Journal of Molecular Structure 981 (2010) 46-53

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis, spectroscopic characterization and X-ray structures of five-coordinate diorganotin(IV) complexes containing 5-hydroxypyrazoline derivatives as ligands

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ARTICLE INFO

Article history: Received 4 May 2010 Received in revised form 15 July 2010 Accepted 15 July 2010 Available online 22 July 2010

Keywords: Diorganotin(IV) complexes Pyrazoline derivatives Crystal structure

ABSTRACT

Four new diorganotin(IV) complexes have been prepared from R_2SnCl_2 (R = Me, Ph) with the ligands 5-hydroxy-3-metyl-5-phenyl-1-(S-benzildithiocarbazate)-pyrazoline (H₂L₁) and 5-hydroxy-3-methyl-5-phenyl-1-(2-thiophenecarboxylic)-pyrazoline (H₂L₂). The complexes were characterized by elemental analysis, IR, ¹H, ¹³C, ¹¹⁹Sn NMR and Mössbauer spectroscopies. The complexes [Me₂SnL₁], [Ph₂SnL₁] and [Me₂SnL₂] were also studied by single crystal X-ray diffraction and the results showed that the Sn(IV) central atom of the complexes adopts a distorted trigonal bipyramidal (TBP) geometry with the N atom of the ONX-tridentate (X = O and S) ligand and two organic groups occupying equatorial sites. The C-Sn-C angles for [Me₂Sn(L₁)] and [Ph₂Sn(L₁)] were calculated using a correlation between ¹¹⁹Sn Mössbauer and X-ray crystallographic data based on the point-charge model. Theoretical calculations were performed with the B3LYP density functional employing 3–21G(*) and DZVP all electron basis sets showing good agreement with experimental findings. General and Sn(IV) specific IR harmonic frequency scale factors for both basis sets were obtained from comparison with selected experimental frequencies.

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1. Introduction

NNO-, ONO- and specially ONS-tridentate Schiff bases, synthesized from 2-acetylpyridine, 2-hydroxyacetophenone, salicylaldehyde with hydrazides are among the most extensively chelating agents investigated over the past several years [1-5]. These chelating semicarbazones and thiosemicarbazones compounds are of considerable interest, most because of their pharmacological applications and ability to form interesting chelates with heavy metals, which in some cases possess enhanced biological activity compared with the uncomplexed ligand [6–8]. Recently the ONO-coordination behavior of 4-phenyl-2-4-butanedionebenzoylhydrazone (5-hydroxypyrazoline derivative) towards diorganotin(IV) derivatives have been reported [4]. However, diorganotin(IV) complexes prepared from ONS-tridentate thiohydrazones have been much less studied [6,9]. In view of this, we are reporting the synthesis and characterization of four new five-coordinated diorganotin(IV) complexes, $[R_2Sn(L_1)]$ and $[R_2Sn(L_2)]$ (R = Me and Ph), in which the H₂L₁ is [5-hydroxy-3-metyl-5-phenyl-1-(S-benzildithiocarbazate)-pyrazoline] and H₂L₂ is [5-hydroxy-3-methyl-5-phenyl-1-(2-thiophenecarboxylic)-pyrazoline]. As far as we know, the 5-hydroxypyrazolinol (H₂L₁) ligand have been prepared for the first time and similar complexes of the kind [Me₂Sn(L₁)] and [Ph₂Sn(L₁)] have not yet been reported. The structures of H₂L₁ and H₂L₂ are illustrated in Scheme 1.

The C–Sn–C angle (θ) in five-coordinated diorganotin(IV) complexes was first estimated by Bancroft et al. [10] using established point-charge procedures. Sham's group found partial quadrupole splitting (PQS) values of [R] of -1.03 mm/s and -0.98 mm/s for dialkyl- and diaryltin(IV) five-coordinate complexes, respectively. This work allowed us to calculate new refined values for [alkyl] of -0.84 mm/s and [Ph] of -0.77 mm/s in five-coordinated diorganotin(IV) complexes embodying ONS-tridentate ligands using crystallographic data (θ) and quadrupole splitting (Δ) values.

