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# Synthesis and characterization of triphenyltin(IV) 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoates. Crystal and molecular structures of $Ph_3Sn\{O_2CC_6H_3$-*p*-$OH[NN(C_6H_4$-4-$CH_3)]\}$ and the 2,2′-bipyridine adduct $Ph_3Sn\{O_2CC_6H_3$-*p*-$OH[N{=}N(C_6H_4$-2-$CH_3)]\}OH_2 \cdot C_{10}H_8N_2$

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**Abstract**

Triphenyltin 5-[(*E*)-2-(4-methylphenyl)-1-diazenyl]-2-hydroxybenzoate, $Ph_3SnL^2H$, has been prepared and characterized, its structure determined by X-ray crystallography, and the structure compared with those of its homologues. Two polymorphs were isolated from the same crystallization attempt. The reactivity of tetrahedral $Ph_3SnL^1H$ ($L^1H$ = 5-[(*E*)-2-(2-methylphenyl)-1-diazenyl]-2-hydroxybenzoate) towards 2,2′-bipyridine (bipy) has been investigated to ascertain the ability of bipy to coordinate to the Sn-complex and the resultant changes in the molecular architecture. The crystal structure of the product revealed that the bipy moiety does not coordinate to the Sn atom, but forms a cyclic tetrameric adduct of formula $[Ph_3SnL^1H(H_2O)]_2 \cdot bipy_2$ through hydrogen bonding between the water ligand of $Ph_3SnL^1H(H_2O)$ and the bipy N atoms. The interpretation of this structure was further enhanced by IR, NMR ($^1H$, $^{13}C$, $^{119}Sn$) and $^{119m}Sn$ Mössbauer experiments.


*Keywords:* Triphenyltin; Carboxylates; 5-[(*E*)-2-(Aryl)-1-diazenyl]-2-hydroxybenzoic acids; Crystal structure

## 1. Introduction

Triorganotin carboxylates, $R_3Sn(O_2CR')$ are the subject of notable interest because of both their structural diversity in the crystalline state [1,2] and their interesting biological activity [3]. Major structural issues in organotin carboxylates are induced by the higher coordination ability of tin, more specifically its ability to be involved in either weak or strong intra- and inter-molecular coordination [4–7]. In the solid state, four basic motifs have been observed for $R_3Sn(O_2CR')$ when possible additional coordination to tin originates only from the carboxylate oxygen atoms; other motifs arise when other potential donor atoms reside in R′ [1,2]. Essentially, discrete monomeric, distorted tetrahedral (Ia) or discrete, distorted *cis*-trigonal bipyramidal (Ib) [1,2], polymeric,

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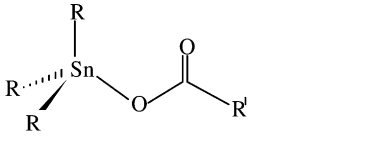
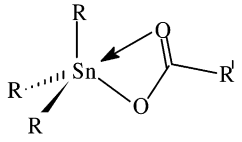
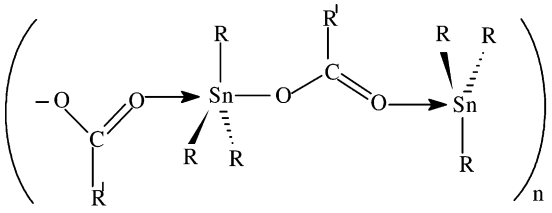
*trans*-trigonal bipyramidal (II) [1,2], cyclotetrameric, distorted *trans*-trigonal bipyramidal (III) [8], and cyclohexameric (IV, similar to II) [9] geometries have been noted. Recently, we have reported a series of triorganotin carboxylates involving azo-organic residues and their crystal structures fall within the boundaries of the motifs specified above [10–13]. In these systems, triphenyltin azocarboxylates invariably display distorted tetrahedral coordination at the Sn atom (motif Ia). In the presence of moisture, a water molecule is able to coordinate to the tetrahedral Sn atom of $R_3Sn(O_2CR')$ complexes. This water molecule can then form a hydrogen bonded adduct with N-donor ligands [14–18] and the Sn atom in these complexes invariably shows a *trans*-$R_3SnO_2$ trigonal bipyramidal geometry. This type of bonding is well known in the study of biochemical systems, particularly in the binding of cations to nucleic acids and their components [19–21]. Examples of such hydrogen bonded adducts involving triorganotin carboxylates are scanty [22,23] and both reports involve the 1,10-phenanthroline moiety. In line with these developments and as part of a comprehensive study on triorganotin azocarboxylates [10,24], the reactivity of triphenyltin(IV) 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoates towards 2,2′-bipyridine (bipy) was investigated. The present paper reports the preparation, characterization and



