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Synthesis and characterization of the first diorganotin(IV) complexes containing mixed arylazobenzoic acids and having skew trapezoidal bipyramidal geometry

Tushar S. Basu Baul [a,*], Wandondor Rynjah [a], Eleonora Rivarola [b], Claudio Pettinari [c], Anthony Linden [d,*]

[a] Department of Chemistry, North-Eastern Hill University, NEHU Permanent Campus, Umshing, Shillong 793 022, India
[b] Dipartimento di Chimica Inorganica e Analitica "Stanislao Cannizzaro" Università di Palermo, Viale delle Scienze, Parco D'Orleans II, Edificio 17, 90128 Palermo, Italy
[c] Dipartimento di Scienze Chimiche, Università di Camerino, Via S. Agostino 1, 62032 Camerino, Italy
[d] Institute of Organic Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

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Abstract

Three diorganotin(IV) complexes of the type, $[R_2Sn(L^aH)(L^bH)]$ (R = ^{n}Bu or Me and, L^aH and L^bH are two different 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoate residues; a: aryl = 4′-Cl- (held constant) and b: aryl = 4′-Me or 4′-Br) have been prepared either by reacting $^n Bu_2SnO$, L^aHH' and L^bHH' (1:1:1) in anhydrous toluene or by reacting Me_2SnCl_2, L^aHNa and L^bHNa (1:1:1) in anhydrous methanol. The products were characterized by microanalysis, IR, NMR (^1H, ^{13}C, ^{119}Sn) and ^{119m}Sn Mössbauer spectroscopy. A full characterization of the structures of the complexes $[^n Bu_2Sn(L^aH)(L^bH)]$ (**1** and **2**) and $[Me_2Sn(L^aH)(L^bH)]$ (**3**) in the solid state were accomplished by single crystal X-ray crystallography. These complexes were found to adopt the usual dicarboxylato structural type with a skew-trapezoidal bipyramidal arrangement around the tin atom.

Keywords: Diorganotin; Mixed azocarboxylates; 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acid; NMR; Mössbauer; Crystal structures

1. Introduction

A rich chemistry of diorganotin dicarboxylate compounds comprising a variance of structural appearance is long known and the compounds are routinely prepared by condensing diorganotin oxide and carboxylic acid in 1:2 molar proportions in suitable solvents. Some members of this class of compounds exhibit catalytic activity on *trans*-esterification, potentially in polymerization [1,2]. Owing to these applications, the structure and mechanisms of action of these diorganotin dicarboxylates remain a matter of great interest [2–5]. In the dominant motif for $[(R_2Sn(O_2CR')_2]$ compounds, the carboxylate ligands chelate the tin atom forming disparate Sn–O bonds distances; the short Sn–O bond distances range from 2.07 to 2.16 Å and the long Sn–O distances range from 2.47 to 2.65 Å [6,7]. The geometry about the tin atom is regarded as skew-trapezoidal bipyramid with the tin-bound organic groups being disposed in pseudo-axial positions over the weaker equatorial Sn–O interactions to give C–Sn–C angles in the range 130–152° [6,7]. Recent systematic studies have been made of a series of $[(R_2Sn(O_2CR')_2]$ compounds

* Corresponding authors. Tel.: +91 364 272 2626; fax: +91 364 2550486/2721000 (T.S. Basu Baul), Tel.: +41 44 635 4228; fax: +41 44 635 6812 (A. Linden).
E-mail addresses: basubaul@nehu.ac.in, basubaul@hotmail.com (T.S. Basu Baul), alinden@oci.unizh.ch (A. Linden).

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where (i) the carboxylic acid residue (R′ = 2-[(*E*)-2-(2-hydroxy-5-methylphenyl)-1-diazenyl]benzoic acid) was held constant and R (R = ^{t}Bu and Ph) was varied [8] and (ii) the carboxylic acid residue was varied (R′ = 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acid where aryl = H (**a**), 2′-Me (**b**), 3′-Me (**c**), 4′-Me (**d**), 4′-Cl (**e**) and 4′-Br (**f**)) and R (^{n}Bu) was held constant [9–11]. In all cases, both participating carboxylate ligands were identical and the geometric parameters about the tin atom for each compound fall within the limits specified (vide supra), thereby testifying to the skew-trapezoidal bipyramid geometry. In series (ii), besides this geometry, weak bridging intermolecular Sn···O contacts were detected in the dibutyltin complexes of **a** and **c**. In these systems, one of the hydroxy oxygen atoms from a neighbouring molecule coordinates weakly with the Sn atom, thereby completing a seventh coordination site in the extended Sn coordination sphere. In **a**, this Sn···O interaction links the molecules into polymeric chains while in **c**, these interactions link pairs of the molecules into head-to-head dimeric units [11].

