrocycle in 1a
and 1b is in contrast puckered in such a way that the space
inside the macrocycle is occupied by the alkyl substituents
of each trimer hereby minimising steric interactions
between the butyl and the phenyl groups. There are no
close contacts other than van der Waals interactions in
1a and 1b.

3. Experimental

3.1. General procedures and reagents

All manipulations were carried out using standard
Schlenk techniques under argon [31]. Solvents were dis-
tilled from the appropriate drying agent prior to use [32]. All other reagents were obtained from Sigma-Aldrich and stored under argon. NMR spectra were recorded on either a Bruker DRX 400 (1H, 400.13 MHz; 31P, 162.0 MHz; 119Sn, 149.2), a Bruker Avance 300 (1H, 300.13 MHz; 13C, 75.5 MHz) or a Bruker AC 200 (1H, 200.13 MHz) spectrometer. NMR spectra were referenced internally to residual solvent resonances (1H and 13C) or externally to 85% H3PO4 (31P) or SnMe4 (119Sn). Infrared spectra were recorded on a Bruker Vario 22 spectrometer. FAB-MS spectra were collected using a VG70-SEQ instrument in positive ion mode. Elemental analyses were determined by the Institute for Soil, Climate and Water, Pretoria, South Africa. The following abbreviations are used throughout Section 3: bs, broad singlet; m, multiplet; mm, multiple multiplets; q, quartet; s, singlet; t, triplet. Coupling constants (J) are given in Hz.

3.2. Synthesis of compound 1a

Triethyl amine (0.25 cm3, 1.58 mmol) was added to a solution of 2,3-bis(diphenylphosphino)maleic acid Æ 2Et2O (0.50 g, 0.79 mmol) in benzene (25 cm3). The reaction mixture was stirred for 15 min and a solution of dimethyltin dichloride (0.17 g, 0.79 mmol) in benzene (20 cm3) was then added dropwise over a period of 15 min. The yellow reaction mixture was then stirred for 16 h. The volatiles were removed in vacuo to give a yellow powder. The residue was partitioned between chloroform (15 cm3) and water (20 cm3). The organic layer was separated, washed with water (20 cm3), dried over MgSO4, filtered and concentrated in vacuo to give the title compound as a yellow powder (0.56 g, 88%). Elemental analysis: Calc. for C30H26O4P2Sn: C, 57.09; H, 4.15%. Found: C, 56.88; H, 4.62%. IR (KBr, cm−1): 1323 s [v(C–O)], 1580 s [v(C=O)], 2912 m, 2930 m, 3000 m, 3049 m [v(C=CH)]. 1H NMR (CDCl3): δ 0.25 [bs, CH3, 2J(119Sn–1H) 77.8 Hz, 6H], 7.32–7.23 (m, o and m-Ar, 16H), 7.43 (bs, p-Ar, 4H); 13C NMR (CDCl3): δ 3.3 (s, CH3), 128.3 [t, Ar, 2J(19P–13C) 3.6 Hz], 128.8 [s, (p-Ar)], 133.9 [t, Ar, 1J(19P–13C) 10.7 Hz], 134.5 [t, Ar, 2J(19P–13C) 2.4 Hz], 149.8 (s, C=O), 174.3 [t, C=O, 2J(19P–13C) 3.7 Hz]; 31P NMR (CDCl3): δ −8.7 (s); 119Sn NMR (CDCl3): δ −83.3; FAB-MS (M+ + H) 632 m/z (8%).

3.3. Synthesis of compound 1aÆ [Ph2P(O)(CH2)2P(O)Ph2]1/6

A mixture of 1a (0.172 g, 0.27 mmol) and a slight excess (stoichiometric ratio of 1a:P-oxide = 6:1.13) of Ph2P(O)(CH2)2P(O)Ph2 (0.022 g, 0.051 mmol) was dissolved in a 1:1 mixture of Et2O and CH2Cl2. Slow evaporation of the solvents resulted in the formation of yellow crystals of the adduct (0.14 g, 74%). M.p. (decomp.): 135–140 °C Elemental analysis: Calc. for C206H180O26P24Sn6Æ (CH2Cl2)1/6: 1H NMR spectroscopy and an uncompleted
X-ray structure suggest the presence of CH$_2$Cl$_2$ which is lost on standing): C, 57.79; H, 4.26%. Found: C, 57.3; H, 4.47%.