2. Experimental

2.1. Materials and methods

Solvents were purified and dried according to standard procedures. The compounds 2,4-pentanedione, 4-phenyl-2,4-butanedione,



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2-thiophenecarboxylic hydrazide, dimethyltin(IV) dichloride and diphenyltin(IV) dichloride were of the highest commercially available grade. The starting material *S*-benzyldithiocarbazate was prepared by a previously reported method [11].

IR spectra were recorded on a BOMEN spectrophotometer in the 4000–400 cm⁻¹ range using KBr pellets. NMR spectra were recorded at room temperature on a Varian Mercury plus spectrometer (7.05 T) operating at 300 MHz for ¹H, at 75.46 MHz for ¹³C and at 134.3 MHz for ¹¹⁹Sn. Compound was dissolved in CDCl₃ containing TMS as internal reference (see Scheme 1 for atom numbering). Chemical shifts were expressed in δ (ppm) and coupling constants as *J* (Hz). ¹¹⁹Sn Mössbauer spectra were collected at 80 K in the transmission geometry on a constant-acceleration conventional spectrometer by using a CaSnO₃ source kept at room temperature. All isomer shift values reported in this work are given with respect to this source. All Mössbauer spectra were computer-fitted assuming Lorentzian line shapes and the resulting isomer shifts and quadrupole splittings are accurate to *ca.* ±0.05 mm/s. CHNS elemental analyses were performed on a FISSONS EA 108 analyzer.

Geometries for both ligands and all four complexes were fully optimized and verified for the absence of imaginary harmonic frequencies. The B3LYP hybrid density functional method was used in all calculations with a fine integration grid and tight energy criterion. Two all electron basis sets, 3-21G(*) and DZVP, were compared against experimental geometries and IR frequencies. Calculations were performed on an personal computer with an Intel Q6600 quad-core processor and the software Gaussian G03W version D01.

2.2. Crystal structure determination

The data collections were performed with Mo K α radiation (λ = 71.073 pm) on a Bruker Kappa APEX II-CCD diffractometer for [Me₂Sn(L₁)], [Ph₂Sn(L₁)] and [Me₂Sn(L₂)]. The structures were solved by the heavy atom method with SHELXS-97 [12] and refined with SHELXL-97 [13]. Hydrogen atom positions were calculated at idealized positions using the riding model option of SHELXL-97 [13]. Additional crystal data and more information about the Xray structural analyses are shown in Table 1. The ORTEP diagrams of the complexes indicating atom numbering scheme with thermal ellipsoids at 30% probability are illustrated in Figs. 1–3. All of relevant crystallographic informations are presented in Table 1, whereas selected bond lengths and angles in Table 2.

2.3. Synthesis

The compounds H_2L_1 and H_2L_2 were prepared as follow: a solution of 1,3-diketone RCOCH₂COMe (4.0 mmol), where R is Me or Ph

groups, in 10 mL of MeOH was added to a solution of the appropriated hydrazide derivative (4.0 mmol) in 10 mL of MeOH. The mixture was refluxed for 1 h, after that yellow solutions for both compounds were obtained. Perfectly clear solutions were obtained after filtration of the original ones and slow evaporation of the solvent led to the appearance of a colorless crystalline product. The crystals were filtered, washed with *n*-hexane and dried in air. The 5-hydroxypyrazoline derivatives H_2L_1 and H_2L_2 can easily be obtained as single crystals using CH_2Cl_2 as solvent of reaction.