The usual synthetic strategy to obtain such [$(R_2Sn(O_2CR')_2$] compounds is quite restrictive. In all of the above-described instances, the Sn atom is always coordinated by two identical carboxylic acid ligands and there are no known reports of [$(R_2Sn(O_2CR')_2$] complexes containing hetero carboxylate residues, except for one involving a Schiff base and anthranilic acid (*o*-aminobenzoato(*o*-(*p*-dimethylaminobenzalidine)benzoato)(*o*-ammoniobenzoate)-dimethyltin(IV)) [12]. To explore the possibility for the formation of [$R_2Sn(L^aH)(L^bH)$], we have studied the reactions of (i) $^{n}Bu_2SnO$, L^aHH' and L^bHH' and (ii) Me_2SnCl_2, L^aHNa and L^bHNa which yielded diorganotin hetero dicarboxylate compounds in moderate yields. The complexes have been characterized (where possible) by microanalyses, IR, ^{1}H, ^{13}C, ^{119}Sn (NMR), ^{119m}Sn Mössbauer and single crystal X-ray crystallography and the results are discussed herein.

2. Experimental

2.1. Materials

$^{n}Bu_2SnO$ (Fluka) and Me_2SnCl_2 (Aldrich) were used as received. All the solvents used in the reactions were of AR grade and dried using standard literature procedures. Toluene 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 ^{1}H 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 ^{1}H, ^{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 ^{1}H, ^{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 analyzer (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 an iron foil as absorber (from Ritverc, St. Petesrburg, Russia).

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

The 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acids (Fig. 1) viz.: L^aHH': aryl = 4′-Cl; L^bHH': aryl = 4′-CH_3 and 4′-Br and their sodium salts were prepared and characterized as described in our earlier report [13,14].

2.4. Synthesis of the diorganotin complexes

The detailed methodology for the preparation of diorganotin complexes of the type [$R_2Sn(L^aH)(L^bH)$] and their work-up procedures are described below.

2.4.1. Synthesis of [$^{n}Bu_2Sn(L^aH)(L^bH)$] (a: aryl = 4′-Cl and b: aryl = 4′-Me) (*1*)

L^aHH' (0.54 g, 1.95 mmol) and L^bHH' (0.50 g, 1.95 mmol) were taken in a 100 ml round bottom flask

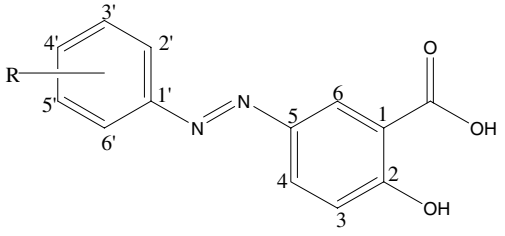

Fig. 1. Generic structure of the acid. Abbreviations: (i) L^aHH': aryl = 4′-Cl; L^bHH': aryl = 4′-CH_3, (ii) L^aHH': aryl = 4′-Cl; L^bHH': aryl = 4′-Br where H and H′ represent hydroxyl and carboxyl protons, respectively.

and mixed thoroughly under vigorous magnetic stirring in order to get a homogeneous powder. To this mixture, a suspension of Bu_2SnO (0.48 g, 1.95 mmol) in 50 ml anhydrous toluene was added and refluxed for 6 h using a Dean and Stark apparatus. The orange coloured solution was filtered while hot, the filtrate was evaporated on a hot plate to one tenth of the initial solvent volume and the compound precipitated with petroleum ether (40–60 °C). The precipitate was separated by filtration, washed with hexane (2 × 5 ml) and dried in vacuo. The dried precipitate was dissolved in a benzene–methanol mixture (v/v 3:1) and filtered. Slow evaporation of the solution at rt yielded orange needles of the desired product (1.04 g, 70%); m.p. 194–195 °C. Anal. Found: C, 55.08; H, 4.80; N, 7.23%. Calc. for $C_{35}H_{37}ClN_4O_6Sn$: C, 55.03; H, 4.88; N, 7.33. IR (KBr: 1630 $\nu(OCO)_{asym}$). ^1H NMR ($CDCl_3$); δ_H: Ligand skeleton: 2.45 [s, 3H, CH_3 (L^b)], 7.13 [d, 9.0 Hz, 2H, H-3 ($L^a + L^b$)], 7.32 + 7.48 [AA′ portion of AA′XX′, 4H, H-2′ &H-6′ ($L^a + L^b$)], 7.86 [m, 4H, H-3′ &H-5′($L^a + L^b$)], 8.12 [dd, 9.0 & 2.1 Hz, 2H, H-4 ($L^a + L^b$)], 8.65 [m, 2H, H-6 ($L^a + L^b$)], 11.0 + 10.9 [brs, 2H, OH ($L^a + L^b$)]; Sn–^{n}Bu skeleton: 0.93 [t, 6H, 4*], 1.45 [m, 4H, 3*], 1.79 [m, 4H, 2*], 1.94 [m, 4H, 1*] ppm. ^{13}C NMR ($CDCl_3$); δ_C: Ligand skeleton: 21.7 [CH_3 (L^b)], 112.9 + 113.0 [C-1($L^a + L^b$)], 118.5 + 118.6 [C-3 ($L^a + L^b$)], 123.0 + 124.2 [C-2′ & C-6′($L^a + L^b$)], 128.4–130.0 (6 complex signals, C-4, 6, 3′ & 5′ ($L^a + L^b$)], 136.8 + 141.5 [C-4′ ($L^a + L^b$)], 145.6 + 145.8 [C-5 ($L^a + L^b$)], 150.8 + 151.1 [C-1′($L^a + L^b$)], 163.8 + 164.3 [C-2 ($L^a + L^b$)], 177.5 + 177.7 [CO_2($L^a + L^b$)]; Sn–^{n}Bu skeleton: 13.7 [C-4*], 26.6 [C-2*], 26.8 [C-1* & C-3*] ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: −116.1 ppm. ^{119}Sn Mössbauer: $\delta = 1.47$, $\Delta = 3.46$, $\Gamma_1 = 0.79$, $\Gamma_2 = 0.79$ mm s^{-1}, C–Sn–C = 141°.

