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Synthesis and spectroscopic studies of diorganotin derivatives with tolfenamic acid. Crystal and molecular structure of the first complex of tolfenamic acid, 1,2:3,4-di-μ_2-2-[(3-chloro-2-methylphenyl)amino]-benzoato-*O*,*O*-1,3-bis-2-[(3-chloro-2-methylphenyl)amino]benzoato-*O*-1,2,4:2,3,4-di-μ_3-oxo-tetrakis[di-*n*-butyltin(IV)]

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Abstract

The complexes $[Me_2LSnOSnLMe_2]_2$ (**1**) $[Bu_2LSnOSnLBu_2]_2$ (**2**) and $Bu_2SnL_2.H_2O$ (**3**), where HL is 2-[bis(3-chloro-2-methylphenyl)amino]benzoic acid (tolfenamic acid), have been prepared and characterized structurally by means of ^{19}Sn Mössbauer, vibrational and ^{1}H- and ^{13}C-NMR spectroscopies. The crystal structure of complex **2** has been determined by X-ray crystallography. Three distannoxane rings are present to the dimeric tetraorganodistannoxanes of planar ladder arrangement with distorted trigonal-bipyramidal geometry about the five-coordinated tin centers. The structure, which has twofold symmetry, features a central Sn_2O_2 unit with two additional tin atoms linked at O. Pairs of tin atoms are bridged by bidentate carboxylate ligands and the external tin atoms have their coordination geometry completed by a monodentate carboxylate ligand. The tin atom geometries are similar and are based on a trigonal bipyramidal arrangement. Significant $\pi\rightarrow\pi$ stacking, C–H–π interactions and intrarmolecular hydrogen bonds stabilize this structure. The polar imino hydrogen atom on N(1) and N(2) participate in a bifurcate intramolecular hydrogen bond. In this case complex **2** is self-assembled via C–H–π and $\pi\rightarrow\pi$ stacking interactions. Tin-119 Mössbauer, vibrational and NMR data are discussed in terms of the crystal structure and the proposed structures for **1** and **3**. From the variable-temperature Mössbauer effect, the Debye temperatures for **1**–**3** were determined.

Keywords: Tin; Tolfenamic acid; Organotin; Mössbauer

1. Introduction

Tolfenamic acid (i.e. 2-[bis(3-chloro-2-methylphenyl)-amino]benzoic acid or *N*-(3-chloro-2-methylphenyl)-anthranilic acid) (Scheme 1) is a potent, well-tolerated non-steroidal anti-inflammatory drug (NSAID) with a low gastroulcerogenicity [1], a low overall toxicity and high therapeutic indices. It possesses analgesic and antipyretic properties as demonstrated in several animal models and has shown good results in long-term treatment of rheumatoid arthritis and osteoarthritis [2]. Chemically, it resembles mefenamic and flufenamic

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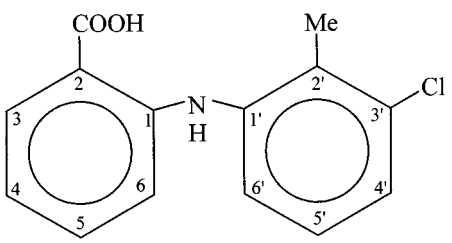
acids, other fenamates in clinical use. Tolfenamic acid inhibits the biosynthesis of prostagladins and has an inhibitory action on prostagladin receptors. Inhibitory effects on the biosynthesis of leukotrienes in vitro and ex vivo have been demonstrated [3]. X-ray crystal structure investigations of tolfenamic acid revealed the existence of two polymorphic forms containing the molecule as different conformers [4]. The poor water solubility of tolfenamic acid is the main difficulty in its pharmaceutical formulation and complexation with various cyclodextrins has been tried in order to circumvent bioavailability problems [5].

Organotin(IV) carboxylates form an important class of compounds and have been receiving increasing attention in recent years, not only because of their intrinsic interest but owing to their varied applications. Some examples find wide use as catalysts and stabilizers, and certain derivatives are used as biocides, as antifouling agents and as wood preservatives [6]. In recent years, investigations have been carried out to test their antitumour activity and it has been observed that indeed several diorganotin species, as well as triorganotin species, show potential as antineoplastic agents [7]. The mechanism of their activity may involve the transportation of the complexed organotin compound into the tumor cells, followed by reaction of uncomplexed organotin and its hydrolysis products at the active sites. This suggestion is supported by the fact that their hydrolysis products are active.