The crystals used for single crystal analysis were obtained in a similar but less reproducible manner (a result of the limited solubility of the phosphine oxide in Et$_2$O) from a solution of the two starting materials in Et$_2$O. A $^{31}$P NMR spectrum of the crystals in CDCl$_3$ at room temperature showed two signals at $\delta_{/C^0}$8.7 and 33.3 in agreement with a dissociation of the adduct in solution into uncoordinated \(1a\) and free \([\text{Ph}_2\text{P(O)}-(\text{CH}_2)_2\text{P(O)Ph}_2]\).

### 3.4. Synthesis of compound \(1b\)

**Method A.** A solution of KOH (0.027 g, 0.85 mmol) in methanol was added to a solution of 2,3-bis(diphenylphosphino)maleic acid · 2Et$_2$O (0.25 g, 0.42 mmol) in t hf (15 cm$^3$). The reaction mixture was stirred for 15 min. A thf solution of dibutyltin dichloride (0.13 g, 0.42 mmol)
was then added dropwise to the dpmaa solution over a period of 15 min at room temperature. The reaction mixture was stirred overnight. The solvent was removed in vacuo, the residue extracted into CHCl₃ (20 cm³) and the solution was washed twice with deionised water (20 cm³). The organic phase was separated, dried over MgSO₄ and then removed in vacuo to give a light yellow solid (0.22 g, 76%).

**Method B.** Dibutyltin oxide (0.60 g, 2.4 mmol) was added to a solution of 2,3-bis(diphenylphosphino)maleic acid·2Et₂O (1.00 g, 1.58 mmol) in benzene (90 cm³). The reaction mixture was heated under reflux for 30 min while continuously removing the formed water by azotropic distillation in a Dean-Stark apparatus. The volatiles were evaporated in vacuo and the residue was recrystallised from diethyl ether to give the title compound as yellow crystals (1.20 g, 88%). Crystals suitable for X-ray analysis were grown from diethyl ether. Elemental analysis: Calc. for C₃₆H₄₈O₄P₂Sn: C, 60.47; H, 5.34%. Found: C, 60.37; H, 5.34%. IR (KBr, cm⁻¹): 1342 s [v(C–O)], 1594 s [v(C–C)], 2856 m, 2915 m, 2959 m, 3055 m [v(C–H)]; ¹H NMR (CDCl₃): δ 0.73 [bs, CH₃(Bu) 6H], 0.92–1.13 [mm, CH₂(Bu), 12H], 3.48 [q, OCH₂(solvent)], 7.07–7.31 (mm, m, p, o-Ar, 20H); ¹³C NMR (CDCl₃): δ 13.5, 13.8 (s, CH₃), 15.3 [s, CH₃(2)], 23.8, 26.1, 26.35, 26.43, 27.0 (s, CH₂), 65.8 [s, OCH₂(2)], 127.9–128.1 (mm, m-Ar), 128.6–128.7 (mm, p-Ar), 133.9–134.3 (mm, o-Ar), 134.9, 135.3 (ipso-Ar) 151.0 (s, C=–C), 172.2 [t, C=O, 2J(¹³P–¹³C) 4.1 Hz], 174.2 [t, C=O, 2J(¹³P–¹³C) 3.6 Hz]; ¹¹¹Sn NMR (CDCl₃): δ −102.3 (s); ¹⁹⁵Sn NMR(d₂-dmso): δ −116.5 (s); FAB-MS (M⁺ – Bu) 660 m/z (12%).

### 3.5. X-ray crystallography

Intensity data were collected on a Bruker SMART 1K CCD area detector diffractometer with graphite monochromated Mo Kα radiation (50 kV, 30 mA). The collection method involved o-scans of width 0.3°. Data was reduced with the program SAINT+ [34] and absorption corrections were made using the program SADABS [34]. The crystal structures were solved by direct methods using SHELXTL [35]. Non-hydrogen atoms were first refined isotropically, followed by anisotropic refinement by full-matrix least-squares calculation based on F² using SHELXTL. Hydrogen atoms were first located in the difference map, then positioned geometrically and allowed to ride on their respective parent atoms. Further crystallographic data are summarised in Table 3. Diagrams and publication material were generated using SHELXTL [35], PLATON [36] and ORTEP3 [37].