2.4.2. Synthesis of [$^nBu_2Sn(L^aH)(L^bH)$] (a: aryl = 4′-Cl and b: aryl = 4′-Br) (2)

Compound **2** was prepared analogously by following the method and conditions described for **1** using L^aHH' (0.50 g, 1.80 mmol), L^bHH' (0.58 g, 1.80 mmol) and Bu_2SnO (0.45 g, 1.80 mmol). The product was recrystallized from a benzene–methanol mixture (v/v 3:1) which upon slow evaporation yielded orange prismatic crystals. Yield: 1.28 g, 85.6%; m.p. 200–202 °C. Anal. Found: C, 49.45; H, 4.20; N, 6.80%. Calc. for $C_{34}H_{34}BrClN_4O_6Sn$: C, 49.28; H, 4.14; N, 6.76. IR (KBr: 1630 $\nu(OCO)_{asym}$). ^1H NMR ($CDCl_3$); δ_H: Ligand skeleton: 7.13 (d, 9.0 Hz, 2H, H-3 ($L^a + L^b$)), 7.50 + 7.67 (m, 4H, H-2′ & H-6′ ($L^a + L^b$)), 7.80 + 7.88 (m, 4H, H-3′ & H-5′($L^a + L^b$)), 8.12 (dd, 9.0 & 2.1 Hz, 2H, H-4 ($L^a + L^b$)), 8.65 (d, 2.1 Hz, 2H, H-6 ($L^a + L^b$)), 11.05 (brs, 2H, OH ($L^a + L^b$)); Sn–^{n}Bu skeleton: 0.93 (t, 6H, 4*), 1.45 (m, 4H, 3*), 1.79 (m, 4H, 2*), 1.94 (m, 4H, 1*) ppm. ^{13}C NMR ($CDCl_3$); δ_C: Ligand skeleton: 113.0 [C-1($L^a + L^b$)], 118.7 [C-3 ($L^a + L^b$)], 124.2 + 124.4 [C-2′ & C-6′($L^a + L^b$)], 128.9–129.6 [4 complex signals, C-4 & C-6 ($L^a + L^b$)], 132.6 [C-3′ & C-5′ ($L^a + L^b$)], 136.8 [C-4′ ($L^a + L^b$)], 145.6 [C-5 ($L^a + L^b$)], 151.1 + 151.5 [C-1′($L^a + L^b$)], 164.30 + 164.34 [C-2 ($L^a + L^b$)], 177.6 [CO_2($L^a + L^b$)]; Sn–^{n}Bu skeleton: 13.7 [C-4*], 26.6 [C-2*], 26.8 [C-1* & C-3*] ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: −116.1 ppm. ^{119}Sn Mössbauer: $\delta = 1.49$, $\Delta = 3.50$, $\Gamma_1 = 0.79$, $\Gamma_2 = 0.81$ mm s^{-1}, C–Sn–C = 142°.

2.4.3. Synthesis of [$Me_2Sn(L^aH)(L^bH)$] (a: aryl = 4′-Cl and b: aryl = 4′-Me) (3)

L^aHNa (0.49 g, 1.77 mmol) and L^bHNa (0.53 g, 1.77 mmol) were dissolved separately in anhydrous methanol (15 ml + 15 ml) and mixed under magnetic stirring in order to get a homogeneous solution. To this mixture, a methanol solution (20 ml) containing Me_2SnCl_2 (0.39 g, 1.77 mmol) was added, refluxed for 5 h and filtered while hot. The filtrate was evaporated at rt under stirring and the residue was dried in vacuo. The orange coloured solid was washed with hexane (2 × 5 ml), dried at rt, extracted into chloroform (20 ml) and filtered to remove NaCl. The chloroform extract was concentrated slowly on a water bath, the compound precipitated with hexane and filtered. The dried precipitate was dissolved in benzene and filtered to remove any particles. The filtrate upon slow evaporation at rt yielded orange prisms of the desired product (0.26 g, 21.3%); m.p. 228–230 °C. Anal. Found: C, 51.20; H, 3.70; N, 8.34%. Calc. for $C_{29}H_{25}ClN_4O_6Sn$: C, 51.25; H, 3.71; N, 8.24. IR (KBr: 1630 $\nu(OCO)_{asym}$). Sensible NMR spectra could not be recorded owing to the poor solubility of the sample even in DMSO-d_6.