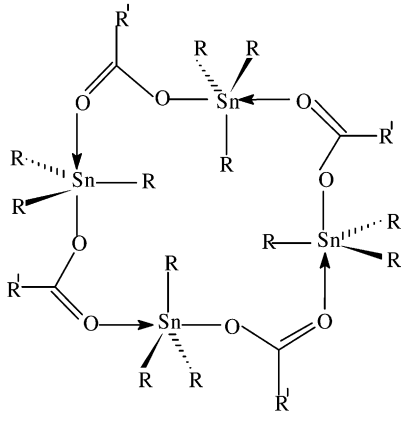
Ia



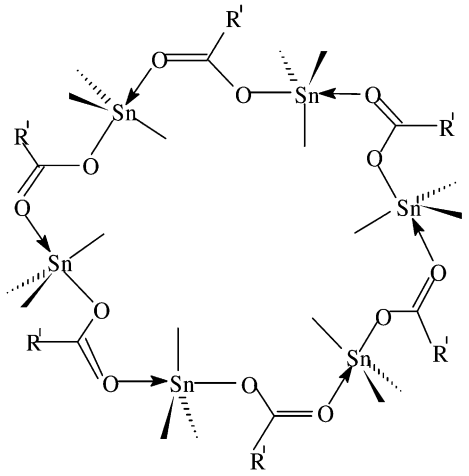
Ib



II



III



IV

crystal structures of two further triphenyltin(IV) complexes, viz., triphenyltin 5-[(*E*)-2-(4-methylphenyl)-1-diazenyl]-2-hydroxybenzoate and the hydrogen-bonded bipy adduct with aqua(5-[(*E*)-2-(2-methylphenyl)-1-diazenyl]-2-hydroxybenzoato-*O*:*O*′)triphenyltin.

## 2. Experimental

### 2.1. Materials

$Ph_3SnCl$ (Fluka AG), salicylic acid (Merck), 2,2′-bipyridine (Merck) and the substituted anilines (reagent grade) were used without further purification. All the solvents used in the reactions were of AR grade and dried using standard literature procedures. Benzene was distilled from sodium benzophenone ketyl.

### 2.2. Physical measurements

Carbon, hydrogen and nitrogen analyses were performed with a Perkin–Elmer 2400 series II instrument. IR spectra in the range 4000–400 $cm^{-1}$ were obtained on a BOMEM DA-8 FT-IR spectrophotometer with samples investigated as KBr discs. The $^1H$ and $^{13}C$ NMR spectra of the ligands were acquired on either a Varian Gemini 2000 spectrometer (operating at 300.13 and 75.47 MHz, respectively) or a Varian Inova spectrometer (operating at 599.91 and 150.85 MHz, respectively). For the organotin compounds, the $^1H$, $^{13}C$ and $^{119}Sn$ NMR spectra were recorded on a Bruker ACF 300 spectrometer and measured at 300.13, 75.47 and 111.92 MHz, respectively. The $^1H$, $^{13}C$ and $^{119}Sn$ chemical shifts were referred to $Me_4Si$ set at 0.00 ppm, $CDCl_3$ set at 77.0 ppm and tetramethyltin set at 0.00 ppm, respectively. Mössbauer spectra were recorded on solid samples at liquid nitrogen temperature by using a conventional constant acceleration spectrometer, coupled with a multichannel analyser (a.e.n., Ponteranica (BG), Italy) equipped with a cryostat Cryo (RIAL, Parma, Italy). A $Ca^{119}SnO_3$ Mössbauer source, 10 mCi (from Ritverc, St. Petersburg, Russia) moving at room temperature with constant acceleration in a triangular waveform was used. The velocity calibration was made using a $^{57}Co$ Mössbauer source, 10 mCi, and iron foil as absorber (from Ritverc, St Petesrburg, Russia).

### 2.3. Synthesis of 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acids

5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acids (Fig. 1) and their sodium salts were prepared and characterized as described in our earlier report [13].

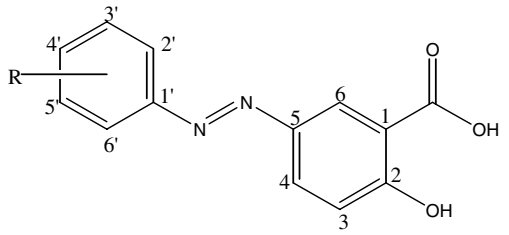



Fig. 1. Generic structure of the acid. Abbreviations: $L^1HH'$, R = 2-$CH_3$; $L^2HH'$, R = 4-$CH_3$, where H and H′ represent hydroxyl and carboxyl protons, respectively.

### 2.4. Synthesis of the triphenyltin complexes, $Ph_3SnL^1H$ (**1**) and $Ph_3SnL^2H$ (**2**)

The triphenyltin complexes (**1** and **2**) of 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acids were prepared by following the general method described earlier [13] and their spectroscopic data were in agreement with that reported previously [13]. Upon crystallization of **2** from petroleum ether (60–80 °C), the compound crystallized simultaneously as two polymorphs, **2a** (orange prism) and **2b** (orange plate).