The complexes were prepared using the methodology reported by Rosair and collaborators [4]. The methyl derivatives were recrystallized using a mixture of MeOH/H₂O (3:1, v/v), whereas the phenyl ones from a mixture of MeOH/CH₂Cl₂ (3:1, v/v). Anal. Calcd for C₂₀H₂₃N₂OS₂Sn (**[Me₂Sn(L₁)]**): C 49.00, H 4.73, N 5.71, S 13.08. Found: C 48.89, H 4.69, N 5.68, S 12.81%, color: yellow, yield: 74%, m.p.: 106–108 °C. Anal. Calcd for C₃₀H₂₆N₂OS₂Sn (**[Ph₂Sn(L₁)**]): C 58.75, H 4.27, N 4.57, S 10.45. Found: C 58.56, H 4.51, N 4.49, S 10.31%, color: yellow, yield: 78%; m.p.: 152– 154 °C. Anal. Calcd for C₁₇H₁₈N₂O₂SSn (**[Me₂Sn(L₂)]**): C 47.15, H 4.19, N 6.47, S 7.40. Found: C 46.81, H 3.98, N 6.35, S 7.29%, color: orange, yield: 74%; m.p.: 160–163 °C. Anal. Calcd for C₃₀H₂₆N₂OS₂Sn (**[Ph₂Sn(L₂]**): C 58.75, H 4.27, N 4.57, S 10.45. Found: C 58.89, H 4.53, N 4.72, S 11.89%, color: orange, yield: 78%, m.p.: 130 °C (dec.)

3. Results and discussion

3.1. Crystal structures of $[Me_2Sn(L_1)]$ and $[Ph_2Sn(L_1)]$

The ORTEP plots of both complexes are shown in Figs. 1 and 2, and their bond lengths and angles are summarized in Table 2. The X-ray structure determination revealed that the substitution of Me group in $[Me_2Sn(L_1)]$ by the Ph group in $[Ph_2Sn(L_1)]$ leads to modifications in the crystal packing of the complex molecules in each case (Table 1). The complex $[Me_2Sn(L_1)]$ crystallizes in the monoclinic $(P2_1/c)$ system while $[Ph_2Sn(L_1)]$ in the triclinic $(P\overline{1})$ one. In both complexes the ligand binds tridentately forming ONS-donor systems containing five- and six-membered chelate rings. The geometry around the Sn(IV) nucleus is well described as a distorted trigonal bipyramid (TBP), with the two organic groups and azomethine N1 atom of the ligand occupying the equatorial positions, the phenolate O1 and thiolate S1 atoms occupy axial sites. As in other complexes [2,5] containing ONS-tridentate thiosemicarbazones, the main distortion from regular TBP geometry comes from the stereochemical constraints imposed by the ligand, which reduce the O1-Sn-S2 angle from the ideal value of 180° to the values of 157.0(2) for [Me₂Sn(L₁)] and 162.85(6)° for [Ph₂Sn(L₁)]. The C19-Sn-C20 and C21-Sn-C31 angles values of 127.1(5) and

Table 1	
Crystallographic data	for Sn(IV) complexes.