2.5. X-ray crystallography

Crystals of the diorganotin compounds suitable for an X-ray crystal-structure determination were obtained from benzene–methanol (**1** and **2**) and benzene (**3**). All measurements were made at 160 K on a Nonius KappaCCD diffractometer [15] 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 [16]. The intensities were corrected for *Lorentz* and polarization effects, and an empirical absorption correction based on the multi-scan method [17] was applied. Equivalent reflections were merged. The data collection and refinement parameters are given in Table 1, and views of the molecules are shown in Figs. 2–4.

The structures of **1** and **2** were solved by direct methods using SIR92 [18] while the structure of **3** was solved by heavy-atom Patterson methods [19]. In all three structures, the terminal 4′-substituent on one azo ligand is disordered with its counterpart on the second azo ligand (i.e., 4′-Cl/4′-Me disorder in **1** and **3** and

Table 1
Crystallographic data and structure refinement parameters for compounds **1**–**3**

	1	**2**	**3**
Empirical formula	$C_{35}H_{37}ClN_4O_6Sn$	$C_{34}H_{34}BrClN_4O_6Sn$	$C_{29}H_{25}ClN_4O_6Sn$
Formula weight	763.75	828.62	679.59
Crystal size (mm)	$0.02 \times 0.07 \times 0.22$	$0.10 \times 0.13 \times 0.13$	$0.10 \times 0.23 \times 0.32$
Crystal shape	Needle	Prism	Prism
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.6836(1)	9.6330(2)	10.0887(1)
b (Å)	12.1294(2)	12.1345(3)	12.9126(2)
c (Å)	15.0381(2)	15.1338(4)	23.0689(2)
α (°)	93.7211(5)	94.043(1)	102.5909(8)
β (°)	99.1943(5)	98.805(2)	94.8953(8)
γ (°)	103.3269(8)	103.522(1)	103.9637(6)
V (Å^3)	1687.13(4)	1689.28(7)	2815.93(6)
Z	2	2	4
D_x (g cm^{-3})	1.503	1.629	1.603
μ (mm^{-1})	0.887	2.072	1.052
Transmission factors (min, max)	0.911, 0.987	0.662, 0.817	0.717, 0.905
$2\theta_{max}$ (°)	60	60	60
Reflections measured	37,869	45,018	72,238
Independent reflection (R_{int})	9847 (0.080)	9815 (0.083)	16,444 (0.053)
Reflections with $I > 2\sigma(I)$	7022	6632	13,071
Number of parameters	449	488	801
Number of restraints	6	123	22
$R(F)$ [$I > 2\sigma(I)$]	0.040	0.043	0.034
$wR(F^2)$ (all data)	0.087	0.095	0.084
Goodness-of-fit on F^2	1.02	1.02	1.04
Maximum, minimum $\Delta\rho$ (e Å^{-3})	0.88, −0.91	0.91, −1.41	1.57, −1.23

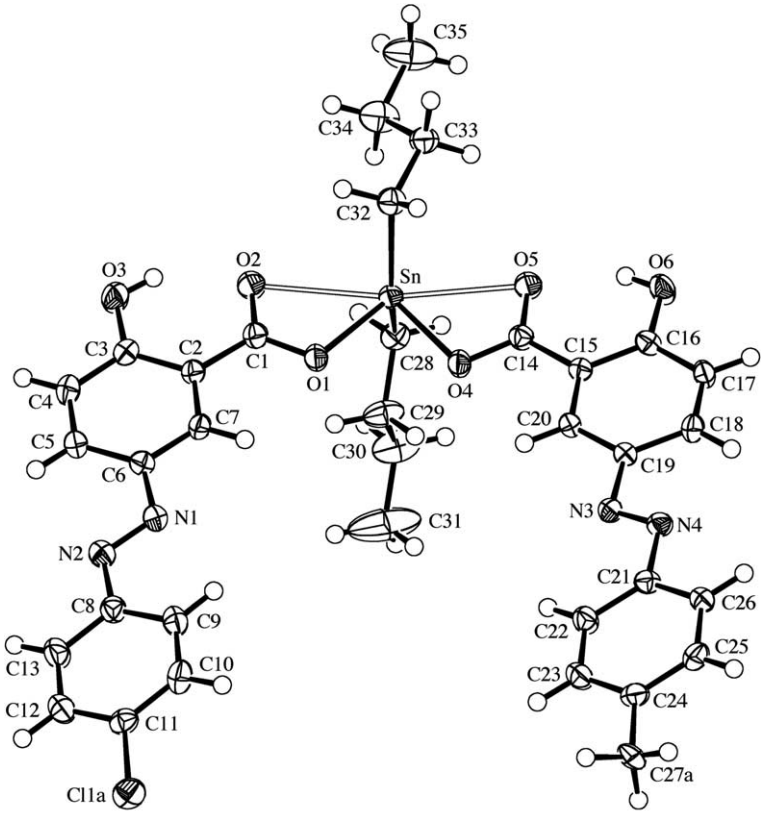

Fig. 2. The molecular structure of one of the disordered conformations of **1** with the atom-labelling scheme (50% probability ellipsoids).