Given the pharmacological importance of tolfenamic acid and the potential biological activity of organotin carboxylates, it was thought of some interest to explore the chemistry of organotin/tolfenamic acid compounds. As a continuation of our studies of biological organotin chemistry [8] and on the coordination chemistry and anti-inflammatory properties of non-steroidal anti-inflammatory drugs [9], we report here the synthesis and spectral characterization of $[R_2LSnOSnLR_2]_2$ (where $R = CH_3$ (**1**), Bu (**2**) and L is deprotonated tolfenamic acid) and $Bu_2SnL_2 \cdot H_2O$ (**3**). The complexes have been structurally characterized in the solid state by means of temperature-dependent ^{119}Sn Mössbauer spectroscopy which allowed the determination of lattice dynamics. Vibrational and ^{1}H- and ^{13}C-NMR spectroscopic studies, and the crystal and molecular structure of **2** is also described.



Scheme 1.

2. Experimental

2.1. General and instrumental

The reagents (Aldrich, Merck) were used as supplied while the solvents were purified according to standard procedures. Tolfenamic acid was a gift from 'ELPEN A.E'. C, H, and N analyses were carried out by the microanalytical service of the University of Ioannina. Melting points were determined in open capillaries and are uncorrected. Infrared and far-infrared spectra were recorded on a Nicolet 55XC Fourier transform spectrophotometer using KBr pellets (4000–400 cm^{-1}) and nujol mulls dispersed between polyethylene disks (400–40 cm^{-1}). The ^{1}H (250.13 MHz), ^{13}C (62.90 MHz), 2D ^{1}H–^{1}H shift correlated spectra (COSY), 2D ^{13}C–^{1}H shift correlated spectra (HETCOR) and 2D long range ^{13}C–^{1}H shift correlated spectra (COLOC) NMR spectra were recorded on a Bruker AC-250E spectrometer equipped with an Aspect 3000 computer (using DISNMR program, version 1991) and a 5 mm ^{13}C/^{1}H dual probe head (^{1}H 90° pulse width = 10.2 μs, ^{13}C 90° pulse width = 10.4 μs). Samples were dissolved in $CDCl_3$ or DMSO-d_6 and spectra were obtained at room temperature with the signal of the free DMSO or $CHCl_3$ (at 2.49 and 7.24 ppm, respectively) as a reference. Mössbauer measurements were carried out using a constant-acceleration Mössbauer spectrometer with a $Ba^{119}SnO_3$ source maintained at room temperature. A Pd filter was used to eliminate the 25.8 keV × radiation. A variable-temperature liquid-nitrogen cryostat (Oxford Instruments) was used for the low temperature measurements. Suitable computer programs have been employed in the fitting procedure of the experimental spectra using Lorentzian line shapes. The estimated errors are ± 0.02 mm s^{-1} for the hyperfine parameters and ± 3% for the spectral areas.

2.2. Synthesis

2.2.1. $[Me_2LSnOSnLMe_2]_2$ (1)

To a solution of di-methyl oxide (0.198 g, 1.2 mmol) in benzene (20 ml) was added a solution of tolfenamic acid (0.262 g, 1 mmol) in benzene (10 ml). The reaction mixture was refluxed for 3 h with azeotropic removal of water via a Dean–Stark trap. The resulting clear solution was rotary evaporated under vacuum to a small volume, chilled and triturated with diethylether to give a white solid; m.p. 190–192°C. Yield 52%. Anal. Found: C, 45.97; H, 3.88; N, 3.18. Calc.: C, 46.04; H, 4.10; N, 3.36%.

2.2.2. $[Bu_2LSnOSnLBu_2]_2$ (2)

Di-*n*-butyl oxide (0.373 g, 1.5 mmol) and tolfenamic acid (0.366 g, 1.4 mmol) and 70 ml of benzene were refluxed overnight with azeotropic removal of water via