	$[Me_2Sn(L_1)]$	$[Ph_2Sn(L_1)]$	$[Me_2Sn(L_2)]$
Empirical formula	$C_{20}H_{23}N_2OS_2Sn$	$C_{30}H_{26}N_2OS_2Sn$	C17H18N2O2SSn
Formula weight	490.21	613.34	433.08
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2 ₁ /c	PĪ	$P2_1/c$
Crystal color	Yellow	Yellow	Orange
Crystal size (mm)	$0.57 \times 0.23 \times 0.04$	$0.12 \times 0.12 \times 0.10$	$0.25 \times 0.08 \times 0.05$
Ζ	4	2	4
Т (К)	293(2)	293(2)	293(2)
a (Å)	7.1391(2)	9.8660(4)	11.9839(2)
b (Å)	25.7575(8)	10.3975(5)	7.75690(10)
<i>c</i> (Å)	11.7189(4)	13.6100(7)	19.5813(4)
β(°)	102.822(2)	80.879(2)	100.2800(10)
V (Å ³)	2101.20(11)	1343.60(11)	1791.02(5)
$ ho_{ m calcd} (m g m cm^{-3})$	1.550	1.516	1.606
Index ranges	$-7 \leqslant h \leqslant 7$	$-14 \leqslant h \leqslant 15$	$-17 \leqslant h \leqslant 17$
	$-26 \leqslant k \leqslant 26$	$-16 \leqslant k \leqslant 16$	$-11 \leq k \leq 11$
	$-12 \leqslant l \leqslant 12$	$-21 \leqslant l \leqslant 20$	$-28 \leqslant l \leqslant 28$
$F(0\ 0\ 0)$	988	620	864
$\mu (\mathrm{mm}^{-1})$	1.426	1.132	1.553
Refinement method	a	a	a
Reflections collected	40,546	29,110	22,810
Data/parameters	2421/235	10,513/325	60/49
Goodness-of-fit on F^2	1.438	1.116	1.108
$\mathbf{R}_1 \left[I > 2\sigma(I) \right]^{\mathbf{b}}$	0.0460	0.0337	0.0469
$wR_2 [I > 2\sigma(I)]^c$	0.1471	0.0982	0.1597
Largest diff. peak and hole $(e\dot{A}^{-3})$	0.636 and -0.784	0.782 and –1.233	1.667 and -1.331

^a Full-matrix least-squares on F 2.

^b R1 = $\sum ||F_0| - |F_c|| / \sum |F_0|$. ^c wR2 = $[\sum_w (|F_0|^2 - |F_c|^2)^2 / \sum_w |F_0^2|^2]^{1/2}$.





Fig. 2. ORTEP plot with atom-labeling scheme of $[Ph_2SnL_1]$ with displacement ellipsoids at the 30% probability level.

The bond lengths values of, respectively, 1.748(11), 1.276(13), 1.412(12), 1.321(12), 1.418(15), 1.373(15), and 1.305(12) Å, found in the skeleton S2-C8-N2-N1-C9-C11-C12-O1 of [Me₂Sn(L₁)], indicate that it has a conjugated double bond character. The shortening of the N2-C8 and C11-C12 bonds and lengthens of the S1-C8 bond upon complex formation, show that the double deprotonation of the ligand results in a conversion from thione to thiolate sulfur. These results were also observed in complex $[Ph_2Sn(L_1)]$

Fig. 1. ORTEP plot with atom-labeling scheme of [Me2SnL1] with displacement ellipsoids at the 30% probability level.

115.14(9)° found, respectively, in $[Me_2Sn(L_1)]$ and $[Ph_2Sn(L_1)]$ also contribute to the distortion.



Fig. 3. ORTEP plot with atom-labeling scheme of [Me₂SnL₂] with displacement ellipsoids at the 30% probability level.

Table 2

Selected bond distances (Å) and angles (°) for Sn(IV) complexes.

