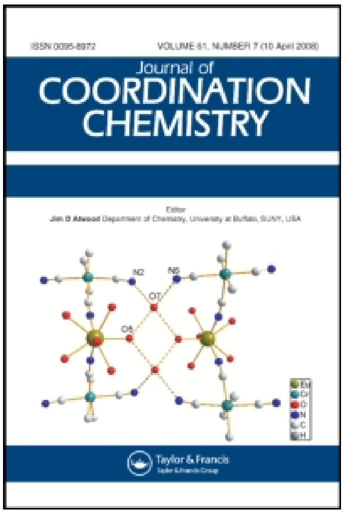

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Structural elucidation for triorganotin derivatives of 3-amino, 4-amino and 3,5-diaminobenzoate. Crystal structures of triphenyltin 4-aminobenzoate and trimethyl and triphenyltin 3,5-diaminobenzoate

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Synthesis and structural investigation of trimethyl and triphenyltin esters of the 3-, 4-amino and 3,5-diaminobenzoic acids are reported as a reinvestigation of their local and overall molecular structure based on crystal structure determinations and on correlation of solid state vibrational and γ-emission spectroscopic evidence. Evidence is provided for the existence of more than one tin environment and therefore different carboxylate coordination modes in the compounds.

Keywords: Triorganotin carboxylates; Mössbauer spectroscopy; Crystal structures

1. Introduction

Triorganotin compounds offer the possibility of studying the coordination to tin of a variety of ligands, mainly those bearing oxygen and nitrogen donor atoms, although coordination to "soft" sulfur and phosphorus is not uncommon. Such compounds have a wide variety of applications including as pesticides, antifouling agents or cytostatic drugs [1], although their generally high toxicity has inhibited extensive use due to enrichment of the environment of the highly toxic R_3Sn^+. The covalent character of Sn–C bonds in triorganotin derivatives is a stabilizing factor as there is little concern for their cleavage or participation in addition or elimination reactions under normal experimental conditions. Carboxylate coordination to metals in general and to tin in particular offers variations of coordination mode, including monodentate, chelate (symmetric or more often asymmetric) or the more subtle bridging [2] which may give rise to oligomeric or polymeric structures [3].

Our current interest lies in synthesis and study of coordinating ability of triorganotin derivatives of substituted aminobenzoates towards metals of main group or transition

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metals, and we have been engaged in the synthesis of simple analogues of unsubstituted acids, which may be regarded as precursors to organotin derivatives. Of special interest is the synthesis and investigation of trimethyl- and triphenyl-tin compounds as they represent the simplest trialkyl and triaryl derivatives. In the process some crystalline compounds were isolated and the solution of their structures provided information which could be related to the abundance of spectroscopic evidence. In the present manuscript we describe the crystal structure of three such compounds, the triphenyl derivatives of 4-aminobenzoic acid and 3,5-diaminobenzoic acid and the trimethyl derivative of 3,5-diaminobenzoic acid. The compounds included in the present study are presented in figure 1.

2. Experimental

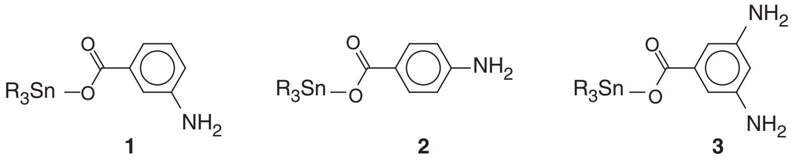
2.1. *Materials and measurements*

The triorganotin chlorides and aminobenzoic acids were obtained from ACROS and were used without purification. The solvents used were of reagent grade and were not subjected to drying prior to use.

Infrared spectra were recorded in KBr pellets on a Perkin–Elmer Spectrum One FTIR spectrometer with a resolution of 2 cm^{-1} following the collection of 16 scans over the range 5000–360 cm^{-1}. Thermal measurements were performed on a Setaram 1200 thermogravimetric analyzer under N_2 flow and at a heating rate of 10° min^{-1}.

Mössbauer spectra were obtained on powder samples at 80 K using a constant acceleration spectrometer and a 10-mCi calcium stannate source kept at room temperature. Spectrometer calibration was effected using a metallic iron foil. Isomer shifts are reported relative to $CaSnO_3$, assuming that they are the same as the $BaSnO_3$ shifts.

X-ray diffraction data were collected with a Kuma KM4CCD diffractometer using graphite-monochromated Mo-Kα radiation. The crystal structures were determined using a Kuma KM4CCD κ geometry diffractometer. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction [4]. Intensity data were corrected for Lorentz and polarization effects, and for absorption. The structures were solved by direct methods with the program SHELXS-97 [5]. Refinement was performed by full-matrix least-squares on F^2, with anisotropic displacement parameters for non-hydrogen atoms using the program SHELXL-97 [6]. Hydrogen atoms were placed in the calculated positions and given isotropic



a: R = Me, b: R = Ph

Figure 1. The triorganotin compounds studied. The simplest coordination environment is depicted in all cases.

displacement parameters equal to 1.2 × U_{eq} of the relevant carbon or nitrogen. In **2b** and **3a** the amino group hydrogen atoms were fully refined. Molecular graphics were generated with the program XP of Stereochemical Workstation and Mercury 1.4.2 software [7]. Crystal data and some further details concerning X-ray analyses are given in table 1. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 678347–678350 for compounds **2b**, **3a**, **3b(RT)** and **3b(LT)**, respectively.

