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Preparations and spectroscopic studies of organotin complexes of diclofenac☆

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Abstract

The reactions of the potent and widely used anti-inflammatory drug diclofenac, HL, with diorganotin(IV) oxides were studied. The dimeric tetraorganodistannoxane complexes $[Me_2LSnOSnLMe_2]_2$, $[Bu_2LSnOSnLBu_2]_2$, $[Ph_2LSnOSnLPh_2]_2$ and the dibutyltin complex $[Bu_2SnL_2]$, have been prepared and structurally characterized in the solid state by means of vibrational and ^{119}Sn Mössbauer spectroscopy. Determination of lattice dynamics by temperature-dependent ^{119}Sn Mössbauer spectroscopy. From the variable-temperature Mössbauer effect, the Debye temperature was determined. The complexes have been characterized in solution by NMR (^{1}H and ^{13}C) spectroscopy. Vibrational, Mössbauer, and NMR data are discussed in terms of the proposed structures.

Keywords: Vibrational spectra; NMR and Mössbauer spectra; Diclofenac acid; Organotin complexes

1. Introduction

Diclofenac, (2-[2,6-dichlorophenylamino]phenylacetate), HL, Scheme 1, is one of the widely used non-steroidal anti-inflammatory drugs (NSAIDs), therapeutically used in inflammatory and painful diseases of rheumatic and non-rheumatic origin. Diclofenac is a potent non-selective inhibitor of cyclo-oxygenase in vitro and in vivo, thereby decreasing the synthesis of prostaglandins, prostacyclin, and thromboxane products. Recently, two different cyclooxygenase isoforms, COX-1 and COX-2, have been characterized. New studies from the last years revealed that in addition to arthritis and pain, cancer and neurodegenerative diseases like Alzheimer's disease, could potentially be treated with COX-2 inhibitors [1,2]. Moser et al. [3] studied 36 congeners of diclofenac as inhibitors of cyclooxygenase and the in vivo inhibition of rat adjuvant arthritis, and found that both activities can be explained by lipophilicity and the twisting of the two aromatic rings (angle of twist, 58–69°). These findings allowed the rationalization of the high activity of diclofenac.

Synthesis and study of metal complexes with anti-inflammatory drugs as ligands is a research area of considerable interest. The synthesis and study of metal complexes with drugs, which exhibit synergistic activity, has concentrated much attention as an approach to new drug development [4,5]. The binuclear copper(II) complex of diclofenac, $[Cu(L)_2(H_2O)]_2{\cdot}2H_2O$ was found to have an anti-inflammatory profile superior to diclofenac when inhibiting inflammations due mainly to the activation of lipooxygenase and or to the complement systems. The most active anti-inflammatory complexes of Co(II), Ni(II), and Pd(II) offered significant protection against lipid peroxidation in vitro, acting as antioxidant compounds, properties that are not demonstrated by diclofenac. Of note is that the complexes of Co(II), Ni(II), and Pd(II) exhibit a superior anti-inflammatory profile, inhibiting inflammations and phagocytosis and act as antioxidant compounds, properties that are absent from diclofenac [4,6]. Crystal structures of organotin and dimeric tetraorganodistannoxane adducts of NSAIDs have been reported by our group [7,8].

☆ Dedicated to the late Professor J.M. Tsangaris for his contribution to Inorganic Chemistry.

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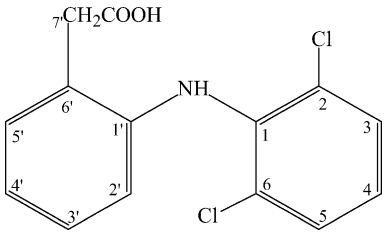

Scheme 1.

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 anti-fouling agents and as wood preservatives [9]. Information on the structures of organotin carboxylates continues to accumulate, and at the same time new applications of such compounds are being discovered in industry, ecology, and medicine. In recent years, investigations have been carried out to test their anti-tumor activity and it has been observed that indeed several diorganotin species, as well as triorganotin species, show potential as anti-neoplastic agents [10] and anti-tuberculosis agents [11].