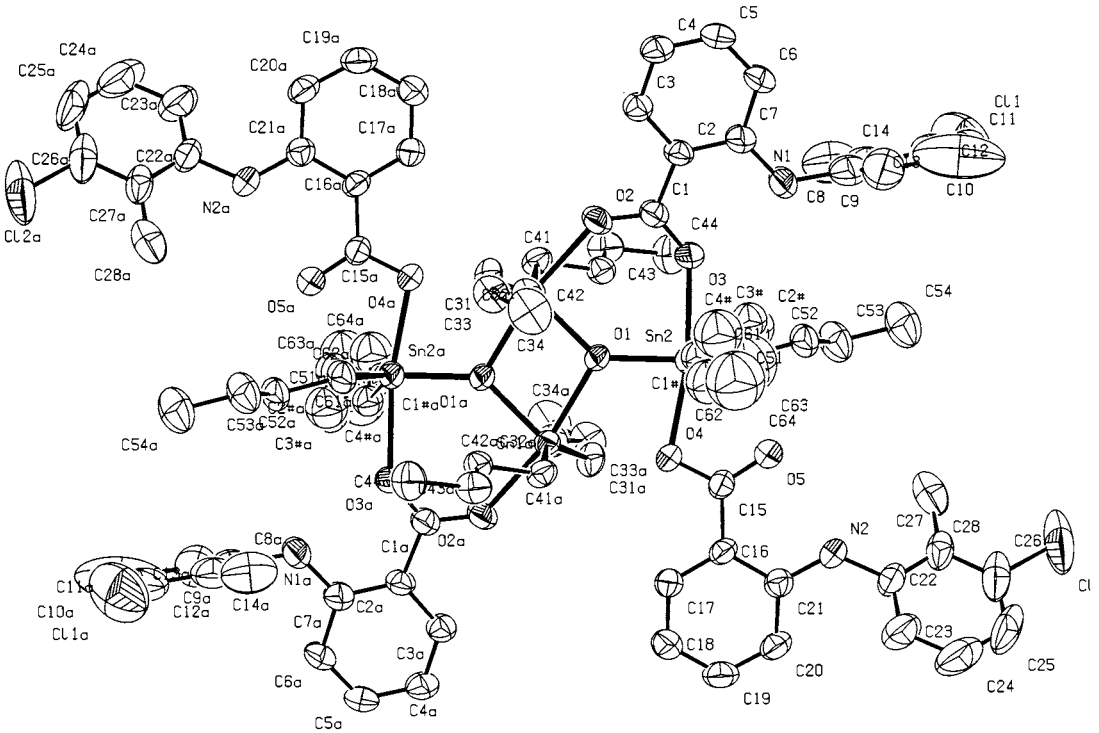


Fig. 1. Perspective view of $[Bu_2SnLOLSnBu_2]_2$ (**2**) showing the atomic numbering scheme.

a Dean–Stark trap. The resulting clear solution was rotary evaporated under vacuum to a small volume. Drops of diethylether were added and after slow evaporation, white crystals were grown. m.p. 99–100°C. Yield 58%. Anal. Found: C, 52.39; H, 5.71; N, 2.78. Calc.: C, 52.68; H, 5.82; N, 2.79%.

2.2.3. $Bu_2SnL_2 \cdot H_2O$ (3)

Di-*n*-butyl oxide (0.373 g, 1.5 mmol) and tolfenamic acid (0.785 g, 3 mmol) and 80 ml of benzene were refluxed overnight with azeotropic removal of water via a Dean–Stark trap. The resulting clear solution was rotary evaporated under vacuum to a small volume, chilled and triturated with diethylether to give a white oil which solidified after 1–2 days in vacuum. The product was washed with acetone and filtered to give a white solid; m.p.: 86–87°C. Yield 55%. Anal. Found: C, 55.24; H, 5.83; N, 3.46. Calc.: C, 55.99; H, 5.48; N, 3.63%.

2.3. X-ray crystallography [10]

$C_{88}H_{116}Cl_4N_4O_{10}Sn_4$, $M = 2006.5$, triclinc, $a = 12.223(2)$, $b = 19.643(3)$, $c = 11.294(2)$ Å, $\alpha = 105.13(1)$, $\beta = 116.59(1)$, $\gamma = 92.24(2)°$, $V = 2302.2(9)$ Å^3, $Z = 1$ (tetramer), $T = 253$ K, $\mu(\text{Mo–K}\alpha) = 12.44$ cm^{-1}, 13830 reflections measured on a Rigaku AFC7R diffractometer, θ_{max} 30.0°, 13247 unique ($R_{int} = 0.042$), 8065 with $I \geq 3.0\sigma(I)$ were used in subsequent calculations: final $R = 0.045$ and $R_w = 0.068$. One butyl chain was found to be disordered over two positions. Refinement showed occupancy ratio 0.67:0.33; H atoms were not included for this group.