	$[Me_2Sn(L_1)]$	$[Ph_2Sn(L_1)]$		$[Me_2Sn(L_2)]$
S1-C7	1.810(11)	1.805(3)	S1-C1	1.680(4)
S1-C8	1.746(11)	1.754(2)	S1-C4	1.658(5)
S2-C8	1.748(11)	1.734(3)	O2-C9	1.297(6)
01- C12	1.305(12)	1.290(3)	01- C5	1.303(5)
N1-C9	1.276(13)	1.276(3)	N1-C5	1.275(5)
N1-N2	1.412(12)	1.396(3)	N1-N2	1.406(4)
N2-C8	1.321(12)	1.335(3)	N2-C6	1.328(5)
C9-C10	1.510(14)	1.509(3)	C6-C7	1.512(6)
C9-C11	1.418(15)	1.410(3)	C6-C8	1.418(5)
C11-C12	1.373(15)	1.374(3)	C8-C9	1.365(5)
C12-C13	1.478(15)	1.484(3)	C9-C11	1.500(5)
Sn-C19	2.120(11)	2.130(3) ^a	Sn-C21	2.088(5)
Sn-C20	2.127(10)	2.149(3) ^b	Sn-C31	2.138(5)
Sn-01	2.135(7)	2.1030(19)	Sn-02	2.100(3)
Sn-N1	2.182(8)	2.1777(19)	Sn-N2	2.136(3)
Sn-S2	2.538(3)	2.5173(7)	Sn-O1	2.122(3)
C7-S1-C8	101.9(5)	102.59(13)	S1-C1-C5	120.5(3)
S1-C8-S2	112.9(6)	111.71(14)	C1-C5-O1	116.5(4)
S2-C8-N2	128.2(9)	128.79(19)	01-C5-N1	125.7(4)
S1-C8-N2	118.9(8)	119.51(19)	C1-C5-N1	117.8(4)
C8-N2-N1	116.6(8)	117.5(2)	C5-N1-N2	111.5(4)
N2-N1-C9	114.2(8)	112.72(19)	N1-N2-C6	115.9(3)
N1-C9-C11	122.8(9)	124.3(2)	N2-C6-C8	122.8(4)
C9-C11-C12	127.4(9)	128.4(2)	C6-C8-C9	127.9(4)
C11-C12-C13	121.5(10)	122.0(2)	C8-C9-C11	120.1(4)
01-C12-C13	115.4(9)	115.5(2)	02-C9-C11	114.5(4)
C19-Sn-N1	103.1(4)	117.75(8) ^c	C21-Sn-N2	117.9(2)
C20-Sn-N1	129.5(4)	126.87(8) ^d	C31-Sn-N2	119.5(2)
N1-Sn-O1	81.4(3)	83.58(7)	N2-Sn-O2	85.22(13)
01-Sn-S2	157.0(2)	162.85(6)	02-Sn-01	158.61(13)
N1-Sn-S2	78.2(2)	79.35(5)	N2-Sn-O1	74.06(12)
C19-Sn-C20	127.1(5)	115.14(9) ^e	C21-Sn-C31	122.3(3)

^a Sn-C21 instead of Sn-C19.

^b Sn–C31 instead of Sn–C20.

^c C21-Sn-N1 instead of C19-Sn-N1.

^d C31-Sn-N1 instead of C20-Sn-N1.

^e C21-Sn-C31 instead of C19-Sn-C20.

and the comparison among the bond parameters found in both complexes is unremarkable.

3.2. Crystal structures of [Me₂Sn(L₂)]

The ORTEP plot of the complex $[Me_2Sn(L_2)]$ is shown in Fig. 3, and their bond lengths and angles are summarized in Table 2. In $[Me_2Sn(L_2)]$ the ligand is ONO-donor tridentate via its O1, O2 and N2 atoms, giving a coordination polyhedron around the Sn(IV) atom described as a distorted trigonal bipyramid with the enolate ligand occupying the two axial positions via O1 and O2 atoms and one equatorial position via N2 nucleus (Fig. 3). The main distortion from regular bipyramidal geometry comes from the stereochemical limitations imposed by the planar tridentate ligand, which reduces the O1-Sn-O2 from the ideal value of 180° to the value of 158.61(13)°. This compression of O1–Sn–O2 is comparable with that found in $[Me_2Sn(L_1)]$ and other reported similar compound, namely Me₂Sn[Ph(O)C=CH-C(Me)=N-N=C(O)Ph] [4]. The angles O1-Sn-N2 = 74.06(12) and $O2-Sn-N2 = 85.22(13)^{\circ}$ are also compressed from 90° and also contribute to the expected distortion. The Sn-O1 = 2.122(3), Sn-O2 = 2.100(3), Sn-N2 = 2.136(3), Sn-C21 = 2.088(5) and Sn-C31 = 2.138(5) Å bond lengths, are very similar with those reported values for Me₂Sn[Ph(O)C=CH-C(Me)=N-N=C(O)Ph] [4], a similar diorganotin(IV) complex containing dinegative ONO-donor tridentate chelating agent.