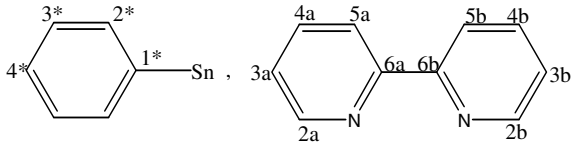
### 2.5. Synthesis of $[Ph_3Sn(L^1H)\ (H_2O)]_2 \cdot bipy_2$ (**3**)

A warm anhydrous benzene solution (5 ml) of 2,2′-bipyridine (0.129 g, 0.83 mmol) was added drop-wise to a hot stirred benzene solution containing $Ph_3SnL^1H$ (**1**) (20 ml, 0.50 g, 0.83 mmol). The reaction mixture was then refluxed for 1 h and filtered while hot. The filtrate was collected, volatiles were removed and the residue was dried in vacuo. The dried residue was extracted into hot petroleum ether (60–80 °C, 20 ml) and filtered to remove any suspended particles. The filtrate was kept for slow evaporation at ambient temperature which furnished orange prismatic crystals of **3** (0.51 g, 80%). m.p. 120–122 °C. Anal. Found: C, 64.70; H, 4.60; N, 7.20%. Calc. for $C_{42}H_{36}N_4O_4Sn$: C, 64.72; H, 4.66; N, 7.19%. In this reaction, it is assumed that the water ligand comes from the solvent or from the reaction apparatus which may have contained adventitious moisture. Several reaction attempts gave identical products and their analytical data were found to be reproducible. IR ($cm^{-1}$): 1587 $\nu(OCO)_{asym}$. $^1H$ NMR ($CDCl_3$); $\delta_H$: 2.71 [s, 3H, $CH_3$], 7.03 [dd, 1H, H-3], 7.23 [td, 2H, H-3a & H-3b], 7.31 [m, 3H, H-3′, H-4′ & H5′], 7.45 [m, 9H, H-3* & H-4*], 7.60 [d, 1H, H-6′], 7.86 [m, 8H, H-2*, H-4a & H-4b], 8.01 [dd, 1H, H-4], 8.40 [dd, 2H, H-5a & H-5b], 8.62 [dd, 3H, H-6, H-2a & H-2b], 11.90 [brs, 1H, OH] ppm. $^{13}C$ NMR ($CDCl_3$); $\delta_C$: 17.4 [$CH_3$], 115.3 [C-1 & C-6′], 117.9 [C-3], 121.1 [C-3a & C-3b], 124.0 [C-5a & C-5b], 126.3 [C-6], 127.7 [C5′], 128.9 [C-3*], 128.7 [C-4], 130.1 [C-4*], 130.3 [C-4′], 131.2 [C-3′], 136.7 [C-2*], 136.9 [C-2′], 137.0 [C-1*], 138.7 [C-4a & C-4b], 145.6 [C-5], 149.1 [C-2a & C-2b], 150.6 [C-1′],

Table 1
Crystallographic data and structure refinement parameters for complexes **2a**, **2b** and **3**

| | **2a** | **2b** | **3** |
|---|---|---|---|
| Empirical formula | $C_{32}H_{26}N_2O_3Sn$ | $C_{32}H_{26}N_2O_3Sn$ | $C_{42}H_{36}N_4O_4Sn$ |
| Formula weight | 605.17 | 605.17 | 779.37 |
| Crystal size (mm) | $0.12 \times 0.17 \times 0.25$ | $0.02 \times 0.10 \times 0.25$ | $0.12 \times 0.15 \times 0.27$ |
| Crystal shape | Prism | Plate | Prism |
| Temperature (K) | 160(1) | 160(1) | 160(1) |
| Crystal system | Triclinic | Monoclinic | Triclinic |
| Space group | $P\bar{1}$ | $P2_1$ | $P\bar{1}$ |
| Unit cell dimensions | | | |
| $a$ (Å) | 10.7054(1) | 10.6835(1) | 11.7870(1) |
| $b$ (Å) | 20.1315(2) | 26.0358(4) | 12.8349(1) |
| $c$ (Å) | 26.8839(2) | 20.1502(3) | 14.5401(2) |
| $\alpha$ (°) | 100.0558(4) | 90 | 67.3018(4) |
| $\beta$ (°) | 99.9225(4) | 91.7335(7) | 89.7559(4) |
| $\gamma$ (°) | 91.8596(4) | 90 | 65.3148(6) |
| $V$ (Å$^3$) | 5607.87(9) | 5602.3(1) | 1811.30(3) |
| $Z$ | 8 | 8 | 2 |
| $D_x$ (g cm$^{-3}$) | 1.433 | 1.435 | 1.429 |
| $\mu$ (mm$^{-1}$) | 0.945 | 0.946 | 0.753 |
| Transmission factors (min, max) | 0.786, 0.896 | 0.797, 0.984 | 0.828, 0.917 |
| $2\theta_{max}$ (°) | 60 | 50 | 56 |
| Reflections measured | 126 124 | 70 363 | 58 177 |
| Independent reflections ($R_{int}$) | 32 727 (0.074) | 19 474 (0.083) | 8635 (0.068) |
| Reflections with $I > 2\sigma(I)$ | 19 270 | 13 692 | 7236 |
| Number of parameters | 1495 | 1471 | 583 |
| Number of restraints | 603 | 514 | 379 |
| $R(F)(I > 2\sigma(I)$ reflections) | 0.043 | 0.075 | 0.037 |
| $wR(F^2)$ (all data) | 0.106 | 0.200 | 0.094 |
| $GOF(F^2)$ | 1.02 | 1.05 | 1.05 |
| Maximum, minimum $\Delta\rho$ (e Å$^{-3}$) | 1.07, −0.82 | 4.64, −0.73 | 1.24, −1.27 |