3. Results and discussion

3.1. Crystal structure of 2

Compound **2** is obtained by azeotropic removal of water from the reaction between the di-*n*-butyl oxide and tolfenamic acid in the molar ratio 1:1 conducted in benzene. The molecular structure is shown in Fig. 1 and selected interatomic parameters are collected in Table 1. Compound **2** is a centrosymmetric dimer built up around the planar cyclic Sn_2O_2 unit. The two oxygen atoms of this unit are tridentate as they link three Sn centres, two *endo*-cyclic and one *exo*-cyclic. Additional links between the *endo*- and *exo*-cyclic Sn atoms are provided by bidentate carboxylate ligands that form essentially symmetrical bridges (Sn(1)–O(2) 2.241(4) Å and Sn(2)–O(3) 2.315(4) Å). Each exocyclic Sn atom is also coordinated by a monodentate carboxylate ligand (Sn(2)–O(4) 2.181(3) Å). The overall geometry found in the structure, allowing for differences in chemistry, is similar to that found in the common motif adopted by compounds with the general formula $[R_2(R'CO_2)SnOSn(O_2CR')R_2]_2$ [11]. To a first approxi-mation, the coordination geometry about each of the Sn atoms is best described as distorted trigonal bipyra-

Table 1
Selected bond lengths (Å) and bond angles (°) for **2** [a]

Bond lengths			
Sn(1)–O(1)	2.037(2)	Sn(2)–O(1)	2.035(3)
Sn(1)–O(1)^{i}	2.178(2)	Sn(2)–O(3)	2.316(3)
Sn(1)–O(2)	2.242(2)	Sn(2)–O(4)	2.181(3)
Sn(1)–C(31)	2.128(3)	Sn(2)–C(51)	2.141(3)
Sn(1)–C(41)	2.124(3)	Sn(2)–C(61)	2. 11(1) [2.24(2)]
Bond angles			
O(1)–Sn(1)–O(1)	76.6(1)	O(1)–Sn(2)–O(3)	88.7(1)
O(1)–Sn(1)–O(2)	91.6(1)	O(1)–Sn(2)–O(4)	80.7(1)
O(1)–Sn(1)–C(31)	109.1(2)	O(1)–Sn(2)–C(51)	111.4(2)
O(1)–Sn(1)–C(41)	108.0(2)	O(1)–Sn(2)–C(61)	112.6(2) [102.9(3)]
O(1)*i*–Sn(1)–O(2)	167.0(1)	O(3)–Sn(2)–O(4)	168.8(1)
O(1)*i*–Sn(1)–C(31)	94.7(2)	O(3)–Sn(2)–C(51)	83.2(2)
O(1)*i*–Sn(1)–C(41)	97.8(2)	O(3)–Sn(2)–C(61)	81.0(2) [95.32(3)]
O(2)–Sn(1)–C(31)	84.0(2)	O(4)–Sn(2)–C(51)	97.5(2)
O(2)–Sn(1)–C(41)	91.0(2)	O(4)–Sn(2)–C(61)	106.0(2) [90.3(3)]
C(31)–Sn(1)–C(41)	142.6(2)	C(51)–Sn(2)–C(61)	132.6(2) [145.6(3)]
Sn(1)–O(1)–Sn(1)*i*	103.4(1)	Sn(1)–O(1)–Sn(2)	135.9(2)
Sn(1)–O(1)–Sn(2)*i*	120.4(1)	Sn(1)–O(2)–C(1)	135.5(3)
Sn(2)–O(3)–C(1)	133.4(2)	Sn(2)–O(4)–C(15)	106.7(2)

[a] Symmetry operation *i*: $-x, -y, 1-z$; parameters given in square brackets are for the minor component of the disordered C(61)–C(64) butyl group.

midal with axial positions occupied by O atoms. Distortions from the ideal geometry arise, in part, owing to the close intramolecular approach of O atoms such that Sn(1)···O(4)^{i} is 2.818(2) Å and Sn(2)···O(5) is 2.729(3) Å; symmetry operation *i*: $-x, -y, 1-z$. While these separations are considered too long to represent significant bonding interactions between Sn and O, they do exert an influence on the respective coordination geometries as seen in the expansion of the C–Sn–C angles to 142.6(2) and 132.6(2)° [145.6(3)° for the minor component of the disordered C(61)–C(64) butyl group] for Sn(1) and Sn(2), respectively. The aminobenzoate portion of each carboxylate ligand is effectively planar presumably so as to facilitate the formation of intramolecular N(1)–H···O(3) and N(2)–H···O(5) interactions of 1.91 and 1.88 Å, respectively. By contrast, significant twists between the aromatic fragments of bidentate and monodentate ligands are noted. The dihedral angles between the aminobenzoate aromatic ring and the other ring are 78.0(3) and 47.8(2)°, respectively. Remarkably, these are comparable to the angles of 73 and 46°, respectively, found in the two white and yellow forms of free tolfenamic acid.