Given the pharmacological importance of sodium diclofenac and the potential biological activity of organotin carboxylates, it was thought of some interest to explore the chemistry of organotin/diclofenac compounds. The novel complexes $[R_2(L)SnOSn(L)R_2]_2$ (where R = CH_3, Ph) and $[R_2SnL_2]$ (where R = Bu) have been prepared and structurally characterized in the solid state by means of ^{119}Sn Mössbauer spectroscopy, the determination of lattice dynamics by temperature-dependent ^{119}Sn Mössbauer spectroscopy and by vibrational and ^{1}H and ^{13}C NMR studies.

2. Experimental

2.1. General considerations

The reagents (Aldrich, Merck) were used as-supplied while the solvents were purified according to standard procedures. Sodium diclofenac was a gift from "HELP 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 correspondingly) 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. $[Me_2SnLOLSnMe_2]_2$, (1)

To a solution of dimethyltin oxide (0.198 g, 1.2 mmol) in benzene (20 ml) was added a solution of diclofenac acid (0.296 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 (caution: benzene is very toxic). 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. 195–197 °C. Anal. found: C, 42.25; H, 4.07; N, 2.97. Calculated: C, 42.44; H, 3.53; N, 3.09.

2.2.2. $[Bu_2SnLOLSnBu_2]_2$, (2)

2 was prepared according to published procedure [8]. m.p. 146–147 °C. Anal. found: C, 49.20; H, 5.21; N, 2.61. Calculated: C, 49.30; H, 5.26; N, 2.61.

2.2.3. $[Bu_2SnL_2]$, (3)

To a solution of di-*n*-butyltin oxide (0.2489 g, 1 mmol) in benzene (20 ml) was added a solution of diclofenac acid (0.65 g, 2.2 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. 103–104 °C. Anal. found: C, 52.03; H, 4.76; N, 3.62. Calculated: C, 52.52; H, 4.62; N, 3.40.

2.2.4. $[Ph_2SnLOLSnPh_2]_2$, (4)

To a solution of diphenyltin oxide (0.332 g, 1.15 mmol) in benzene (20 ml) was added a solution of diclofenac acid (0.296 g, 1 mmol) in EtOH (10 ml) and were refluxed for 4 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. 101–104 °C. Anal. found: C, 54.12; H, 3.65; N, 2.45. Calculated: C, 54.22; H, 3.50; N, 2.43.

3. Results and discussion

Compounds **1–4** are obtained by azeotropic removal of water from the reaction between diorganotin oxide and diclofenac acid in the molar ratio 1:1 and 1:2 conducted in benzene or in a mixture of benzene–EtOH according to the reactions 1–3.

$$4\,R_2SnO + 4HL \xrightarrow{\text{benzene}} [R_2(L)SnOSn(L)R_2]_2 + 2H_2O$$
$$\text{where } R = CH_3, Bu \quad (1)$$

$$4\,Ph_2SnO + 4HL \xrightarrow{\text{benzene, EtOH}} [Ph_2(L)SnOSn(L)Ph_2]_2 + 2H_2O$$
$$\text{where } R = Ph \quad (2)$$

$$Bu_2SnO + 2HL \rightarrow [Bu_2SnL_2] + H_2O \quad (3)$$

Recently the crystal and molecular structure of $[Bu_2(L)SnOSn(L)Bu_2]_2$, **2**, has been reported by some of us [8]. 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 four membered Sn_2O_2 ring of tetraorganodistannoxanes, $[R_2(L)SnOSn(L)R_2]_2$, is formed through interaction of the tin of one distannoxane with the oxide linkage of a second, and the resulting structures are referred as "ladders" or "staircases" depending on their planarity (Fig. 1).