2.2. *Synthesis and characterization of the compounds*

The method for synthesis of the compounds was a slight variation of one previously reported [8], involving deprotonation of the acid by methanolic potassium hydroxide followed by addition of an equivalent amount of triorganotin chloride dissolved in methanol. Better results were obtained when the reaction was not carried out in subsequent steps in a single pot but when the potassium salt of the acid was isolated and used as such in a second reaction. This reaction scheme may be summarized as follows: 2 mM of the acid salt were dissolved under continuous magnetic stirring in methanol (5 mL). To this solution was added dropwise a solution of 2 mM of the appropriate triorganotin chloride in toluene (15 mL) and the solution was refluxed for 2–3 h. During the process there were signs of a microcrystalline deposit on the flask which proved to be KCl. After completion of the reaction the mixture was filtered while hot in order to remove any suspended KCl and the solvent was removed on the rotary evaporator. The solid product was dissolved in hot toluene, filtered, and to the filtrate small amounts of petroleum ether were added and the solution set aside under ambient conditions, upon which crystallization occurred. In the case of the trimethyl and triphenyl derivatives of 4-amino and 3,5-diaminobenzoate crystals suitable for X-ray analysis were obtained by this procedure. For **1a** and **1b** there was need to add molecular sieves to the refluxing mixture and consequently to collect them by filtration along with the KCl formed, in order to avoid turpidity of the reacting solution and undesired by-products.

Of the compounds synthesized the one reported for the first time, to our knowledge, is **3a**, for which the obtained analytical data are as follows: Anal. Calcd for $C_{10}H_{16}O_2N_2Sn$(%): H, 5.12; C, 38.13; N, 8.89. Found: H, 5.02; C, 38.80; N, 9.42. Melting points for this compound and for the corresponding triphenyl derivative, **3b**, for which no literature data is reported, were recorded at 205 and 178°C, respectively.

3. Results and discussion

Several attempts have been made to elucidate the structure of triorganotin carboxylates, especially since the coordination of the carboxylate may be monodentate, bridging or chelating. A compilation of spectroscopic evidence is needed in every case, the most relevant being infrared and Mössbauer spectra of the compounds. In the IR spectrum one has to identify the symmetric and asymmetric stretching modes of the carboxylate moiety and apply the widely known and accepted criterion of the spacing, $\Delta\nu$, of the two bands. Generally, differences of 235–245 cm^{-1} indicate bridging or chelating modes

Table 1. Crystal data and structure refinement for the studied compounds. Compound **3b** was solved at room and at low temperature, the measurements being identified as RT and LT, respectively.

	2b	**3a**	**3b(RT)**	**3b(LT)**
Empirical formula	$(C_6H_5)_3SnC_7H_6NO_2$	$(CH_3)_3SnC_7H_7N_2O_2$	$(C_6H_5)_3SnC_7H_7N_2O_2$	$(C_6H_5)_3SnC_7H_7N_2O_2$
Formula weight	486.12	314.94	501.14	501.14
Temperature (K)	100	120	294	100
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pna2_1$	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
Unit cell dimensions (Å, °)				
a	9.5057(2)	7.4295(2)	11.4179(2)	19.7117(5)
b	15.0676(3)	9.8929(3)	10.3050(2)	30.6932(8)
c	14.9693(3)	16.8053(4)	19.8047(3)	22.2872(6)
α	90	90	90	90
β	90	90	102.054(2)	100.903(2)
γ	90	90	90	90
V (Å^3)	2144.02(8)	1235.18(6)	2278.87(7)	13240.7
Z, Z′	4, 1	4, 1	4, 1	24, 6
Absorption coefficient (mm^{-1})	1.212	2.053	1.144	1.181
Crystal size (mm^3)	0.5 × 0.4 × 0.15	0.3 × 0.3 × 0.08	0.5 × 0.3 × 0.3	0.5 × 0.3 × 0.3
θ range for data collection (°)	4.28–26.37	4.12–26.37	4.09–27.10	4.09–25.03
Reflections collected	18984	12701	34281	92744
Independent reflections	4265 [$R_{int} = 0.0204$]	2521 [$R_{int} = 0.0175$]	4942 [$R_{int} = 0.0199$]	23294 [$R_{int} = 0.0435$]
Completeness up to θ (max)	0.995	0.995	0.979	0.995
Data/restraints/parameters	4265/1/271	2521/0/153	4942/0/271	23294/18/1621
Goodness-of-fit on F^2	1.156	1.077	1.075	1.274
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0174$; $wR_2 = 0.0370$	$R_1 = 0.0130$; $wR_2 = 0.0289$	$R_1 = 0.0223$; $wR_2 = 0.0522$	$R_1 = 0.0512$; $WR_2 = 0.0787$
R indices (all data)	$R_1 = 0.0196$; $wR_2 = 0.0379$	$R_1 = 0.0163$; $wR_2 = 0.0305$	$R_1 = 0.0346$; $wR_2 = 0.0622$	$R_1 = 0.1267$; $wR_2 = 0.1469$
Largest diff. peak and hole (e Å^{-3})	0.33–0.36	0.48–0.37	0.58–0.55	2.45–1.63