The unit cell of **2** comprises one centrosymmetric, dimeric distannoxane molecule. Translationally related (along *a*) molecules associate via π–π stacking interactions so that slightly displaced C(2)–C(7) and C(16)–C(21) rings face each other. The average separation between the two rings is 3.56 Å (dihedral angle 5.6°), however, the closest separation of 3.522(8) Å occurs between the C(3) and C(19) atoms. Evidence for a C–H···π interaction is also found in the structure. The C(24)–H atom is directed towards the symmetry related $(-1-x, -1-y, -z)$ aromatic ring containing the C(8)–C(13) atoms but in particular towards the C(10)–C(12) atoms of this ring. The closest contact of 2.78 Å occurs between the H and C(11) atoms. Further, intramolecular hydrogen bonds stabilize this structure. The polar imino hydrogen atom on N(1) and N(2) participate in a bifurcate intramolecular hydrogen

Table 2
C–H-π, π–π and intra-hydrogen bonds for **2**

			H···Cg	C···Cg	C–H···Cg
C(42)–H(42B)→Cg(1)^{i}			3.200	3.581	105.35
C(24)–H(24)→Cg(4)^{ii}			3.081	3.910	133.88
C(32)–H(32)→Cg(1)^{i}			3.058	3.526	111.12
Cg(I)→Cg(J) [a]		Cg–Cg [b]	*β* [c]	CgI-Perp [d]	CgJ-Perp [e]
Cg(3)→Cg(5)^{iii}		3.779	19.13	3.570	3.439
Cg(5)→Cg(3)^{iv}		3.786	24.93	3.439	3.570
D	H	A [f]	D···A	H···A	D–H···A
N(1)	H(1)	O(3)	2.635(5)	1.9490	131.71
N(2)	H(2)	O(5)	2.631(5)	1.8781	134.23
C(14)	H(14)	N(1)	2.839(8)	2.3638	104.85
C(28)	H(28)	N(2)	2.860(4)	2.3588	106.54

[a] Where Cg(1), Cg(3), Cg(4) and Cg(5) are referred to the centroids Sn1–O1–Sn1a–O1a, C3–C4–C5–C6–C7, C8–C9–C10–C11–C12–C13, and C16–C17–C18–C19–C20–C21, respectively.

[b] Cg–Cg is the distance between ring centroids; symmetry transformations: *i*, $-x, -y, 1-z$; *ii*, $-1-x, -1-y, -z$; *iii*, $1+x, y, z$; and *iv*, $-1+x, y, z$.

[c] Where *β* is the angle Cg(I)→Cg(J) or Cg(i)→Me vector and normal to plane I (°).

[d] CgI-Perp is the perpendicular distance of Cg(I) on ring J

[e] CgJ-Perp is the perpendicular distance of Cg(J) on ring I.

[f] D, donor; A, Acceptor.