In the structure of 1a one of the phenyl groups was found to be disordered (C11B–C16B). This was refined isotropically over two positions as C11B–C16B and C11F–C16F with site occupancies of 0.60(2) and 0.40(2),

### Table 3

Crystal data and structure refinement details for 1a and 1b

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>1b (Polymorph A)</th>
<th>1b (Polymorph B)</th>
</tr>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₂₈H₁₂₂O₃₈P₁₄Sn₆</td>
<td>C₁₁₂H₁₂₈O₃₈P₁₄Sn₆</td>
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<td>173(2)</td>
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<td>173(2)</td>
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<td>Wavelength (Å)</td>
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<td>0.71073</td>
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<td>P₁</td>
<td>P2₁/n</td>
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<td>α (Å)</td>
<td>13.5228(13)</td>
<td>15.1482(7)</td>
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<td>25.780(3)</td>
<td>15.8531(8)</td>
<td>19.4003(7)</td>
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<td>γ (Å)</td>
<td>29.962(3)</td>
<td>24.6201(12)</td>
<td>35.4638(11)</td>
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<tr>
<td>γ (°)</td>
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<td>63.835(3)</td>
<td>90</td>
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<td>Volume (Å³)</td>
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<td>36940/20292 [0.063]</td>
<td>45573/18496 [0.060]</td>
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<td>Z, calculated density (Mg m⁻³)</td>
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<td>2, 1.409</td>
<td>2, 1.385</td>
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<td>Absorption coefficient (mm⁻¹)</td>
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<td>0.848</td>
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<td>F(000)</td>
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<td>2280</td>
<td>4560</td>
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<tr>
<td>Crystal size (mm)</td>
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<td>0.26 × 0.20 × 0.18</td>
<td>0.30 × 0.30 × 0.22</td>
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<td>Completeness to 2θ (°)</td>
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<td>98.6</td>
<td>98.7</td>
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<td>Maximum and minimum transmission</td>
<td>0.8296 and 0.6976</td>
<td>0.8602 and 0.8086</td>
<td>0.8331 and 0.7880</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>22499/108/1206</td>
<td>16449/69/1169</td>
<td>18496/67/1253</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.001</td>
<td>1.061</td>
<td>1.061</td>
</tr>
<tr>
<td>Final R indices</td>
<td>R₁ = 0.037, wR₂ = 0.089</td>
<td>R₁ = 0.045, wR₂ = 0.125</td>
<td>R₁ = 0.039, wR₂ = 0.102</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.053, wR₂ = 0.098</td>
<td>R₁ = 0.072, wR₂ = 0.142</td>
<td>R₁ = 0.055, wR₂ = 0.111</td>
</tr>
<tr>
<td>Largest difference peak and hole/e Å⁻³</td>
<td>1.263 and −1.015</td>
<td>1.289 and −0.669</td>
<td>1.171 and −0.774</td>
</tr>
</tbody>
</table>
respectively. In addition, one of the diethyl ether molecules was also found to be disordered and was refined anisotropically in two positions with site occupancies of 0.501(11) and 0.499(11), respectively.

Polymorph A of 1b contains disordered ether molecules (1 per main molecule). A treatment of SQUEEZE [38] accounted for 53 electrons per unit cell, less than the 84 electrons two ether molecules would account for, but not unexpected as the data collection was done at room temperature, allowing some of the solvent molecules to escape. Though coordinates of the ether molecules have not been added to the final structure, their contribution to \( I(000) \), the sum formula and density has been accounted for with full occupancy.

Polymorph B of 1b contains several disordered butyl groups. These have each been refined over two positions, using free variables for the occupancy of each position (the occupancies of the two positions being summed up to unity), as well as SADI and DFIX restraints on the molecular geometries of each disordered fragment.

The RMS difference values for the two polymorphs of 1b were calculated with x8 [35].

4. Supplementary material

Full crystallographic data (CCDC 267677 for 1a, 267678 for polymorph A and 267679 for polymorph B of 1b) have been deposited at the Cambridge Crystallographic Database Centre and are available on request from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or on the web http://www.ccdc.cam.ac.uk).

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References

(c) D.L. Caulder, K.N. Raymond, Acc. Chem. Res. 32 (1999) 975;
(d) P.J. Langley, J. Hulliger, Chem. Soc. Rev. 28 (1999) 975;
(e) M. Fujita, Struct. Bond. 96 (2000) 177;
(g) G.F. Swiegard, T.J. Malefetse, Chem. Rev. 100 (2000) 3483;


(c) For related diorganotin(IV) monocarboxylates with a cycloligomic structure formed through intermolecular Sn-O interactions see: T.P. Lockhart, Organometallics 7 (1988) 1438;
(d) J. Meunier-Piret, M. Boualam, R. Willem, M. Gielen, Main Group Met. Chem. 16 (1993) 329.


(c) T.P. Lockhart, J.C. Calabrese, F. Davidson, Organometallics 6 (1987) 2479.


    (b) S.W. Ng, V.G.K. Das, W.-H. Yip, R.-J. Wang, T.C.W. Mak, J. Organomet. Chem. 393 (1990) 201;