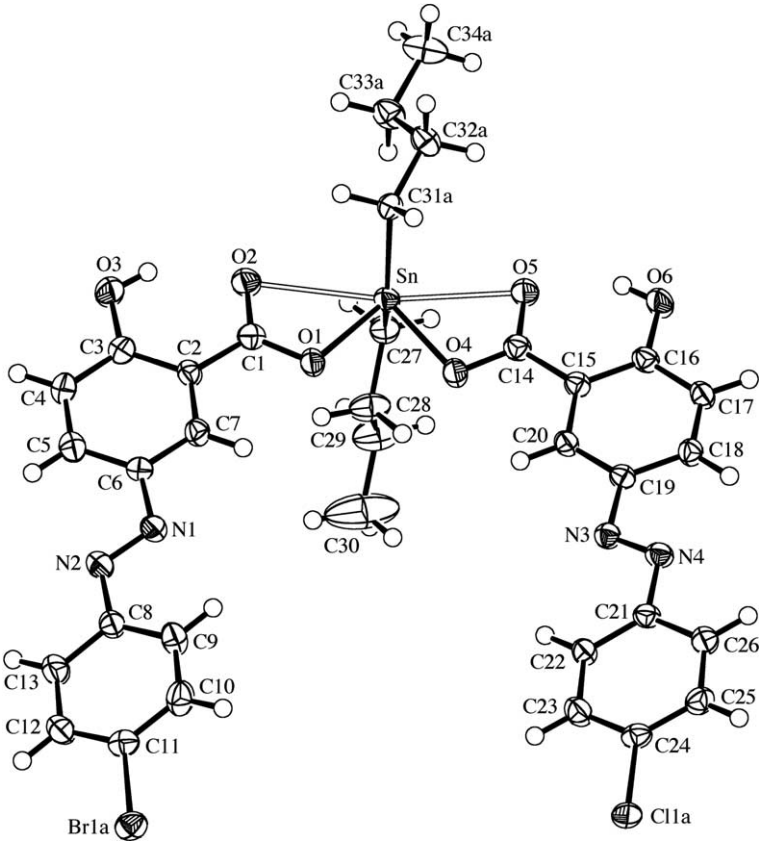

Fig. 3. The molecular structure of one of the disordered conformations of **2** with the atom-labelling scheme (50% probability ellipsoids).

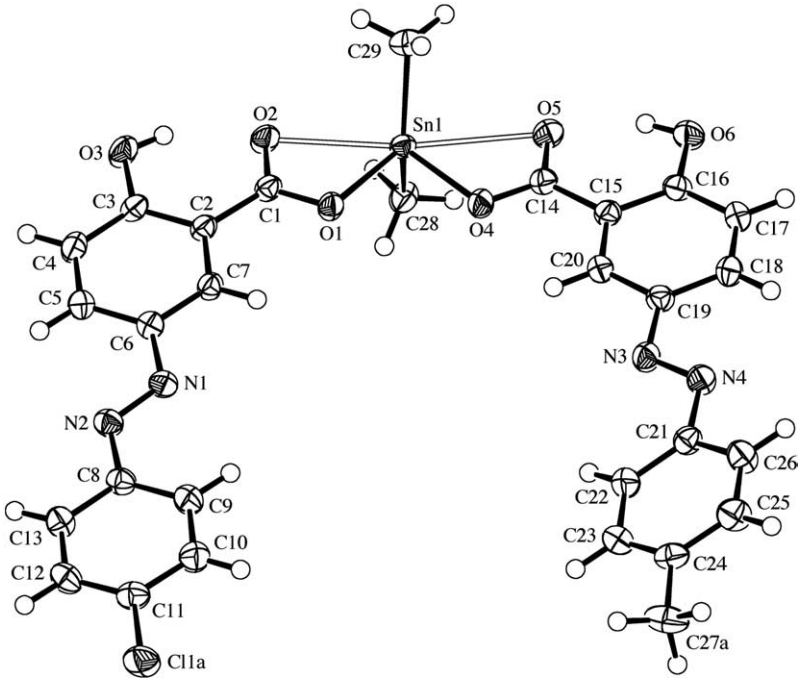

Fig. 4. The molecular structure of one of the disordered conformations of one of the two symmetry-independent molecules (molecule A) of **3** with the atom-labelling scheme (50% probability ellipsoids).