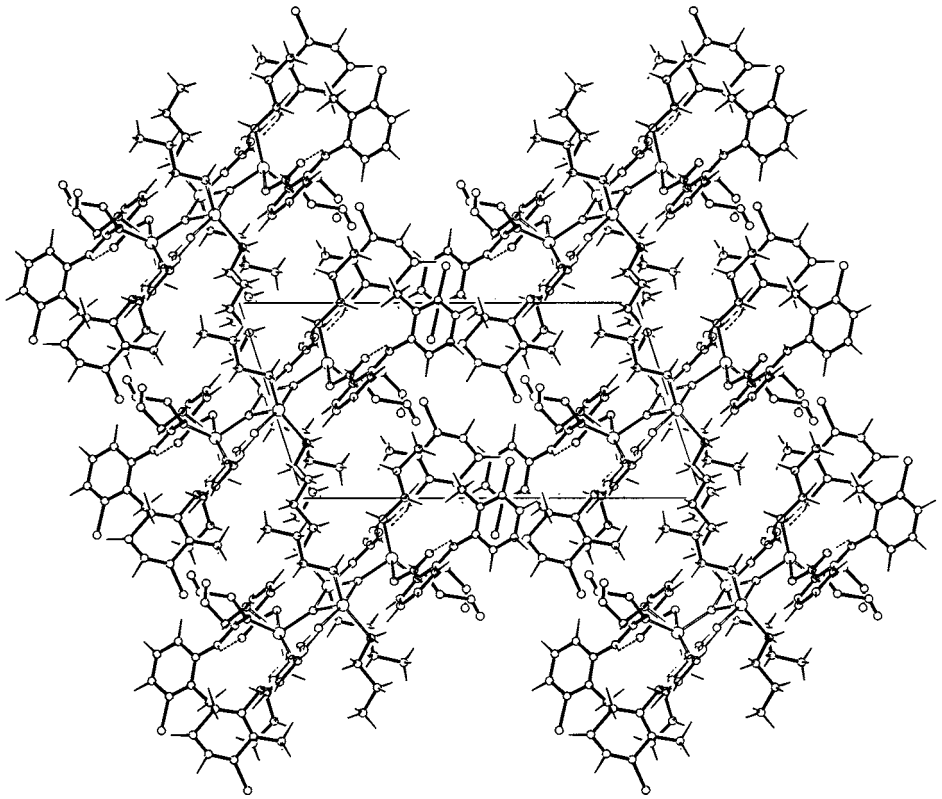


Fig. 2. Packing diagram of the complex $[Bu_2SnLOLSnBu_2]_2$ viewed along the α.

bond, Table 2. In this case complex **2** is self-assembled via C–H–π and π→π stacking interactions and a different packing arrangement from bis(2-[(2,6-dichlorophenyl)amino]phenyl]acetate) oxide results [7f]. A view of the crystal packing along the α axis is shown in Fig. 2.

3.2. Spectroscopy

3.2.1. Infrared spectroscopy

The IR of the diorganotins, **1**, **2** and **3** gave bands at ν 3340 and 3290 cm^{-1} attributable to intramolecular NH···O hydrogen bonds. The $\nu_{as}(COO)$ and $\nu_{sym}(COO)$ bands appear at ν 1615, 1580 cm^{-1} and ν 1450 and 1370 cm^{-1}, respectively, for **1** and **2**, and appear at ν 1662 and 1374 cm^{-1} for **3**. The difference between these bands for **1** and **2**, Δ [$\Delta = \nu_{as}(COO) - \nu_{sym}(COO)$], is close to that found for a unidentate carboxylate ligand (ca. 215 cm^{-1}) and a bidentate bridging carboxylate (ca. 170 cm^{-1}), respectively [8,12]. The difference between these two bands for **3**, i.e. 288 cm^{-1}, is close to that observed for asymmetric bidentate chelate mode [12]. Two bands at 490–480 and 446–427 cm^{-1}, for **1** and **2**, are assigned to $\nu_{as,sym}(SnO)_2$, indicating non-linear Sn–O moieties, while the bands at 230–190 cm^{-1} are assigned to the tin–oxygen (COO) bridging and unidentate stretching modes, respectively [8,12].

3.2.2. NMR spectra

The ^{1}H- and ^{13}C-NMR data for tolfenamic acid, Scheme 1 and **1**–**3** are summarized in Table 3. The lack of published information on tolfenamic acid made it necessary to perform ^{1}H (250.13 MHz), ^{13}C (62.90 MHz), 2D ^{1}H–^{1}H shift correlated spectra (COSY), 2D ^{13}C–^{1}H shift correlated spectra (HETCOR) and 2D long range ^{13}C–^{1}H shift correlated spectra (COLOC) NMR spectra in order to completely assign the resonances in the tolfenamic acid and **1**–**3**. Involvement of the carboxyl group in bonding to Sn is confirmed by the resonance ascribed to C1, which either disappears or exhibits the greatest shift upon coordination. The existence of the NH resonance in the ^{1}H-NMR spectra indicates that the nitrogen atom remains protonated in **1**–**3**. The small downfield shift of the NH resonance in $CDCl_3$ solution suggests that no significant participation in intermolecular hydrogen-bonding takes place.

The remaining resonances due to the aromatic carbon atoms for **1** do not shift considerably after binding to Sn, with C3′ exhibiting the greatest upfield shift (1.3 ppm). No resonance attributable to the carbonyl C nucleus was found, behaviour that has been noted previously for related systems [13]. Three resonances attributed to the tin-bound methyl carbons are found, a result that is consistent with the presence of a dimer in solution by analogy with related compounds [14]. In the ^{1}H-NMR spectrum of **1**, three singlets appear in the