156.0 [C-6a & C-6b], 164.2 [C-2], 173.9 [$CO_2H$] ppm. $^{119}$Sn NMR ($CDCl_3$) $\delta_{Sn}$: −133.1 ppm. $^{119}$Sn Mössbauer: $\delta = 1.24$, $\Delta = 3.07$, $\Gamma \pm = 0.79$ mm s$^{-1}$). For assignments of NMR signals, refer to Fig. 1 for the numbering schemes of the ligand skeleton, while for Sn–Ph and bipy skeletons as shown below:




### 2.6. X-ray crystallography

Crystals of compounds **2** (two polymorphs, **2a** and **2b**) and **3** suitable for an X-ray crystal-structure determination were obtained from petroleum ether (60–80 °C). All measurements were made at low temperature on a Nonius KappaCCD diffractometer [25] with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [26]. The intensities were corrected for *Lorentz* and polarization effects, and an empirical absorption correction based on the multi-scan method [27] was applied. Equivalent reflections were merged. The data collection and refinement parameters are given in Table 1. The structures were solved by direct methods using SHELXS97 [28] for **2a** and SIR92 [29] for **2b** and **3**. In each structure, the non-hydrogen atoms were refined anisotropically, while employing restraints when necessary as described below.

The asymmetric unit in **2a** and **2b** contains four symmetry-independent molecules. The atomic coordinates of the four independent molecules were tested carefully for a relationship from a higher symmetry space group by using the program PLATON [30], but none could be found. In three of the independent molecules in each polymorph, one phenyl substituent is disordered over two positions. Two sets of positions were defined for each of these phenyl rings and the site occupation factors of the major conformations refined to 0.615(9), 0.67(1) and 0.547(3) for molecules A, B and D, respectively, in **2a**, and to 0.72(1), 0.64(4) and 0.74(1) for molecules A, B and C, respectively, in **2b**. In molecules A and B of **2a**, the disordered phenyl rings were constrained to be rigid hexagons, while in molecule D, the disordered rings were restrained to be planar with all C–C bond lengths equivalent. Each of the disordered

phenyl rings in **2b** was constrained to be a rigid hexagon. For both polymorphs, neighboring atoms within and between each of the disordered conformations were restrained to have similar atomic displacement parameters, and the Sn–C bonds involving disordered C atoms were restrained to have similar lengths. All of the H atoms were placed in geometrically calculated positions and refined using a riding model where each H atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent atom ($1.5U_{eq}$ for the methyl and hydroxy groups). The orientation of the hydroxy O–H vector was optimized to correspond with the direction that would bring the H atom closest to the nearest hydrogen bond acceptor.

In **3**, the asymmetric unit contains one molecule of the $[Ph_3Sn(L^1H)(H_2O)]$ complex plus one bipy molecule. The entire bipy molecule is disordered over two conformations and two positions were defined for all atoms of this moiety. Refinement of constrained site occupation factors for the two orientations yielded a value of 0.549(7) for the major conformation. Similarity restraints were applied to the chemically equivalent bond lengths and angles of the two conformations of the bipy molecule. Furthermore, neighboring atoms within and between each conformation of the disordered molecule were restrained to have similar atomic displacement parameters. Some of the atomic displacement ellipsoids in two of the phenyl rings of the Sn-complex are elongated, which suggests that these rings might also be slightly disordered. However, a logical disordered model could not be developed successfully. The hydroxy and water H atoms were placed in the positions indicated by a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters. Bond length restraints applied to the O–H bonds of the water ligand. All remaining H atoms were treated as for **2a**.

The refinement of each structure was carried out on $F^2$ using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in the case of **2a** and **3**. Five reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement of **2a**. Refinement of the absolute structure parameter [31] for **2b** yielded a value of 0.41(3), which indicates that the crystals are inversion twins. For **2b**, eight residual electron density peaks of more than 2.0 e $Å^{-3}$ remain, of which four are close to Sn atoms, but the remaining four, including the two largest at 4.6 e $Å^{-3}$ are located near C atoms. No satisfactory explanation can be found for these features, other than that they might be attributed to the quality of the data, because the crystal was very weakly diffracting and yielded broad reflection profiles. Attempts to isolate a better crystal led to the discovery of polymorph **2a**. All calculations were performed using the SHELXL97 [32] program.