3.1. Spectroscopy

3.1.1. Infrared spectroscopy

The most prominent IR absorptions are shown in Table 1. The IR of the tetraorganodistannoxanes, **1** and **2** gave bands at ~3320 and 3240 cm^{-1} attributable to intramolecular hydrogen bonds NH–O and NH–Cl. The ν_{as}(COO) and ν_{sym}(COO) bands appear at 1623, 1575 cm^{-1}, and 1444 and 1358 cm^{-1} for **1**, respectively. The difference between these bands, Δ [$\Delta = \nu_{as}(COO) - \nu_{sym}(COO)$], are 179 and 217 and are close to that found for sodium diclofenac (170 cm^{-1}) and less than 217 cm^{-1} found for the unidentate carboxylate group [6,11–14]. The difference between these bands, Δ [$\Delta = \nu_{as}(COO) - \nu_{sym}(COO)$], are 171, 220, and 171, 210 for **2** and **4**, respectively. Two bands at 490 and 466 cm^{-1}, assigned to $\nu_{as,sym}(SnO)_2$ are observed, indicating non-linear Sn–O moieties, while the bands at 226, 200sh, and 189 cm^{-1} are assigned to the tin–oxygen (COO) bridging and unidentate stretching modes, respectively [6,11–14]. The bands at 487, 465, and 461, 436 cm^{-1} are assigned to $\nu_{as,sym}(SnO)_2$ for **2** and **4**, respectively. From the infrared spectra the same coordination mode, bridging and monodentate, is proposed for **1**, **2**, and **4**. The ν_{as}(COO) and ν_{sym}(COO) bands appear at 1575 and 1305 cm^{-1}, respectively for **3**. The difference between these two bands for **3** is close to that observed for asymmetric bidentate chelate mode [14]. The bands at 260–190 cm^{-1} are assigned to the tin–oxygen (COO) stretching modes [11–14] (see Table 1).

3.1.2. ^1H and ^{13}C NMR spectra

Previous NMR assignments of the ligand, performed in Tris buffer [15] or DMSO-d_6 [16], were based on standard

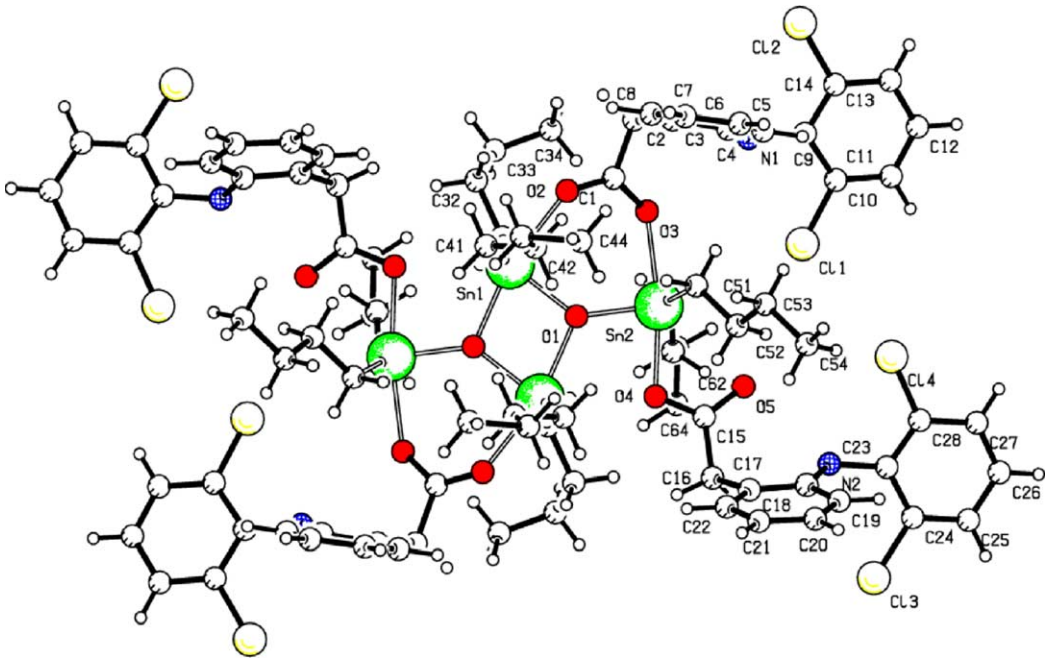

Fig. 1. Perspective view of $[Bu_2(L)SnOSn(L)Bu_2]_2$, **2**, showing the atomic numbering scheme [8].

Table 1
Selected IR absorption bands (cm^{-1}) of organotin(IV) complexes

Sample	ν(NH)	ν_{as}(COO)	ν_{sym}(COO)	Δ	ν(Sn–C)	ν(Sn–O)$_2$	ν(Sn–O) (COO)
HL		1694 1587	1507 1453				
Na L	3388s 3260s	1572s	1402vs	170			
1	3328m 3239s	1623vs 1575s	1444vs 1358vs	179 217	582ms 525ms	490s 466m	226 200sh
2	3335s 3253s	1616vs 1578s	1445vs 1358vs	171 220	588m 529m	487s 465m	252m 211m
3	3266vs	1575s	1305s	275	566s 529m		227m 201m
4	3320m 3240br	1600m 1577ms	1429ms 1367sh	171 210	323ms 274ms	452s 410m	225 209

decoupling sequence or comparisons with a number of related ligands and complexes. However these assignments were tentative. In the present study, ^{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), were used to assign the diclofenac acid resonances in $CDCl_3$. In this manner the assignments were more complete. ^{1}H and ^{13}C NMR data for diclofenac (Scheme 1), complexes **1**–**4** are summarized in Tables 2 and 3.