and larger ones (255–275 $\mathrm{cm^{-1}}$) indicate monodentate carboxylate [9]. However, one cannot draw a clear line between these two categories and in most cases in the absence of structure determination only speculation can be made. Structural data allow more sophisticated treatment of the observables, i.e. a difference exceeding the normally accepted boundaries for bridging coordination may be attributed to asymmetric bridging [10]. In addition, individual peak positions have been used as indication for the presence of specific coordination modes, i.e. the existence of a carboxylate band at 1630 $\mathrm{cm^{-1}}$ is related to the asymmetric bridging of the carboxylate [11].

The Mössbauer spectra of the triorganostannyl esters of carboxylates are more subtle in their interpretation as the range over which the quadrupole splittings are observed may be shifted and the observed values for specific cases may lie outside the well-documented boundaries, therefore calling again for speculation. It is generally assumed that higher quadrupole splitting values correspond to higher coordination numbers, the accepted ranges being 2.0–2.4, 2.6–3.0 and around 3.5 $\mathrm{mm\,s^{-1}}$ for coordination numbers 4, 5 and 6, respectively [12]. With high coordination numbers occurring with amino-substituted acids, one may not exclude the participation, in addition to the carboxylic oxygen atoms, of the amino substituent to the formation of the tin coordination sphere. This has received little or no attention with attempts always being focused on the bridging or chelating character of the carboxylate of the benzoate ligands.

3.1. *Structural considerations*

At room temperature the triphenyltin 3,5-diaminobenzoate derivative, **3b**, crystallizes in the space group $P2_1/c$ with one molecule in the asymmetric unit (figure 2 left). The distances between Sn and oxygen from the carboxylic group are 2.0590(17) and 2.8124(18) Å pointing to a carboxylate lying at the borderline between monodentate and asymmetrically chelating bonding modes. All three Sn–C bonds are very similar in length, varying between 2.120(2) and 2.127(2) Å (table 2) and the Sn deviates by 0.5816(14) Å from the plane defined by the three bonded C atoms. Compound **3b** has a temperature-dependent solid-to-solid phase transition on cooling to 100 K weak reflections are registered which correspond to the monoclinic supercell, space group $P2_1/n$, with the six-fold larger volume of the unit cell and the following relation between the unit-cell axes: $a_{LT} = 2c_{HT}$, $b_{LT} = -3b_{HT}$, $c_{LT} = a_{HT}$. The observed phase transition is reversible. The structural changes accompanying the phase transition are small but cannot be ignored. In the low-temperature phase the Sn–C distances are in the range 2.100(9)–2.142(10) Å and the Sn–O distance remains practically unchanged [2.056(6)–2.069(6) Å]. As the interaction of the Sn with the second O atom of the carboxylate group is much weaker, the longer Sn···O distance is more significantly altered by the phase transition; in two molecules it is 2.73 Å, whereas in the remaining four it ranges from 2.78–2.82 Å (figure 2 right).

The closely related 3,4-diamino substituted acid has been reported to coordinate to Sn(IV) and the observed bond lengths of Sn–O being 2.069(2) and 2.680(3) Å and the corresponding Sn–C ones between 2.121(3) and 2.146(3) Å categorized the compound as tetrahedral tin carboxylate, although the second oxygen is referred to as possessing strong interaction to tin [13]. The structure in the above case was confirmed to be stabilized by intermolecular hydrogen bonds between the amino groups and the neighboring carboxylate oxygens.