## 3. Results and discussion

### 3.1. Syntheses

The reaction of **1** with bipy in benzene yielded **3** essentially quantitatively. The synthesis of **3** is of interest in order to understand its structure and bonding. The microanalysis and NMR data revealed the composition of the product. At first, it was contemplated that the Sn atom in **3** is hexa-coordinated by three phenyl groups, one O atom of the $L^1H$ ligand and both N atoms of the bipy moiety, while the crystal lattice included water molecules of solvation. After recrystallization from petroleum ether, an X-ray crystal structure analysis revealed that **3** was a hydrogen-bonded adduct between $Ph_3Sn(L^1H)(H_2O)$ and bipy (see Section 3.3). This furnishes the first example of adduct formation between bulky triphenyltin azocarboxylates and the bipy moiety. The attempted reaction of **1** with 1,10-phenanthroline under similar conditions appears to be inhibited by steric hindrance and did not provide the desired product. Complexes **2** and **3** are quite stable in air and can successfully be recrystallized from common organic solvents.

### 3.2. Spectroscopy

Compound **3** was characterized by means of IR, NMR ($^1H$, $^{13}C$, $^{119}Sn$) and $^{119}Sn$ Mössbauer spectroscopic techniques. The $^1H$ and $^{13}C$ chemical shift assignments of the triphenyltin moiety and the ligands were made from the multiplicity patterns and/or resonance intensities and also by standard distortionless enhancement by polarization transfer (DEPT) experiments (Section 2.5). The $^1H$ and $^{13}C$ NMR spectra show the expected resonances and integration. The $^{119}Sn$ NMR spectra reported for compounds **1** and **2** in solution reveal a single intense $^{119}Sn$ resonance in the range −89.3 to −89.9 ppm [10,13,33]. In **3**, the $^{119}Sn$ resonance is shifted upfield to −133.0 ppm in $CDCl_3$ solution. The difference between the $\delta$ $^{119}Sn$ shift of **3** and those of compounds **1** and **2** can be attributed to the differences in the electronic effect of the ligand environments caused by the additional water ligand in **3** and the value for **3** falls within the limit specified for tetrahedral geometry [33]. Thus, the $^{119}Sn$ NMR result indicates that the five-coordinate Sn atom in the solid state structure (as revealed by X-ray and Mössbauer, vide infra) is lost upon dissolution giving rise to a four-coordinate Sn atom in solution.

The Mössbauer spectra of the tetrahedral triphenyltin carboxylates, **1** and **2**, exhibit quadrupole splitting ($\Delta$) values at around 2.60 mm $s^{-1}$ [13]. In **3**, the $\Delta$ value is expected to increase owing to the increased coordination number and was found to be 3.07 mm $s^{-1}$. This value falls in the range 3.0–4.1 mm $s^{-1}$ usually expected for

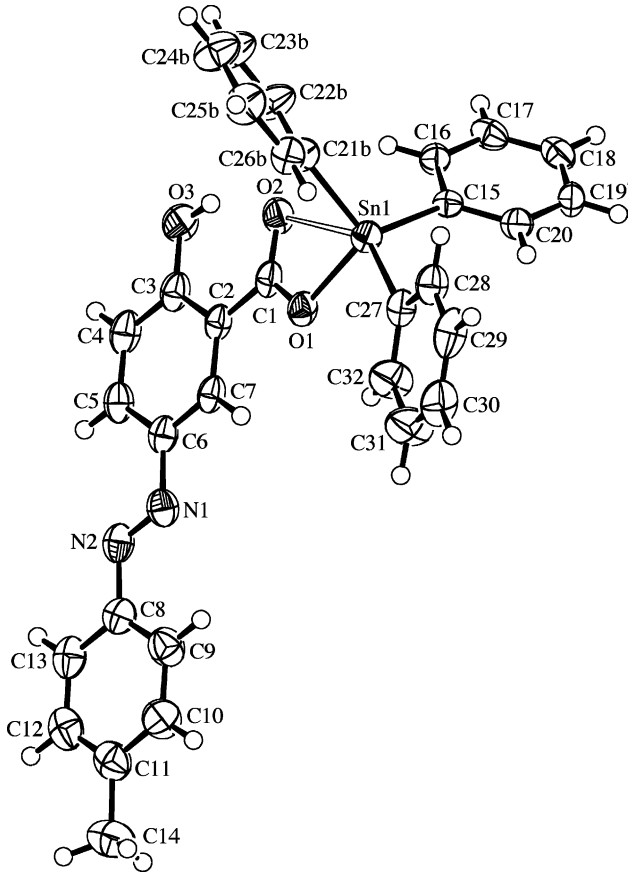



Fig. 2. The molecular structure of the major conformation of one of the four symmetry-independent molecules in the structure of $Ph_3SnL^2H$ (**2a**; 50% probability ellipsoids).

a *trans*-trigonal bipyramidal geometry with a planar equatorial $Ph_3Sn$ unit and two axial O atoms (carboxylate and water) [34,35]. This conclusion is in excellent agreement with the structure determined by X-ray crystallography (see Section 3.3). The isomer shift ($\delta$) value of 1.24 mm $s^{-1}$ is indicative of typical quadrivalent organotin derivatives [10,13].