4′-Cl/4′-Br disorder in **2**). As the microanalyses confirmed that each compound was a proper 1:1 complex of the two distinct carboxylate ligands, it was assumed that the disorder results from random positioning of these ligands in each molecule in the crystal and that the total Cl/Me or Cl/Br ratios are always 1:1. Based on this assumption, two set of overlapping Cl/Me or Cl/Br positions were defined for each of these disordered groups and the site occupation factor of the major conformation refined to 0.576(3) and 0.534(2) for **1** and **2**, respectively. In **3**, there are two independent molecules in the asymmetric unit, both of which display the aforementioned disorder. The site occupation factors of the major conformations refined to 0.579(3) and 0.598(3) for molecules A and B, respectively. A pseudo-isotropic restraint was applied to the atomic displacement parameters of the minor position of the disordered methyl C atom in **1** and **3**, in order to maintain a reasonable shape for the atomic displacement ellipsoid. In addition, for **3**, similarity restraints were applied to the chemically equivalent bond lengths involving disordered C and Cl atoms and C–C bond length restraints were applied to the bonds involving the disordered methyl groups. For **2**, quite tight C–Cl and C–Br bond length restraints were applied in order to retain sensible geometry for these disordered substituents.

The atoms of one butyl group in **2** are disordered over two conformations. Two sets of overlapping positions were defined for each of the atoms of this butyl group and the site occupation factor of the major conformation refined to 0.62(4). Similarity restraints were applied to the chemically equivalent bond lengths and angles of all disordered butyl C atoms, while neighbouring atoms within and between each conformation of the disordered butyl group were restrained to have similar and pseudo-isotropic atomic displacement parameters. The terminal methyl C atom of one butyl substituent in **1** has an elongated atomic displacement ellipsoid, which suggests that this methyl group might also be slightly disordered. However, attempts to develop a disordered model for this group did not lead to any improvement in the refinement results or the atomic displacement ellipsoids, so the ordered model was retained.

In all the structures, the non-hydrogen atoms were refined anisotropically. The hydroxy H atoms were initially placed in the positions indicated by difference electron density maps. For **3**, the hydroxy H atoms were allowed to refine together with individual isotropic displacement parameters, but for **1** and **2**, the positions of the hydroxy H atoms could not be refined successfully. Subsequently, their positions were geometrically optimized and the directions of the idealized O–H vectors were allowed to rotate to the orientation that was closest to the observed difference electron density peaks. All remaining H atoms for each compound 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 C atom ($1.5U_{eq}$ for the methyl and idealized hydroxy groups).

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 **2**. Three reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement of **3**. All calculations were performed using the SHELXL97 [20] program.

3. Results and discussion

3.1. Syntheses

Diorganotin hetero dicarboxylate compounds of the type $[R_2Sn(L^aH)(L^bH)]$ can be prepared by reacting either the acid form of the ligands with R_2SnO or by reacting sodium salts of the ligands with R_2SnCl_2. The detailed methodologies for the preparation of compounds **1**–**3** are reported in Section 2.4. The complexes are all orange coloured crystalline solids and stable for months. Complexes **1** and **2** are soluble in chloroform, dichloromethane, methanol, ethanol, acetonitrile, benzene, toluene and DMSO while **3** is only partly soluble in DMSO.

3.2. Spectroscopy

The ^1H and ^{13}C NMR data of the ligands are reported in [13,14]. The signals were assigned by the use of correlated spectroscopy (COSY), heteronuclear single-quantum correlation (HSQC) and Constant time Inverse-detection Gradient Accordion Rescaled (CIGAR) heteronuclear multiple-bond connectivities (HMBC) [21] experiments using gradient coherence selection. The conclusions drawn from the ligand assignments have subsequently been extrapolated to the complexes owing to the similarity in the data. The ^1H and ^{13}C chemical shift assignments of the butyltin moiety are readily deducible from the multiplicity patterns and resonance intensities. The assignments of the signals for compounds **1** and **2** are reported in Section 2.4. The OH signals in **1** appeared as two separate singlets at 11.0 and 10.9 ppm, while in **2**, they appeared as one unresolvable singlet. The integration values are consistent with the structures. Both complexes displayed only one set of aromatic ^1H signals whereas the ^{13}C NMR reflected the individual signals for each carbon atom of the ligand skeletons (refer to Section 2) on the NMR time scale. These results are consistent with the presence of two different ligands in the complexes. A sharp singlet at −116.1 ppm is observed in the ^{119}Sn NMR spectra

Table 2
Selected bond lengths (Å), bond angles (°), and torsion angles (°) for compounds **1**–**3**[a]