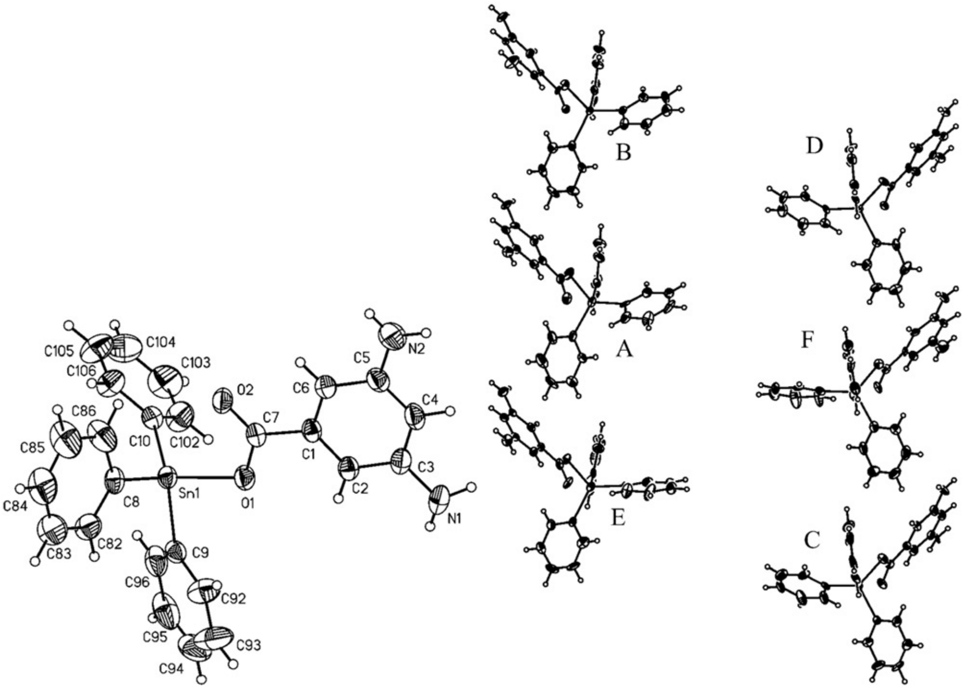


Figure 2. ORTEP representation of **3b** at room- (left) and low-temperature phase (right). Displacement ellipsoids are shown at the 50% probability level. The letters A–F indicate six symmetry independent molecules in the asymmetric unit of **3b(LT)**.

Table 2. Selected bond lengths (Å) and angles (°), for the studied compounds.

Bond/angle	**2b**	**3a**	**3b(RT)**
Sn–O^a	2.062(2)	2.160(1)	2.059(2)
Sn–O^b	2.706(2)	3.122(2)	2.812(2)
Sn–C	2.123(2)	2.127(2)	2.120(2)
	2.123(2)	2.134(2)	2.121(3)
	2.129(2)	2.128(2)	2.126(2)
Sn–N′		2.623(2)	
O^a–Sn–C	86.25(8) 109.55(8)	94.51(7)	111.52(8) 106.56(8)
	147.68(9) 95.16(8)	88.29(7)	112.29(8) 87.48(8)
	81.65(97) 111.96(7)	96.64(6)	92.22(8) 143.09(8)
C–Sn–C	115.43(9)	124.27(1)	116.19(1)
	109.36(9)	116.49(9)	112.34(1)
	113.63(9)	118.27(9)	109.81(1)
N′–Sn–C		86.59(1)	
		89.23(1)	
		84.55(1)	

In all cases the directly bonded oxygen atom is denoted by superscript a, while the asymmetrically chelated, if present, receives superscript b. The carbon atoms bonded to tin are not identified but all observed values are listed.

In the triphenyltin 4-aminobenzoate **2b** (figure 3) the two Sn–O distances are 2.0618(16) and 2.7060(15) Å and are in general agreement with the values of 2.072(2) and 2.629(2) Å reported for the benzene-solvated structure of the same compound, which has been reported earlier [14]. In both cases the longer Sn–O distances are well

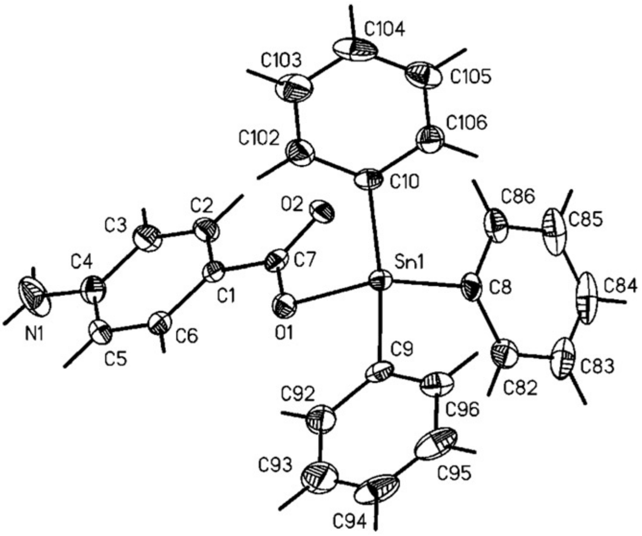


Figure 3. ORTEP representation of **2b**. Displacement ellipsoids are shown at the 50% probability level.