### 3.3. X-ray crystallography

Compound **2** was found to crystallize as two polymorphs, **2a** and **2b**, with a crystal of each polymorph being obtained serendipitously from the same batch of crystals. The unit cell volumes are the same and the lengths of the unit cell axes are very similar. However, the unit cell angles differ considerably, so that polymorph **2a** belongs to the triclinic crystal system, while polymorph **2b** is monoclinic. Furthermore, the crystal symmetry of **2a** is centrosymmetric, while that of **2b** is non-centrosymmetric. Despite these differences, the asymmetric unit in each polymorph contains four symmetry-independent molecules and, other than small differences in the orientations of the phenyl substituents, there are no significant differences in the conformations

Table 2
Selected geometric parameters (Å, °) for a representative molecule from the triphenyltin complex **2a**

| | | | |
|---|---|---|---|
| Sn(1)–O(1) | 2.073(2) | Sn(1)–C(21b) | 2.131(3) |
| Sn(1)–O(2) | 2.806(2) | Sn(1)–C(27) | 2.131(3) |
| Sn(1)–C(15) | 2.127(2) | O(1)–C(1) | 1.301(3) |
| Sn(1)–C(21a) | 2.115(5) | O(2)–C(1) | 1.245(3) |
| O(1)–Sn(1)–O(2) | 51.38(6) | O(2)–Sn(1)–C(27) | 146.27(9) |
| O(1)–Sn(1)–C(15) | 109.55(9) | C(15)–Sn(1)–C(21a) | 113.5(3) |
| O(1)–Sn(1)–C(21a) | 113.8(3) | C(15)–Sn(1)–C(21b) | 115.5(2) |
| O(1)–Sn(1)–C(21b) | 108.0(2) | C(15)–Sn(1)–C(27) | 113.5(1) |
| O(1)–Sn(1)–C(27) | 95.0(1) | C(21a)–Sn(1)–C(27) | 110.2(3) |
| O(2)–Sn(1)–C(15) | 84.64(8) | C(21b)–Sn(1)–C(27) | 113.1(2) |
| O(2)–Sn(1)–C(21a) | 85.5(3) | C(1)–O(1)–Sn(1) | 110.4(2) |
| O(2)–Sn(1)–C(21b) | 80.2(2) | C(1)–O(2)–Sn(1) | 77.2(2) |

of the independent molecules both within and between the two polymorphs. Both structures even have one disordered phenyl ring in three of the four independent molecules. The disorder results from a small twist about the Sn–C bond. The extensive similarities in the two structures suggests that the structures may actually be the same and that an inappropriate definition of the unit cell has been chosen for one of them, but it has not been possible to find any transformation matrix that would convert one structure to the other.

The molecular structure of one of the four symmetry-independent molecules in the asymmetric unit of **2a** is depicted in Fig. 2 and selected geometric parameters for this molecule are given in Table 2. The view and geometric parameters are completely representative of all independent molecules in the structures of **2a** and **2b**. To a first approximation the Sn atom is four-coordinate, existing in a distorted tetrahedral geometry defined by a $C_3O$ donor set. The range of tetrahedral angles for the eight symmetry-independent molecules in **2a** and **2b** is 93.5(4)–117.2(3)°, with the narrow and wide angles reflecting the influence of the more weakly coordinating O(2) atom. The O(2) atom approaches the tin atom at distances in the narrow range of 2.770(8)–2.828(8) Å. As expected, the disparity in the lengths of the carboxylate C–O bonds (Table 2) correlates inversely with the lengths of the Sn–O bonds involving the same O atoms. Other parameters within the molecules are as expected [19,13,24]. The hydroxy group in each molecule forms an intramolecular hydrogen bond with the carboxylate carbonyl O atom of the same ligand and the azo ligand in each molecule is essentially planar. There is no evidence in the crystal structures of the two polymorphs for significant stacking via $\pi\cdots\pi$ contacts, with the shortest separation between parallel ring centroids being 4.11 Å in **2a**.

The structural motif found for **2a** and **2b** resembles one of the four predominant motifs for structures of the general formula $R_3Sn(O_2CR')$, this being the monomeric distorted tetrahedral type Ia motif. The crystal structures of three analogous $Ph_3SnLH$ complexes have

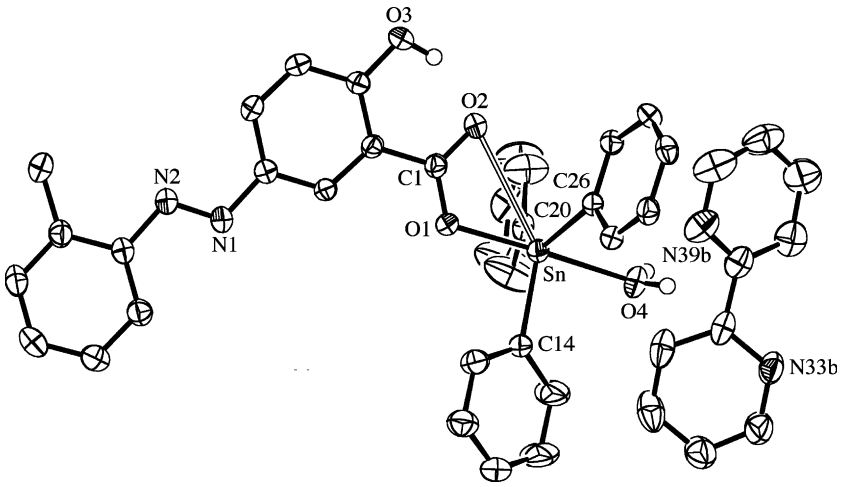



Fig. 3. The molecular structure of $Ph_3Sn(L^1H)(H_2O) \cdot bipy$ (**3**; 50% probability ellipsoids; only the major conformation of the disordered bipy moiety is shown and most H atoms have been omitted for clarity).