Upon interaction of ligand with metal, for all complexes studied, no significantly large shifts were evident for the proton atoms of both the phenyl and the 2,6-dichlorophenyl rings. This implies a lack of direct bond involvement of these rings with organotin. Two further observations were evident. The phenyl ring protons generally show larger shifts than the dichlorophenyl ring protons. The largest shift evident (0.11 ppm), was for H(5′) of complex **1**. These observations could be indicative of bond formation in the vicinity of the phenyl rings.

With respect to the imino group it remains protonated in all the complexes synthesized. The shifts exhibited upon complexation, are consistent with a lack of interaction between this group and organotin. In contrast, H(7′) of complexes **1** and **2** exhibit significant upfield shift values (0.22 and 0.15 ppm, respectively). This is suggestive of bonding of the metal to the carboxylate group of complexes **1** and **2**. The results presented are in agreement with previous studies of diclofenac complexes with Zn(II), Cd(II), Hg(II) in which the coordination of a metal center to the carboxylato group of diclofenac mainly influenced the CH_2 protons while it also had a minor effect ($\Delta\delta \sim 0.1$ ppm) on the protons of the phenyl rings [16].

The ^{13}C NMR spectrum of complex **1** reveals a broadened peak of diminished intensity at 178.5 ppm. This is attributed to the carboxylato group and is indicative that it is not free. The exocyclic methylene carbon shifts by 3.1 ppm towards lower field values, while C(6′) shifts in the same direction but by 1.8 ppm. All the other carbon atoms of the ligand exhibit 0.1–0.8 ppm shifts. These data are indicative of interaction of the metal through the carboxylic group.

Inferences concerning the structure of methyltin(IV) compounds in solution, can also be drawn from the coupling constants of the methyl carbons bonded to tin and from

Table 2
Proton NMR data recorded in $CDCl_3$

Compound		NH	H3,5	H4	H(2′)	H(3′)	H(4′)	H(5′)	H(7′)
HL		6.78	7.32d	6.96t	6.55d	7.13td	6.95td	7.24dd	3.84s
1	Me_2Sn 0.71s/0.69s $^{2}J(^{119/117}Sn–H) = 90.2/86.9$ $^{2}J(^{119/117}Sn–H) = 87.5/83.8$	6.93s	7.30d	6.94t	6.48d	7.06td	6.89td	7.13d	3.62s
2	Bu_2Sn Hδ: 0.81t/0.73t; Hγ: 1.21 m/1.18 m; Hα,β: 1.58 m/1.46 m	7.22s	7.31d	6.93t	6.52d	7.08t	6.90t	7.16d	3.81s/3.69s
3	Bu_2Sn Hα: 0.69t; Hγ: 1.19 m; Hβ: 1.48 m; Hα: 1.63 m $^{3}J(^{119/117}Sn–H) = 138.0/125.4$	7.17s	7.28d	6.93t	6.51d	7.09td	6.92td	7.23dd	3.82s
4	Ph_2Sn Ho: 7.67 m; Hm,p: 7.40 m	7.03s	7.33d/7.27d	6.97t	6.54d/6.51d	7.12td/7.09td	6.91t	7.23dd/7.21dd	3.90s/3.80s