Table 3
Proton and ^{13}C-NMR data

	OH	NH	H3	H4	H5	H6	H4′	H5′	H6′	CH_3				
Tolf [a]	13.12	9.57	7.91dd, $J(3–4) = 7.8$, $J(3–5) = 1.8$	6.76td, $J(4–6) = 0.9$	7.35td, $J(4–5) = 8.3$	6.81dd, $J(6–5) = 8.3$	7.28d	7.22	7.20d	2.24s				
Tolf [b]		9.15	8.01dd, $J(3–4) = 7.7$, $J(3–5) = 1.7$	6.73t, $J(4–6) = 0.8$	7.31td, $J(4–5) = 8.1$	6.75d, $J(6–5) = 8.5$	7.25d	7.12t, $J(5′–4′) = 7.7$, $J(5′–6′) = 7.7$	7.25d	2.32s				
1 [b]	Me_2Sn, 0.99s/1.07s, 1.15s/1.15s	9.43br	8.10br	6.61br	7.17td, $J(4–5) = 8.2$	6.84d, $J(6–5) = 8.2$	7.31d	7.11t, $J(5′–4′) = 7.7$, $J(5′–6′) = 7.7$	7.31d	2.32s				
2 [b]	Bu_2Sn, Hδ:0.90, Hγ: 0.76; Hβ: 1.66, Hα: 1.29	9.52s/9.27	8.12d/7.88d, $J(3–4) = 7.7$	6.57t	7.27t, $J(4–5) = 8.2$	6.90d/6.80d, $J(6–5) = 8.8$	7.20d	7.11t, $J(5′–4′) = 7.7$ $J(5′–6′) = 7.7$	7.20d	2.33s/2.31s				
3 [b]	Bu_2Sn, Hδ: 0.89; Hγ: 1.41; Hα, β: 1.77	9.28s	8.13d, $J(3–4) = 7.7$	6.76t	7.13t	6.90d, $J(6–5) = 8.3$	7.30d	7.17t, $J(5′–4′) = 7.7$, $J(5′–6′) = 7.7$	7.30d	2.34s				
	COOH	C1	C2	C3	C4	C5	C6	C1′	C2′	C3′	C4′	C5′	C6′	Me
Tolf. [a]	170.1	112.2	147.5	131.8	117.3	134.2	113.6	140.5	129.8	134.4	122.1	124.9	127.5	14.7
Tolf [b]	172.9	109.9	149.4	132.5	117.0	135.3	113.8	140.1	132.2	135.7	123.7	126.2	127.0	15.1
1 [b]	Me_2Sn: 5.0/7.5/10.2		148.4	131.2	117.0	135.6	113.8	140.7	132.3	133.8	122.6	125.3	126.8	15.1
2 [b]	175.0; Bu_2Sn, Cδ: 13.5; Cγ: 26.9/26.8; Cβ: 27.9/27.5; Cα: 29.8/28.6	114.6	148.4	132.4	116.7	133.6	113.7	140.9	131.6	135.6	123.0	125.4	126.9	15.1
3 [b]	Bu_2Sn, Cδ: 13.5; Cγ: 26.3; Cβ: 26.7; Cα:25.8; COOO: 177.3	112.0	148.3	133.4	117.2	134.6	113.7	140.7	131.0	135.6	122.2	125.3	126.8	14.9

[a] Spectrum recorded in DMSO-d_6.
[b] Spectrum recorded in $CDCl_3$, tolfenamic acid acid is poor soluble in $CDCl_3$.

region of the tin-bound methyl groups, but integration shows that in the case of the signal emerging at 1.15 ppm, two methyl groups are present indicating accidental equivalence. The most significant chemical shift difference between the ^{1}H spectra of the free drug and **1** is observed for the H5 atom.

For **2**, the appearance of two resonances for each of NH, H3, H6 and CH_3, in the ratio 1:3, shows the existence of two inequivalent ligands in solution. The NH, H3, H6 and H4 resonances associated with least abundant ligand exhibit the greater shifts compared with those found for the free drug. All shifts are downfield except for the that due to H4 which is shifted upfield by 0.16 ppm. Two resonances also appear for the Cα,β,γ atoms of the butyl group, with the Cα resonances being separated by 73 Hz, the Cβ by 24 Hz and the Cγ by 5 Hz. This result is expected as the more remote the C nucleus is from the Sn centre, the less susceptible it is to different Sn-atom environments. Multiplicity of the butyl protons is also observed in proton NMR spectrum as a result of their non-equivalence [14]. In the ^{13}C-NMR spectra, the greatest downfield shift is exhibited by the C1 atom (4.7 ppm) while the carbonyl C shifts downfield by 2.1 ppm. The C5 resonance, by contrast, shifts upfield by 1.7 ppm.

The shifts of the benzoic ring proton resonances in **3** are similar to those observed in the other complexes. The ^{13}C-NMR spectrum reveals a small resonance assignable to the CO_2 nucleus and coordination is confirmed by the fact that this resonance exhibits the most important shift (4.4 ppm downfield). A downfield shift is also observed for the C1 nucleus (2.1 ppm) while smaller resonance shifts are found for the rest of the carbon atoms. The value of the ^1J(Sn–Cα) and ^2J(Sn–Cβ) coupling constants are 563.7 and 36.5 Hz, respectively. Based on the coupling constants and according to Holeček equation the C–Sn–C angle is estimated to be 131° [15]. An assignment of the structure for **3** can be made based on literature data as similar values for C–Sn–C angles have been determined (in $CDCl_3$ solution) for hexacoordinated dibutyltin(IV) compounds for which skewed-trapezoidal bipyramidal geometries were found.