3.3. IR spectroscopy

Tables 5 and 6 show the assignments of the main IR absorption bands for 5-hydroxypyrazoline derivatives H₂L₁ and H₂L₂, respectively, and Tables 7 and 8 for their Sn(IV) complexes. The IR spectra of the four complexes, when compared with that of the free ligands, show that the v(O-H) = 3356, v(C=N) = 1629 and $\delta(CH_2) =$ 1440 cm⁻¹ absorptions observed in H₂L₁, and v(O-H) = 3411, v(C=N) = 1630 and $\delta(CH_2) = 1445$ cm⁻¹ bands observed in H₂L₂ disappear, suggesting double deprotonation of the ligands upon complex formation. However, new bands observed at 1585 for $[Me_2Sn(L_1)]$, at 1586 for $[Ph_2Sn(L_1)]$, at 1590 for $[Me_2Sn(L_2)]$ and at 1593 cm⁻¹ for $[Ph_2Sn(L_2)]$ are attributed to v(C=N-N=C)stretching vibration [4]. The IR spectra of complexes also exhibit v(C=N) bands shifted to both higher and lower wave numbers { $[Me_2Sn(L_1)]$: 1553/1517; $[Ph_2Sn(L_1)]$: 1554/1528; $[Me_2Sn(L_2)]$: 1572/1537; [Ph₂Sn(L₂)]: $1573/1542 \text{ cm}^{-1}$ }, evidencing double deprotonation and tridentate bibasic behavior of the ligands [2,5,14]. The v(S–C–S) absorption at 981 cm⁻¹ observed in H_2L_1 spectrum, is observed at lower frequencies on complexation { $[Me_2Sn(L_1)]$: 970; $[Ph_2Sn(L_1)]$: 967 cm⁻¹}, indicating that this group takes part in the chelating process [15].

3.4. NMR spectroscopy

The ¹H NMR spectra of the derivatives H₂L₁ and H₂L₂ measured in CDCl₃ (Table 3 and Scheme 1 for atom numbering) show that they exist exclusively in the cyclic (5-hydroxypyrazoline) form. The signal of the terminal ${}^{1}CH_{3}$ appears at 2.09 ppm for $H_{2}L_{1}$ and at 2.15 ppm for H_2L_2 ; whereas the magnetically and chemically nonequivalent ³CH₂ methylene hydrogens appear as double doublet at 3.23 ppm (J_{HH} = 18.8 Hz) for H₂L₁ and at 3.16 ppm $(J_{HH} = 18.0 \text{ Hz})$ for H_2L_2 , similar results have been reported by Zelenin and collaborators [15,16]. The spectrum of H₂L₁ also showed ¹⁰CH₂ methylene signal at 4.35 ppm as a double doublet due to geminal ${}^{2}J$ coupling (J_{HH} = 13.2 Hz). The OH proton appears as a broad peak at 6.47 ppm in H₂L₁ and at 5.29 ppm in H₂L₂. For these compounds, the phenyl hydrogen signals are observed as a multiplet in the region at 7.26–7.40 ppm and the thiophene hydrogens ¹¹CH, ¹²CH, and ¹³CH appear as doublet of doublet at 8.10, 7.10, and 7.60 ppm, respectively. The ¹H NMR spectra (CDCl₃) of the four diorganotin(IV) complexes showed the disappearance of the signals assigned to methylene (³CH₂) and hydroxy (OH) hydrogens

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111, (C) and 511 with chemical single and $1(C)$ $511-11$ and $1(C)$ $511-C$ for invariating derivatives and then $511(10)$