Table 3
^{13}C NMR data recorded in $CDCl_3$

Compound		COOH	C1	C2,6	C3,5	C4	C(5′)	C(6′)	C(7′)
HL		177.7	137.7	129.4	128.9	124.0	130.9	123.6	38.1
1	Me_2Sn 9.5/6.6	178.5	137.9	129.7	128.8	123.9	130.6	125.4	41.2
2	Bu_2Sn Cδ: 13.6/13.5; Cγ: 26.8/26.7; Cβ: 26.4/26.1; Cα: 27.6/27.2	178.2	138.1/138.0	129.4	128.8	123.7	130.7/130.5	125.8	41.0
3	Bu_2Sn Cδ: 13.3; Cγ: 26.1; Cβ: 26.4; Cα: 25.5 $^1J(^{119/117}Sn–C\alpha) = 564.6/540.8$, $^2J(^{119/117}Sn–C\beta) = 35.6$, $^3J(^{119/117}Sn–C\gamma) = 96.6$	182.3	137.9	129.5	129.2	123.8	130.8	124.3	38.6
4	Ph_2Sn Co: 136.8; Cm: 128.9; Cp: 130.2; Ci: 137.9 $^2J(C–Sn) = 48.3$, $^3J(C–Sn) = 74.6$, $^4J(C–Sn) = 12.7$	172.3	138.0/137.9	129.4/129.1	128.8/128.7	124.0/123.6	130.8	124.4	38.7

the tin–hydrogen coupling. In both the ^{1}H and ^{13}C NMR spectra of complex **1**, two peaks of equal height appear for the organotin methyl groups. This is suggestive either of their non-equivalence or of the existence of two types of Sn centres. Taking into account the similarities in the NMR data of this complex with complex **2**, whose structure has been crystallographically determined [8], and the IR data which proposes bridging and monodentate coordination mode of the carboxylate group to organotin, it is presumed that two types of Sn centres are present, with complex **1** adopting a structure similar to that of complex **2**. The coupling constants $^2J(^{119/117}Sn–^1H)$ of the complex **1**, compared to those found for free $[Me_2SnCl_2]$ in $CDCl_3$ are greater by approximately 20 Hz, indicating an increase in the s-character of the Sn–C bond. The magnitude of $^2J(^{119/117}Sn–^1H)$ is dependent upon the percent s electron character of the tin–carbon bond. As electronegative groups repel s-character, substitution by a more electronegative group will produce an increase in $^2J(^{119/117}Sn–^1H)$. The change in $^2J(^{119/117}Sn–^1H)$ value implies a charge flow from the tin atom to the ligand.

Use of the Lockhart and Manders equation [17], which for $^2J > 83$ Hz indicates the Me–Sn–Me angle, gives C–Sn–C angles of 145 and 141° for $[Me_2SnLOLSnMe_2]_2$, (complex **1**) in solution. Both the magnitude of the Fermi contact contribution to $|J|$ and the magnitude of the Me–Sn–Me angle, are believed to be primarily determined by the hybridization of tin orbitals directed toward carbon [18]. If, in a dimethyltin(IV) compound, tin does not employ identical orbitals in bonding to methyl, then methyl groups can have individual values of $|J|$ [19]. In the case of $[Me_2SnLOLSnMe_2]_2$, (complex **1**) dissimilar bonding environments around tin resulted in individual J coupling values of the methyl groups.

The proton peaks of complex **2** are broader in comparison to those of $[Me_2SnLOLSnMe_2]_2$ (complex **1**). No $^2J(^{119/117}Sn–^1H)$ fine couplings could be observed. Two signals emerge in the region of H(7′) NMR spectrum. These could arise either from two inequivalent protons of $C(7')H_2$ or from two $C(7')H_2$ groups close to differently coordinated carboxylates. Since there is no diastereoisotopic splitting of the two peaks, different binding modes of the carboxylate are suggested. Bidentate and monodentate binding could be the case, as supported by the resolved crystal structure of this complex [8]. The C(6′) and C(7′) atoms move to lower fields by 2.1 and 2.9 ppm, implying a decrease of their electronic density and coordination of the tin atom to the exocyclic carboxylic group. Minor changes of 0.0–0.7 ppm appear for the other carbon atoms of the ligand. A significant difference is observed when comparing the ^{13}C NMR spectra of complexes **1** and **2**. In the latter complex, ($[Bu_2SnLOLSnBu_2]_2$, complex **2**), some of diclofenac's carbon signals appear as duplicates, implying inequivalence of the two ligand molecules. As expected from the crystallographic data of complex **2**, and in accordance with the ^{1}H NMR spectrum, two distinct peaks appear for the alkyltin carbon atoms, reflecting the existence of two differently coordinated tin atoms. The organotin Cα, Cβ, Cγ, and Cδ double signals are separated by 26.3, 13.8, 9.3, and 3.4 Hz, respectively. The more remote the carbon nucleus from the tin center, the less susceptible it is to a difference in the tin environment.