3.2.3. Mössbauer spectra

Mössbauer spectra were obtained between 78 and 200 K for **1**–**3** and are reported in Table 4. The isomer shift is correlated to the partial atomic charges (Q_{Sn}) acting on the Sn nucleus by means of the σ-electron density; δ increases as Q_{Sn} decreases. The increase in δ with increase of alkyl chain length follows the expected pattern of +I inductive effect of the alkyl groups. The fitting of the experimental data points by two symmetric Lorentzian doublets for **1**, shows the occurrence of two distinct crystallographic enviroments around tin atoms. From the quadrupole splitting value (QS) and the point-charge approach, the relation $QS = 4[R]\ (1-3\sin^2\theta\cos^2\theta)^{1/2}$ gives an estimate of θ, where $180°-2\theta$ is the R–Sn–R bond angle [16b]. In the present compound the bond angles calculated for the two tin sites are 142° for the coordination with the high QS value and 131° for low QS value. The presence of the two different tin sites with almost equal spectral areas can consequently propose for this compound the formula $[Me_2LSnOSnLMe_2]_2$. The values of the corresponding hyperfine parameters are very similar to that already reported for the adduct $[(Me_2SnOOCR)_2O]_2$ (where R = *m*-$CH_3C_6H_4CH$=CH and $\delta = 1.30$, 1.13 mm s^{-1}; $\Delta E_Q = 3.65$, 3.14) [17b]. The spectra of **2** and **3** are each characterized by a large quadrupole split doublet with a relatively high isomer shift and a narrow linewidth. This fact is indicative of pure compounds with a single Sn site. At first inspection, the presence of a single quadrupole split resonance for **2** at all temperatures suggests the equivalence in the environments about the two crystallographically dissimilar Sn nuclei and reflects the relative insensitivity of the i.s. and q.s to subtle changes in atomic environment. The Mössbauer parameters for **2** are however very similar to those reported for the adducts $[ClR_2SnOSnR_2Cl]_2$ [16a]. A C–Sn–C bond angle of 149° for **2** is calculated from the Mössbauer analysis. The X-ray crystal structure for **2** indicates C–Sn(1)–C and C–Sn(2)–C bond angles of 142.6(2) and 132.6(2)° [145.6(3)° for minor component], respectively. The infrared and NMR spectroscopy suggest a distorted octahedral environment for **3**, there-

Table 4
Mössbauer effect spectral data at 80.0 K [a]

No.	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	$\Gamma/2$ (mm s^{-1})	A [b]	A [c] ($\times 10^{-2}$) (K^{-1})	Θ_D (K)	C–Sn–C [d] (°)
1	1.37	3.58	0.38	48	−1.59	106	142
	1.00	3.21	0.40	52	−1.60	106	131
2	1.33	3.34	0.39	100	−2.17	91	149, 142.6(2) [e], 132.6(2) [e]
3	1.34	3.32	0.40	100	−2.17	91	149

[a] Estimated errors ±2 in the last significant figures.
[b] Full width at half maximum.
[c] Slope of the best fit straight lines (-10^2 d ln $A(T)$/dT).
[d] Values calculated from Mössbauer spectra.
[e] Values from crystallographic data.

fore, the low value of q.s. for **3** points to a rather trans octahedral or skew-trapezoidal bipyramidal stereochemistry.

Variable temperature spectra were recorded for complexes **1**, **2** and **3** in order to extract molecular dynamics information; the procedure has been previously described [8b]. The plot of $\ln A(T)$ versus T gives a straight line with slope $-\mathrm{d}\ln A(T)/\mathrm{d}T$ that characterizes the tightness by which the tin atom is bounded into the lattice. The experimental slope is -2.17×10^{-2} K^{-1} for both **2** and **3** with correlation coefficients r better than -0.997. These values correspond to an arrangement of noninteracting molecules in the solid state for **2** and **3**, and of interacting molecules by hydrogen bonds or polymeric for **1** [17c]. The crystal structure of **2** shows that C–H–π and π > π stacking interactions are responsible for the value of -2.17×10^{-2} K^{-1}.

4. Supplementary material

Crytallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC, no. 149406 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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