	1	**2**	**3**	
			Molecule A	Molecule B
Sn–O(1)	2.084(2)	2.079(2)	2.095(1)	2.084(1)
Sn–O(2)	2.692(2)	2.704(2)	2.553(2)	2.663(2)
Sn–O(4)	2.092(2)	2.086(2)	2.079(2)	2.088(1)
Sn–O(5)	2.634(2)	2.635(2)	2.703(2)	2.605(2)
Sn–C(a)	2.117(2)	2.120(3)	2.098(2)	2.091(2)
Sn–C(b)	2.118(3)	2.11(3), 2.13(2)	2.094(2)	2.095(2)
O(1)–C(1)	1.292(3)	1.291(3)	1.293(3)	1.295(2)
O(2)–C(1)	1.249(3)	1.255(3)	1.254(2)	1.254(2)
O(4)–C(14)	1.299(3)	1.291(3)	1.291(3)	1.292(2)
O(5)–C(14)	1.252(3)	1.256(3)	1.261(3)	1.254(2)
O(1)–Sn–O(2)	53.05(5)	52.92(6)	55.35(5)	53.78(5)
O(1)–Sn–O(4)	82.22(6)	82.11(7)	83.32(6)	83.40(6)
O(1)–Sn–O(5)	135.95(5)	135.66(6)	136.52(5)	137.86(5)
O(1)–Sn–C(a)	105.24(8)	105.26(9)	105.80(8)	104.55(9)
O(1)–Sn–C(b)	104.70(8)	105.4(7), 103.8(4)	107.02(8)	105.97(9)
O(2)–Sn–O(4)	135.23(6)	135.02(6)	138.65(5)	137.10(5)
O(2)–Sn–O(5)	170.05(5)	170.01(6)	168.13(5)	168.09(5)
O(2)–Sn–C(a)	89.68(8)	90.05(9)	88.46(7)	87.68(8)
O(2)–Sn–C(b)	88.28(8)	86.2(8), 88.8(5)	91.34(8)	86.52(8)
O(4)–Sn–O(5)	54.11(5)	54.01(6)	53.21(5)	54.45(5)
O(4)–Sn–C(a)	102.42(8)	102.40(9)	103.13(8)	107.86(8)
O(4)–Sn–C(b)	106.50(8)	109.5(6), 104.7(4)	103.32(9)	105.17(8)
O(5)–Sn–C(a)	91.06(8)	91.59(9)	87.25(7)	90.48(8)
O(5)–Sn–C(b)	84.86(8)	86.0(8), 83.9(5)	84.81(8)	86.81(8)
C(a)–Sn–C(b)	140.6(1)	138.1(5), 142.4(3)	139.7(1)	136.9(1)
C(1)–O(1)–Sn	107.2(1)	107.9(2)	102.7(1)	106.0(1)
C(1)–O(2)–Sn	79.7(1)	79.4(2)	82.5(1)	80.0(1)
C(14)–O(4)–Sn	105.2(1)	105.6(2)	107.5(1)	104.7(1)
C(14)–O(5)–Sn	81.1(1)	80.8(2)	79.1(1)	81.6(1)
N(1)–N(2)–C(8)–C(9)	5.8(4)	8.1(4)	−4.9(3)	−11.0(3)
N(2)–N(1)–C(6)–C(5)	7.6(3)	8.1(4)	8.3(3)	−12.6(3)
N(3)–N(4)–C(21)–C(22)	−1.3(4)	−1.5(4)	15.7(3)	−5.9(3)
N(4)–N(3)–C(19)–C(18)	14.7(3)	13.5(4)	5.1(3)	−6.6(3)

[a] Entries with two values correspond to disordered conformations in the structure. Atoms C(a) and C(b) correspond with the C atoms bonded to Sn shown in Figs. 2–4 with the lowest numbered C atom being assigned to C(a) in each case.

in $CDCl_3$ solution and the values are consistent with those reported for other $R_2Sn(O_2CR')_2$ systems [11,22–24].

The quadrupole splitting (Δ) value of the Mössbauer spectra for complexes **1** and **2** is around 3.50 mm s^{-1} indicative of an octahedral configuration at the tin atom with *trans*-alkyl groups [10,25]. This conclusion is in excellent agreement with the structures determined by X-ray crystallography (see below). The isomer shift (δ) values are in the range 1.47–1.49 mm s^{-1}, which is typical for quadrivalent organotin derivatives and the full width of half maximum ($\Gamma\pm$) of these resonance absorptions are ≈0.80 mm s^{-1}, further suggesting the presence of a single tin centre in the complexes [25]. Both complexes display similar Mössbauer parameters, which indicates that they are isostructural in the solid state. Using the Parish relationship between the Δ parameter value and the C–Sn–C bond angle [26], the latter has been calculated. The calculated angles are 141° and 142° for **1** and **2**, respectively, which indicate a distortion from the ideal *trans*-R_2Sn octahedral structure and correspond closely with the values found in the crystal structure determinations (see below).

3.3. X-ray crystallography

The molecular structures of compounds **1**, **2** and **3** are depicted in Figs. 2–4, respectively, while selected geometric parameters are given in Table 2. Complexes **1** and **2** are isostructural with one another, as well as with the corresponding dibutyltin complexes of *bis*(4′-chloro-)-, *bis*(4′-bromo-)- and *bis*(4′-methyl-)-azocarboxylates [10,11]. In **3**, the asymmetric unit contains two molecules of the Sn-complex. The conformations of the two symmetry-independent molecules in **3** are very similar and the overall molecular geometry is quite

akin to that of complexes **1** and **2**. In all three structures, the terminal 4′-substituent on one azocarboxylate ligand is disordered with its counterpart on the second azocarboxylate ligand (i.e., 4′-Cl/4′-Me disorder in **1** and **3** and 4′-Cl/4′-Br disorder in **2**). The disorder results from random and approximately equally distributed positioning of the azocarboxylate ligands in each molecule in the crystal. Further details are given in Section 2.5.