Concerning complex **3**, it gives simplified ^{1}H and ^{13}C NMR spectra, similar to those of complex **1**. The hydrogen atoms of the organotin(IV) butyl group are shifted upfield compared to the free organometal. The interaction of dibutyltin(IV) with the ligand causes a clear separation in the Hα and Hβ peaks, which appear as one multiplet at $\delta = 1.80$ ppm in the free metal. The most significant carbon shift is exerted by the carboxylic group which moves to lower field values by 4.6 ppm, implying coordination of the metal through this group. Smaller shifts, ranging between

0.0 and 0.7 ppm, are observed for the rest of the carbon signals of diclofenac. According to elemental analysis, the ratio Bu_2Sn:L is 1:2 in the molecule of this complex. NMR data shows that the two bound ligands have identical binding environments. This equivalence is also confirmed by the presence of a single peak for each of the butyltin proton and carbon signals. A *trans* arrangement around the tin atom is thus inferred and a monomeric structure is strongly supported by the NMR data. Similar structures have been found for $[Me_2Sn(OAc)_2]$ and $[Bu_2Sn(OAc)_2]$ in solution [20]. The ^1J(Sn–C) values for these complexes were found to be 665 and 630 Hz, respectively. In the present study $^1J(^{119/117}\text{Sn–C}\alpha) = 564.6/540.8$ Hz. Using the Holecek equation for di-*n*-butyltin(IV) derivatives [21] the C–Sn–C angle, θ, was calculated as 131°. An irregular trapezoidal bipyramidal structure (skew) was attributed to dibutyltin carboxylates [22] with a value of θ lying between 129 and 146°. The same structure was also proposed for $[Bu_2SnL_2{\cdot}H_2O]$ (L = tolfenamic acid), where a C–Sn–C angle of 131° was estimated [6]. The values of θ and the coupling constant $^1J(^{119/117}\text{Sn–C})$ are determined not only by the coordination number of the central tin atom but also by steric and electronic factors. The coupling constant $^3J(^{119/117}\text{Sn–H})$ is larger by 13 Hz for the adduct than for the free $[Bu_2SnCl_2]$. Considering the literature data and our NMR findings, the skew structure is proposed for $[Bu_2SnL_2]$.

Finally in complex **4**, almost all the carbon signals of diclofenac appear as duplicates, showing inequivalence of the two ligand molecules. Carbon signal shifts range between 0.2 and 0.8 ppm, with the exception of the carboxylate carbon which shows a considerable shift to higher fields by 5.4 ppm, confirming coordination of the metal through this group. Only one resonance emerges for each of the phenyltin carbon atoms. The coupling constant ^1J of the ipso carbon could not be detected and no C–Sn–C angle could be calculated. Taking into consideration the NMR spectra and the elemental analysis, complexes **4** and **2** would be expected to possess similar structures. It is noteworthy however, that although upon complexation the carbon of the carboxylic groups of complexes **1**–**3** move downfield, in the case of complex **4** this shift is realized in the opposite direction. This could probably be due to charge delocalization by the phenyl ring of organotin, making the carbonyl carbon less electron deficient.

3.1.3. Mössbauer spectra

Mössbauer spectra for all the complexes were obtained between 80 and 180 K and are reported in Table 4. The ρ (QS/IS) values of all complexes, strongly indicate a higher than four-coordination at the tin atom [23]. The increase in the IS values on going from the methyl- to the butyl- derivative dictates a corresponding increase in the s-character of the tin–carbon bonds consistent with the expected pattern of +I inductive effect of the alkyl groups and is lower for the phenyl-complexes due to the electronegativity of the Ph group.

The spectra of **1** and **2** are each characterized by a single quadrupole split resonance indicating the equivalent of the environment of the dissimilar tin nuclei. This is due to the relative insensitivity of the IS and QS to subtle changes in atomic environment [24]. According to the calculations performed by applying the point-charge model formalism, 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 [25]. A C–Sn–C bond angle of 130°, for **2**, is calculated from the Mössbauer analysis. The X-ray crystal structure for this compound indicates C–Sn(1)–C and C–Sn(2)–C bond angles of 134.9 and 143.5°, respectively [8]. In keeping with the X-ray results as well as with published work [26] the values of IS and QS are compatible with dimeric structures with the two tin atoms both pentacoordinate and occupying very similar trigonal bipyramidal environments. The comparably parameters of **1** support the hypothesis that the methyl-derivative adopts the same configuration.