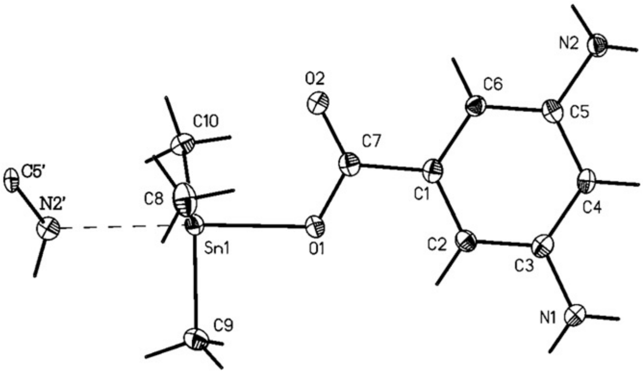


Figure 4. ORTEP representation of **3a**. Displacement ellipsoids are shown at the 50% probability level. N2′ and C5′ are symmetry equivalents of N2 and C5 (symmetry code: $1.5-x$, $1-y$, $-1/2+z$).

within the range for van der Waals interactions by approximately 1 Å. Neither compound approaches the ideal trigonal bipyramidal or square pyramidal arrangement around the metal center, being more of the distorted tetrahedral type with the two oxygen donors of the carboxylate ligand squeezed close to one of the tetrahedron apexes.

The trimethyltin derivative of 3,5-diaminobenzoic acid, **3a**, on the other hand, reveals some interesting features in its structure (figure 4). There is only one molecule in the asymmetric unit cell and coordination of the carboxylate is clearly monodentate, with Sn–O bond length of 2.1598(13) Å, whereas the non-bonded oxygen lies 3.122 Å away from the metal center (figure 4). Closer inspection of the structure reveals that the Sn–O bond is approximately perpendicular to the three Sn–C bonds [C–Sn–O angles ranging from 88.28(7)° to 96.64(6)°] and, furthermore, the C–Sn–C angles are ranging within the margins of 116.51(9)° and 124.26(10)° with a total slightly less than 360°. These observations clearly indicate a trigonal SnC_3 core with an apical Sn–O bond to which a close contact to the neighboring N2 lone pair may be assumed on the basis of the atom's proximity to the Sn [interatomic distance of 2.6234(18) Å]. Of special importance is the O–Sn–N angle of 177.52(5)°, as well as the observation that the assumed Sn–N contact lies almost perpendicular to the aforementioned SnC_3 core plain [N–Sn–C angles ranging between 84.55(7)° and 89.24(7)°]. In the solid state, therefore, one may refer to this compound as forming a trigonal bipyramidal environment around tin with an O and an N at the apical positions.

Hydrogen bonding may account, at least in part, for the overall crystal structure stabilization. In the case of **3b**, at room temperature a wide range of weak intermolecular N–H···N and N–H···O hydrogen bonds are observed involving the amino groups and the non-directly bonded carboxylate oxygen (figure 5). In the structure of **2b** there is apparently hydrogen bonding from the amino group to a neighboring non-coordinated carboxylate O with a N···O distance of 2.878 Å (figure 6).

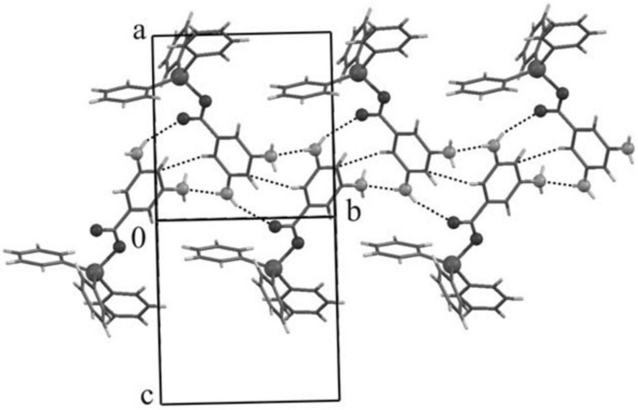


Figure 5. 1-D assembly of **3b** molecules via the N–H···N and N–H···O hydrogen bonding and C–H···π interactions (the room-temperature form). The O, N and Sn atoms are represented as spheres.

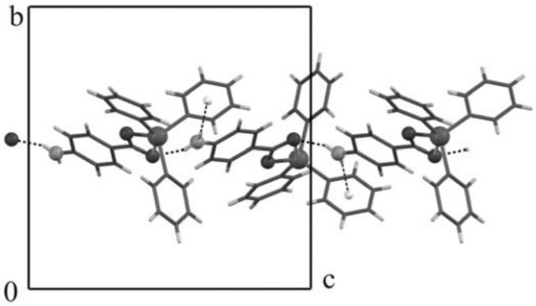


Figure 6. 1-D assembly of **2b** molecules via the N–H···O hydrogen bonding and N–H···π interaction shown with dashed lines. The O, N and Sn atoms are represented as spheres.

This interaction appears to be of the same order as the corresponding one in the free acid where the same interaction was observed at a distance of 2.985 Å [15].

In the case of **3a**, there is again an extensive intermolecular N–H···N (2.49 Å) and N–H···O (2.28 Å) interaction network, presented in figure 7. This is again an observation common with the one in the free acid where all the above interactions are observed but slightly weaker as the corresponding distances are calculated to be 3.230(3)–3.431(3) Å and 3.054(2) Å, respectively [16].