When only the primary coordination sphere is considered, all three complexes adopt the same skew-trapezoidal bipyramidal structural motif about the Sn atom and reveal a monomeric molecule. The carboxylate O atom of each azocarboxylate ligand coordinates strongly with the Sn atom, while the carbonyl O atom is much more weakly bound (Table 2). The coordination is such that the four O atoms lie in the equatorial plane, but the strongly bound O atoms lie *cis* to one another with a very acute angle, while the weakly bound O atoms lie only 10° (12° in **3**) from being linearly disposed to one another. The alkyl ligands lie in axial positions, thereby completing six-coordination about the Sn atom, but they are distorted some 38–43° from a true *trans* position so as to better occupy the open space left by the skew trapezoidal arrangement of the equatorial ligands. These observations are in excellent agreement with the coordination geometry determined from the ^{119}Sn Mössbauer results and the structures conform with the predominant motifs found for compounds with the general formula $[(R_2Sn(O_2CR')_2]$ [6,7,9–11].

In the structure of **3**, the open side of the Sn coordination sphere actually allows one of the hydroxy O atoms from the 2-hydroxybenzoate moiety of one ligand of symmetry-independent molecule B to form a bridge and coordinate very weakly with the Sn atom of molecule A, thereby completing a seventh coordination site in the extended Sn coordination sphere of molecule A. The Sn···O distance is 3.537(2) Å, which is about 0.24 Å shorter than the sum of the van der Waals radii of the Sn and O atoms, so the interaction is significant. There is no corresponding interaction between a hydroxy O atom from molecule A and the Sn atom of molecule B. The bridging Sn···O interaction links pairs of A and B molecules into head-to-head dimers (Fig. 5) and thereby fills the open side of the Sn-coordination sphere which is left open by the methyl ligands in **3**. Similar intermolecular Sn···O interactions have been observed in some related tin azocarboxylates [11]. In contrast, in the structures of **1** and **2**, one butyl group extends perpendicular to the plane of the azocarboxylate ligands, while the other butyl group bends so that it is mainly antiparallel to the azocarboxylate ligands, thereby closing off access to the open side of the Sn atom and precluding intermolecular Sn···O interactions. This arrangement has also been observed previously in related compounds [11].

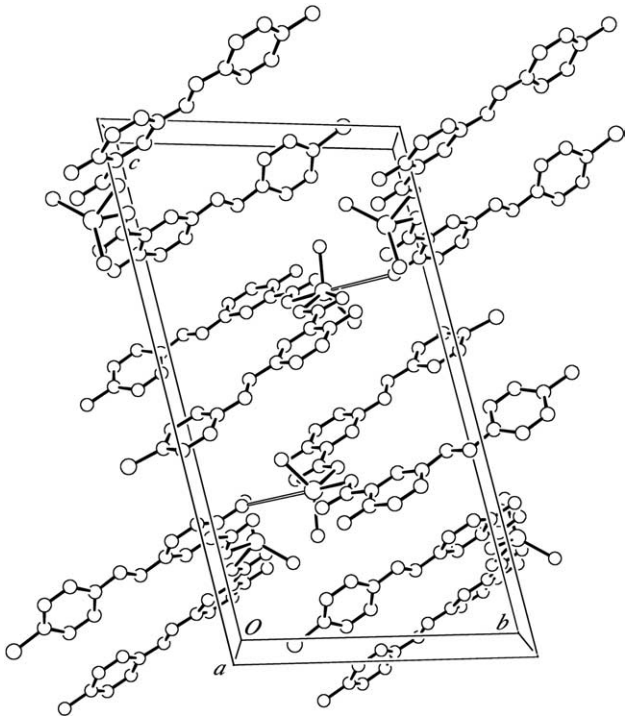

Fig. 5. The unit cell packing of **3** showing the dimers formed by the intermolecular Sn···O contact.

In each complex, the two azocarboxylate ligands are almost coplanar, and each ligand is planar up to the C–N bonds, but small twists about the C–N bonds result in each 4′-substituted phenyl group being twisted slightly from the plane of the remainder of its ligand. These twists amount to about 13° for each ligand in **1**, 11° and 17° in **2**, 4° and 21° for molecule A in **3** and 19° and 23° for molecule B. In each structure, each 2-hydroxybenzoate hydroxy group forms an intramolecular hydrogen bond with the carboxylate carbonyl oxygen atom of the same ligand.

4. Supplementary material

CCDC-255647–CCDC-255649 contain the supplementary crystallographic data for complexes **1**–**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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