The spectrum of **3** shows a single quadrupole split doublet with a narrow linewidth, consistent with there being just a single tin site. The values of the corresponding hyperfine parameters for this compound are very similar to that already reported for the adduct diethyltin-bis(2-methylthio-3-pyridinecarboxylate) (IS = 1.48 mm sec^{-1} $\kappa\alpha\iota$ QS = 3.61 mm sec^{-1}) [27] which is monomeric with a six-coordinate tin atom and two equivalent carboxylate groups chelating the tin atom adopting a *trans* highly distorted octahedral or skewed trapezoidal bipyramidal stereochemistry responsible for the rather low value of QS.

Both values of isomer shift and quadrupole splitting obtained for the **4**, indicate that the phenyl groups are in *cis* positions. (Within the limits of the point-charge model the calculated value of the QS is 2.25 mm sec^{-1}. The

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

No.	IS (mm s^{-1})	QS (mm s^{-1})	$\Gamma/2$ (mm s^{-1})	A[b]	A[c] ($\times10^{-2}$ K^{-1})	Θ_D (°K)	C–Sn–C[d] (°)
1	1.243	3.374	0.395	100	−1.89	98	130
2	1.348	3.374	0.400	100	−1.38	114	130
3	1.491	3.511	0.385	100	−1.55	108	142
4	0.700	1.890	0.570	92.8	−1.10	128	141

[a] Estimated errors ±2 in the last significant figures.
[b] Spectral area.
[c] Slope of the best fit straight lines $-\mathrm{d}\ln A(T)/\mathrm{d}T$.
[d] Calculated from Mössbauer spectra.

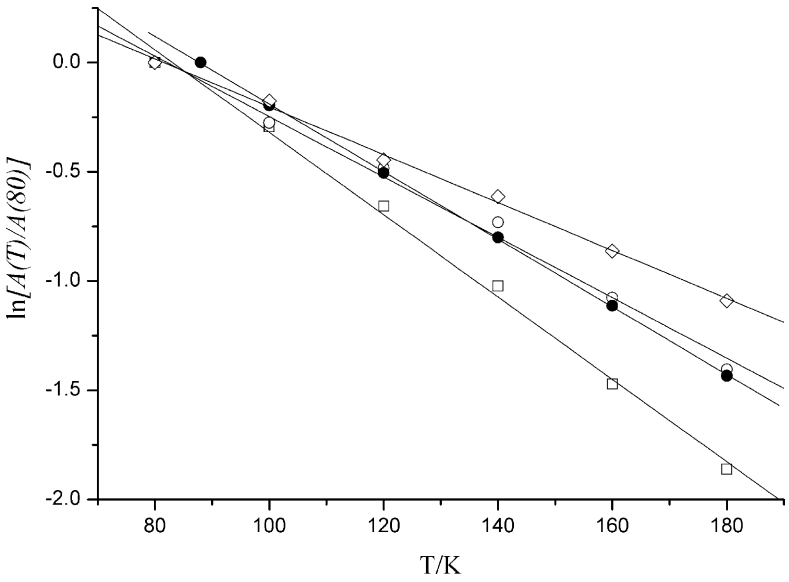

Fig. 2. Temperature coefficient (area vs. temperature) for organotin complexes **1** (□), **2** (○), **3** (●), and **4** (◇).

derivation from the experimental value is $0.36\,\mathrm{mm\,sec^{-1}}$ within the limit of $0.4\,\mathrm{mm\,sec^{-1}}$ normally accepted).

Variable temperature spectra were recorded in order to investigate the molecular dynamics of the complexes. The treatment of temperature-dependent data and the calculation of related functions were performed as previously described [28]. 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 correlation coefficients for all experimental slopes are better that -0.997, Fig. 2. The value of $-1.10 \times 10^{-2}\,\mathrm{K^{-1}}$ for **4** is in line with the probable existence of polydimensional networks characterized by extensive hydrogen bonding [29]. The values for the other compounds correspond to an arrangement of non-interacting molecules in the solid state although the presence of hydrogen bonds in **2** cannot be ruled out.

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