ⁿ C	H_2L_1	$[Me_2Sn(L_1)]^a$	$[Ph_2Sn(L_1)]$	H_2L_2	$[Me_2Sn(L_2)]^b$	$[Ph_2Sn(L_2)]$
¹ C	2.09 d (16.0)	2.51 s (23.5)	2.35 s (26.3)	2.15 d (16.1)	2.51s (23.5)	2.50 s (24.0)
² C	(158.4)	(161.0)	(161.4)	(155.0)	(161.0)	(161.2)
³ C	3.23 dd (54.6)	5.62 s (94.3)	5.79 s (94.6)	3.16 dd (53.5)	5.62 s (94.2)	5.78 s (95.0)
⁴ C	(97.3)	(169.5)	(173.0)	(94.5)	(169.4)	(169.5)
⁵ C	(142.3)	(138.5)	(136.7)	(143.5)	(138.6)	(138.4)
⁶ C	(128.3)	(128.4)	(128.5)	(126.8)	(128.1)	(128.2)
⁷ C	(128.0)	(128.0)	(128.1)	(128.0)	(128.0)	(128.0)
⁸ C	(123.8)	(126.5)	(126.9)	(128.6)	(126.4)	(126.6)
⁹ C	(191.2)	(173.6)	(177.1)	(160.2)	(173.6)	(173.6)
¹⁰ C	4.35 dd (39.2)	4.35 s (36.1)	4.37 s (36.1)	(135.0)	(138.5)	(138.4)
¹¹ C	(135.5)	(138.6)	(137.7)	8.10 dd (134.8)	7.76 dd (130.1)	7.77 dd (130.3)
¹² C	(129.3)	(130.2)	(130.0)	7.10 dd (123.8)	7.04 dd (127.2)	7.11 dd (127.3)
¹³ C	(128.6)	(128.8)	(129.2)	7.60 dd (133.4)	7.61 dd (128.0)	7.60 dd (128.0)
¹⁴ C	(127.2)	(127.1)	(127.1)			

Abbreviations and attributions: s = singlet, d = doublet, dd = double doublet, qd = quartet deformated. ^a $\delta(^{1}H) = 0.79$, $\delta(^{13}C) = 1.3$, $\delta(^{119}Sn) = -149.4$ ppm, $^{2}J(^{119/117}Sn^{-1}H) = 78.7/75.3$, $^{1}J(^{119/117}Sn^{-13}C) = 644/617$ Hz.

^b $\delta^{(11)} = 0.79, \, \delta^{(13)} C = 1.3, \, \delta^{(119Sn)} = -147.2 \, \text{ppm}, \, ^2 J \, (^{119/117} \text{Sn}^{-1}\text{H}) = 78.6/75.3, \, ^1 J \, (^{119/117} \text{Sn}^{-13}\text{C}) = 647/618 \, \text{Hz}.$

Table 4

Selected observed and calculated IR absorptions bands for H₂L₁.

Vibration mode	DZVP	3-21G(*)	H_2L_1
v(C9-N1) + v(C2-C3) + v(C5-C6)	1655	1635	1628
δ (C10–H) _s umbrela	1422	1464	1440
δ (C–H) in plane ; C14 to C18	1361	1385	1378
δ (C–H); C11 + δ (C–H); C7 + v (C12–C13)	1276	1290	1256
δ (C–H); C11 + v(C9–C10)	1246	1246	1220
$v(S1-C8-S2)_a$	1000	1116	981
v(C7-S1-C8) _a	793	772	789
v(C7–S1–C8) _s	784	705	776
(N1–N2) ring breath	701	716	707
δ(O-H)	621	626	593

Table 5

Selected observed and calculated IR absorptions bands for H₂L₂.

Vibration mode	DZVP	3-21G(*)	H_2L_2
$v(C6-N2) + \delta(C7-H) + \delta(C8-H)$	1704	1648	1630
$v(C5-O1) + \delta(O2-H)$	1662	1609	1610
v(C1-C2) + v(C3-C4)	1563	1554	1514
λ (C7–H) _a umbrela + v(C5–N1) + v(C2–C3)	1464	1450	1445
λ (C7–H) _s umbrela + v(C5–N1) + v(C2–C3)	1420	1435	1414
v(N1-C5) + v(C1-C2) + v(C3-C4)	1379	1393	1377
v(C–C); phenyl ring	1359	1321	1338
v(C6-C8)	1347	1314	1313
v(C6-C8) + v(C9-N1)	882	859	861
Molecule breath	834	821	829

in the free ligands and appearing of absorptions in the range 5.79-5.62 ppm attributed to the sp² hydrogens (³CH). These observations suggest that double deprotonation give rise the tridentate bibasic behavior of the ligands H_2L_1 and H_2L_2 .