3.2. *Infrared spectra*

The trivial vibrational analysis of carboxylates makes use of the wavenumber difference between the asymmetric and symmetric carboxylate stretching modes, $\Delta\nu = \nu_{as}$COO–ν_{sym}COO, to draw conclusions on the coordination mode of the carboxylate. The calculated $\Delta\nu$ values for the compounds under investigation are reported in table 3 along with the most relevant of vibrational spectral features.

Following the general trends for tin carboxylates [17], one may conclude that the methyl derivatives have consistently higher $\Delta\nu$ values than the corresponding phenyl ones, therefore suggesting a tendency for predominant monodentate coordination where these approach 250 wavenumbers. Asymmetric chelating coordination may be assumed in the case of the phenyl derivatives on the basis of their generally small $\Delta\nu$ values, which lie around and below 200 wavenumbers.

In view of the observed crystal data for the compounds of 3,5-diaminobenzoic acid and the existence of the aminobenzoates in asymmetric chelating coordination to the triphenyltin centers, it is interesting to examine more carefully the vibrational spectra of the compounds. The existence of similar but not identical molecules within each unit cell is pointing at the possibility of observing a range of ν_{as}COO and ν_{sym}COO bands

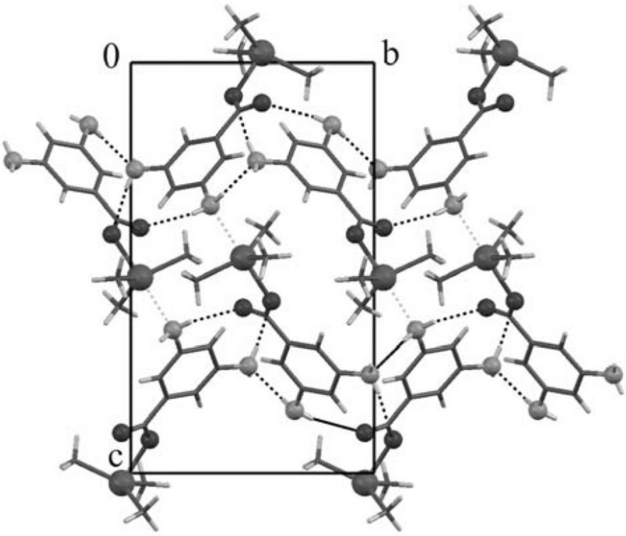


Figure 7. Projection of the crystal packing for **3a**. Hydrogen bonding and Sn–N contact are shown with dashed lines. The O, N and Sn atoms are represented as spheres.

Table 3. Infrared spectral data for the ligands and their trimethyl and triphenyltin derivatives.

Compound	ν_{as}(COO)	ν_{sym}(COO)	$\Delta\nu$	$\nu(NH_2)$	ν(Sn–O)
L1	1634	1388	246	3444 br	–
1a	1580	1349	231	3450, 3363	450
1b	1617	1429	188	3451, 3376	451
L2	1664	1422	242	3460, 3382, 3364	–
2a	1588	1365	223	3484, 3444, 3389, 3347	440
2b	1558	1359	199	3440, 3339	456
L3	1631	1394	237	3432, 3350	–
3a	1595	1368	227	3430, 3353, 3316	405
3b	1592	1373	219	3432, 3352	446

All the band maxima are given in wavenumbers. The free aminobenzoic acids are referred to by using the notation L followed by the index of the appropriate organotin group in figure 1.

close in energy, forming an envelope, as has been the case in some recent studies. In our case the asymmetric bands may be located in the region of 1620 to 1530 and the symmetric ones in the region 1430 to 1340 cm^{-1}, in general agreement with a previous study of **3b** [10]. Furthermore, the amino groups in the two compounds appear in the same region as for the free ligand with those of the methyl derivative appearing split. Finally, only the asymmetric Sn–C stretching vibration for the methyl derivative appears in the spectra, in line with the suggestion that this implies a planar SnC_3 moiety [8] with two apical ligands bearing non-carbon atom donors. The splitting of the amino group bands may be attributed to deviation from their symmetric arrangement within the backbone of the compound, something that may be achieved in a variety of ways, one of which is the slight pyramidalization of one amino group upon its participation in coordination to the tin center of a neighboring molecule. Simple participation in an intermolecular hydrogen bond is by no means uncommon in analogous compounds but would generally lead to broadening of the corresponding spectral lines.

Identical observations are made for the compounds of 4-aminobenzoic acid (**2a** and **2b**) implying that for this ligand, as well, the triphenyl derivative does not bear any amino group participation in the coordination environment of tin. A slight broadening in the amine bands may be indicative of their participation in hydrogen bonding.

For 3-aminobenzoate, there is no apparent splitting in the amino group bands for the methyl derivative (**1a**), therefore making it impossible to identify the local tin structure on the basis of vibrational evidence alone.