Table 3
Selected geometric parameters (Å, °) for the triphenyltin-bipy adduct **3**

| | | | |
|---|---|---|---|
| Sn–O(1) | 2.159(2) | Sn–C(20) | 2.125(3) |
| Sn–O(2) | 3.049(2) | Sn–C(26) | 2.121(2) |
| Sn–O(4) | 2.369(2) | O(1)–C(1) | 1.287(3) |
| Sn–C(14) | 2.142(2) | O(2)–C(1) | 1.252(3) |
| O(1)–Sn–O(2) | 47.00(6) | O(4)–Sn–C(14) | 87.75(9) |
| O(1)–Sn–O(4) | 176.95(7) | O(4)–Sn–C(20) | 82.13(8) |
| O(1)–Sn–C(14) | 91.42(8) | O(4)–Sn–C(26) | 83.16(8) |
| O(1)–Sn–C(20) | 95.56(8) | C(14)–Sn–C(20) | 114.3(1) |
| O(1)–Sn–C(26) | 99.85(8) | C(14)–Sn–C(26) | 114.0(1) |
| O(2)–Sn–O(4) | 134.12(6) | C(20)–Sn–C(26) | 128.51(9) |
| O(2)–Sn–C(14) | 137.95(8) | C(1)–O(1)–Sn | 116.0(1) |
| O(2)–Sn–C(20) | 81.11(8) | C(1)–O(2)–Sn | 74.0(1) |
| O(2)–Sn–C(26) | 74.83(7) | | |

been reported [13], where L is the 2-Me, 3-Me and 4-OMe analogue of the ligand (4-Me substituted) used in **2a** and **2b**. All five structures have the same type Ia motif of coordination to the Sn atom and very similar molecular structures overall. The 4-OMe structure [13] even has four symmetry-independent molecules in the asymmetric unit, as found in **2a** and **2b**, and the same space group and quite similar unit cell dimensions to those of **2b**.

Compound **3** is a co-crystal, the asymmetric unit of which contains one molecule of the $Ph_3Sn(L^1H)(H_2O)$ complex plus one bipy molecule (Fig. 3). Apart from hydrogen bonding interactions these moieties are discrete. The effective geometry around the Sn atom in **3** is essentially a *trans*-$R_3SnO_2$ trigonal bipyramid (Table 3), where one O atom from the carboxylate group of the $L^1H$ ligand and a coordinated water molecule occupy the axial positions, and phenyl groups are located in the trigonal equatorial plane. The sum of the angles subtended at the Sn atom by the *ipso*-carbon atoms of the phenyl rings is 356.8(2)° and the distortions of the trigonal bipyramidal geometry are small. The carbonyl O atom of the carboxylate group of the $L^1H$ ligand coordinates even more weakly to the Sn atom than in the structures of **2a** and **2b**, so has only a very small influence on the coordination geometry about the Sn atom established by the other coordinating atoms. Although the Sn–O(2) distance is 3.049(2) Å, this is still significantly shorter than the sum of the van der Waals radii of the Sn and O atoms (~3.8 Å), so the interaction cannot be considered to be truly non-bonding. The Sn–O(4) bond involving the water ligand is about 0.2 Å longer than the Sn–O(1) bond and is consistent with the Sn–$OH_2$ bond lengths of 2.299(3) and 2.527(5) Å in the related complexes, $\{[Ph_3Sn(C_2ClF_2O_2)OH_2]_2 \cdot 2C1_2H_8N_2\}$ [23] and $\{Ph_3Sn[O_2CC_6H_4(N{=}N(C_6H_3\text{-}4\text{-}OH\text{-}5\text{-}CHO))\text{-}o]OH_2\}$ [36], respectively, and with the range 2.25–2.35 Å in other related $R_3SnR'(H_2O)$ complexes [14,18], all

Table 4
Hydrogen bonding geometry (Å, °) for the triphenyltin-bipy adduct **3**

| D–H···A atoms | D–H (Å) | H···A (Å) | D···A (Å) | D–H··· A (°) |
|---|---|---|---|---|
| O(3)–H(3)···O(2) | 0.85(4) | 1.77(4) | 2.552(3) | 151(4) |
| O(4)–H(42)···N(33a)$^{i}$ | 0.83(1) | 2.38(4) | 2.813(7) | 113(4) |
| O(4)–H(41)···N(33b)$^{ii}$ | 0.83(1) | 2.15(2) | 2.872(6) | 144(3) |
| O(4)–H(41)···N(39a)$^{ii}$ | 0.83(1) | 2.03(2) | 2.730(7) | 142(3) |
| O(4)–H(42)···N(39b)$^{i}$ | 0.83(1) | 2.05(2) | 2.821(6) | 153(5) |

Symmetry codes: (i) $x$, $1 + y$, $z - 1$; (ii) $1 - x$, $2 - y$, $1 - z$.