In assignment of the asymmetric carbonyl stretching we were aided by previous assignments for 3,5-diaminobenzoic acid [16] and by computations and their correlation to experimental data [18]. Furthermore, we carried out similar computations assuming single molecules using the PM6 Hamiltonian [19] as implemented in the MOPAC2007 program [20]. This is needed since, in general and especially in the aryl carboxylic compounds, this stretching is expected to lie near or within the envelope of the ring C=C vibrations, and furthermore, is generally strongly coupled to them. Of course, simple semiempirical computations are not expected to result in accurate vibration eigenvalues and there is always need for scaling in order to approach the experimental observations, however, the correct ordering of the normal coordinate analysis cannot be overruled especially when it consistently determines higher frequencies for the C=O relative to the neighboring C=C bonds. In our case, both the free acids and their idealized trimethyl and triphenyltin derivatives were investigated applying tight convergence criteria (setting the SCF convergence to 1.0×10^{-12} and the gradient norm to 0.01 for the geometry optimization which preceded the FORCE calculation). In all cases the carbonyl-dominated frequency was computed to be by approximately 150 wavenumbers in the free acids and by approximately 70 wavenumbers in the tin derivatives higher than the nearest ring-dominated one. Furthermore, in attempting to provide a single C=O scaling factor for the whole group of compounds, correlation of the higher frequency in the region 1700–1600 wavenumbers with the computed carbonyl stretching, gave a scaling factor of 1.095 giving an average of $17.1\,\mathrm{cm}^{-1}$ difference between the scaled and the experimentally observed frequencies. Assuming that the higher observed frequency in this region corresponds to ring stretches gave a scaling factor of 1.023 with an average deviation of $105.9\,\mathrm{cm}^{-1}$ between computational and experimental data, proving that this is not a suitable assumption. It should be noted at this point that analogous treatment of the data for Sn–O bonds gave a scaling factor of 1.137 with an average difference between observed and scaled calculated frequencies of $47.6\,\mathrm{cm}^{-1}$. The Sn–C vibrations are more subtle because they are expected, and are actually computed, to be strongly coupled with neighboring bonds. Furthermore, our computations assumed a single tetrahedral environment for each tin within a single organotin molecule, and therefore, cannot be directly related to the exact solid state environment where the spectra are recorded. On these grounds the several computed Sn–C vibrations ranging from 604 to $565\,\mathrm{cm}^{-1}$ were correlated to the experimental findings. Since no uniform correlation could be applied, efforts were made to correlate the extreme computed bands with the experimental ones, yielding different scaling factors, namely 1.103 and 1.035 but with almost identical coincidence with the experimental values, the average differences being less than $1\,\mathrm{cm}^{-1}$. These observations, and especially the use of scaling factors approaching unity, account for the applicability of the above semiempirical method in the study of such compounds, even though in our computations we did not assume intermolecular interactions or any specific environment observed by the X-ray diffraction study, i.e. the acid molecules are not forming hydrogen bonded dimers and the tin environments are in all cases tetrahedral with monodentate carboxylate.

3.3. *Mössbauer evidence*

The ^{119m}Sn Mössbauer parameters are generally used, with reasonable efficiency in the elucidation of organotin compound structures in the absence of structural information, or in correlation with them when possible. Both quadrupole splitting, QS, and isomer shift, IS, as well as their ratio, ρ, have been used as a measure of the coordination number of tin and of the asymmetry in it, being directly or indirectly related to the coordination mode of the ligands present in the tin coordination sphere [8, 17, 21].

Some of the compounds under investigation have been previously subjected to analogous studies and their Mössbauer spectra recorded and discussed [8]. The observed isomer shift and quadrupole splitting values were attributed to a monodentate bonding of the aminobenzoate and an overall tetrahedral tin environment in the case of the phenyl derivatives, while chelate coordination and trigonal bipyramidal environment was assumed for their methyl counterparts. The results obtained within the present study are presented in table 4 and the spectra of the two compounds which

Table 4. Mössbauer spectroscopic data for the studied compounds.

Compound	IS	QS	ρ (QS/IS)	$\Gamma_{1/2}$
1a	1.34	3.37	2.51	0.88
	1.43[a]	3.49[a]	2.44[b]	1.13[a]
1b	1.37	3.72	2.72	1.02
	0.72	2.41	3.35	1.02
	1.18[a]	2.60[a]	2.20[b]	2.11[a]
2a	1.35	3.39	2.50	0.96
	1.38[a]	3.02[a]	2.19[b]	1.48[a]
2b	1.20	2.29	1.91	0.90
	1.01[a]	2.46[a]	2.44[b]	1.66[a]
3a	1.32	3.26	2.47	0.96
3b	1.17	2.74	2.34	0.96
	0.92	1.83	1.99	0.96

[a]Values from reference [8]. [b]Values calculated from reference [8].
Quadrupole splittings, isomer shifts and spectral line half widths are reported in mm s^{-1}.

reveal more than one tin environment, namely **1b** and **3b**, are also shown in figures 8 and 9, respectively.

For **2b**, correlation of the crystal structure with the infrared spectra in the solid state indicate the presence of a Sn(IV) environment where the carboxylate is chelating in its bonding mode, however, the overall structure around the tin center may be regarded as pseudotetrahedral with the fourth apex of the tetrahedron being located roughly towards the carboxylate carbon atom. The single environment presented in the crystallographic unit cell is also reflected in the single tin species observed by Mössbauer, with indications that the asymmetry imposed on the tin nucleus by the chromophore atoms is moderate if the QS and the ρ values are to be considered. A close analogy by one of the tin environments is envisaged in the study of **3b**, where the quadrupole splitting becomes less, probably due to less interaction with the non-directly bonded oxygen of the carboxylate, which has on average a larger separation than the corresponding one in **2b**. The second tin environment observed in the spectra of **3b** can be assigned to molecules, which in the unit cell, appear to possess a marginally monodentate carboxylate and a more typical tetrahedral arrangement of the ligands around tin. The proximity of single oxygen to tin, however, must be responsible for the elevation of the asymmetry around the nucleus, as reflected in the elevated QS value (2.771 relative to 1.861 for the previous conformer).

Compound **3a** is different in that there is an apparent higher asymmetry in the electronic distribution around tin, something that is common in trigonal bipyramidal compounds which reveal measurable QS values even in the case of a set of five chemically equivalent ligands. This observation is further accompanied by a slightly higher ρ value of around 2.50, which is indicative of a coordination number higher than four [21]. The above results are in good agreement with the structural information available for the compound, as well as with the infrared spectra. Furthermore, the similarity of the values of the same observables in all the methyl derivatives makes it possible to propose similar structures for all of them, i.e. monodentate carboxylate and overall trigonal bipyramidal environment with the participation of an amino donor from a neighboring molecule. Based on the correlations drawn so far, the information retrieved for **1b** is insufficient to make a solid conclusion, however, the existence of discrete environments in the solid sample is apparent and their attribution to tin

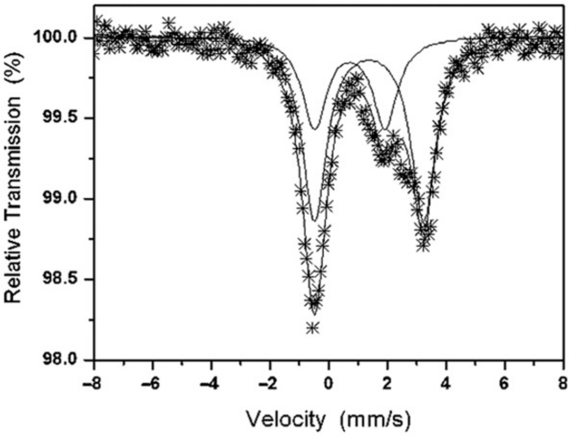


Figure 8. Experimental and simulated Mössbauer spectrum of **1b** at 80 K.

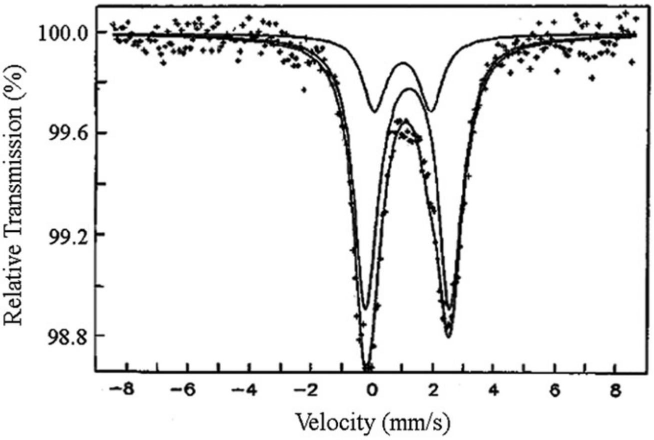


Figure 9. Experimental and simulated Mössbauer spectrum of **3b** at 80 K.

compounds with high coordination number, even octahedral, where both chelating and bridging carboxylates are present, is most plausible. There is an overall agreement in the Mössbauer parameters obtained in the current study with the ones determined previously [8] but there are also some differences originating first of all, from the subtle way of crystallization of organotin compounds from different media, as well as of the resolution of the two studies under concern; in the present one the larger line-width is about 20% smaller than the minimum and almost two times smaller than the maximum width reported previously. This may account, in part, for the observed discrepancies and justifies to some extent re-investigation of the structure of the studied compounds.

Thermal studies of fresh samples of the triorganotin compounds under consideration were carried out under dinitrogen at a heating rate of 5°C min^{-1} up to 300°C on a SETARAM TG-DSC 15 thermogravimetric analyzer using Pt crucibles. The temperature limit was set low as our interest was mainly on the appearance of any endothermic procedure prior to the melting point of the compounds and not on their further thermal decomposition. No significant phenomenon was observed in the DTA curve besides minor endothermic peaks accompanying the slight mass loss (1% to 2%) which was observed in two cases and was ascribed to solvent residues. It is, therefore, not possible to suggest that the compounds under study undergo any conformational change at ambient temperature, whereupon they break any intermolecular interactions or change from chelate to monodentate carboxylate coordination, becoming purely tetrahedral at the tin center prior to their melting.

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