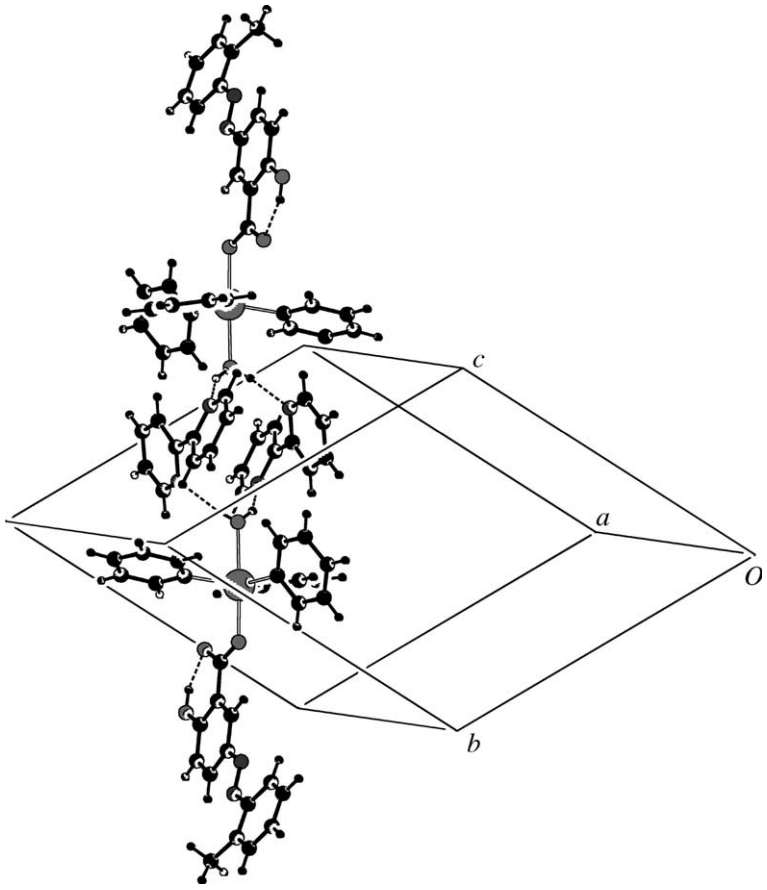



Fig. 4. The hydrogen-bonded tetrameric motif in the molecular structure of $Ph_3Sn(L^1H)(H_2O) \cdot bipy$ (**3**), consisting of two $Ph_3Sn(L^1H)(H_2O)$ and two bipy molecules.

of which also feature trigonal bipyramidal coordination at the Sn centers with water ligands in axial positions.

The bipy molecule is disordered over two conformations with the major conformation existing in approximately 55% of the molecules (see Section 2.5). The N atoms lie in an almost *anti* position with the angle between the planes of the two pyridine rings being 26.0(6)° and 37.2(6)° for the two disordered conformations. The disorder serves to flip the entire bipy molecule about its longitudinal axis (see Table 4).

The two structural moieties in the crystal have coalesced into an adduct by virtue of intermolecular hydrogen bonds. The water ligand, through each of its H atoms, forms intermolecular hydrogen bonds with the N atoms of two neighboring bipy molecules, each of which accepts a further hydrogen bond from the water ligand of another molecule of the $Ph_3Sn(L^1H)(H_2O)$ complex. This pattern links two molecules of the Sn-complex and two bipy molecules into a centrosymmetric tetrameric loop (Fig. 4). The hydrogen bonding motif thus formed can be described by the graph set motif of $R_4^4(14)$ [37], and the formula of the adduct can be depicted by $[Ph_3Sn(L^1H)(H_2O)]_2 \cdot bipy_2$. The disorder in the bipy molecule does not affect the pattern of intermolecular hydrogen bonds and merely changes the conformation of the tetrameric loop. The hydroxy group of the carboxylate ligand forms an intramolecular hydrogen bond with the carboxylate carbonyl O atom of the same ligand. Similar hydrogen-bonded adducts involving 1,10-phenanthroline or terpyridine and $R_3SnR'(H_2O)$ complexes have been reported previously [14,16–18,23]. The crystal structure of the adduct between aqua(chlorodifluoroacetato-*O*)triphenyltin and 1,10-phenantroline [23] displays a hydrogen-bonded tetrameric $[R_3SnR'(H_2O)]_2 \cdot phen_2$ unit very similar to that in **3**.

## 4. Supplementary material

CCDC-249827–CCDC-249829 contain the supplementary crystallographic data for complexes **2a, 2b** and **3**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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