According to the ¹³C NMR spectroscopy, the spectra of compounds H_2L_1 and H_2L_2 showed signal arising from ³C atom at 54.6 and 53.5 ppm, respectively, whereas the asymmetrical ⁴C atom signal was observed at 97.3 and 94.5 ppm (Zelenin's group has been observed at 93-95 ppm) [16]. The ¹³C NMR spectra of the complexes showed that both signals relative to the ³C and ⁴C in the uncomplexed ligand H₂L₁ and H₂L₂, are shifted downfield from its original positions upon coordination (see Table 3). This is due to the rehybridization process of these atoms from Csp³ to Csp² with ring-opening reaction upon complex formation. According to the Lochart's [17] equation ${}^{1}J({}^{119}Sn-{}^{13}C) = 10.7\theta-778$, the C-Sn-C angles of $[Me_2Sn(L_1)]$ and $[Me_2Sn(L_2)]$ were calculated as being 133.2° and 133.5°, respectively. However, using the alternative Locart's [18] equation $\theta = 0.0161(|^2I({}^{119}Sn-{}^{1}H)|)^2 - 1.32(|^2I)$ (¹¹⁹Sn-¹H)]) + 133.4, the C-Sn-C angles were calculated as being 128.6° and 128.5°, closer to the values found by X-ray diffraction, $127.1(5)^{\circ}$ and $122.3(3)^{\circ}$, respectively. The ²J (¹¹⁹Sn-¹H) = 78.6 Hz and ${}^{1}I$ (${}^{119}Sn - {}^{13}C$) = 647 Hz coupling constants observed for our complex $[Me_2Sn(L_2)]$ are comparable with the values of 78.5 and 649.9 Hz found to Me₂Sn[Ph(O)C=CH-C(Me)=N-N=C(O)Ph] [4].

¹¹⁹Sn chemical shifts, δ (¹¹⁹Sn), relative to Me₄Sn in five-coordinate dimethyltin(IV) derivatives have been empirically reported by Otera [19] located between -90 and -330 ppm, while Holecek et al. [20] have been reported that five-coordinated diorganotin(IV) adducts have $\delta(^{119}\text{Sn})$ values of -90 to -190 ppm. However, values of $\delta(^{119}Sn)$ for [Me₂Sn(L₁)] and [Me₂Sn(L₂)] of -149.4 and -147.2 ppm are inside these range, suggesting that both our methyl complexes do not dissociate in solution. The five-coordinated complexes Me₂Sn [Ph(O)C=CH-C(Me)=N-N=C(O)Ph] and $Ph_2Sn[Ph(O)C=CH-C(Me)=N-N=C(O)Ph]$ showed $\delta(^{119}Sn)$ signal at -146.8 and -151.5 ppm [4].

3.5. Mössbauer spectroscopy

¹¹⁹Sn Mössbauer spectral parameters for the diorgantin(IV) complexes are reported in Table 4, which includes parameters from the literature for comparison, and the spectra of the complexes are shown in Fig. 4. The line-width (Γ) values of the complexes 1, 2, 6 and 7 were found in the range 0.80–0.83 (±0.05) mm/s, removing any possibility of the existence of a second Sn(IV) atom with different coordination. The isomer shift (δ) is very sensitive to the first coordination sphere and it is correlated to the change of s-electron density on the metal by means of +I inductive effect imposed by the ligands. A result of this is the inverse dependence of δ with electronegativity [4]. Thus, δ decrease on replacing the phenyl by alkyl groups (Table 4). This behavior can clearly be seen in complexes 1-5 (1.12-1.31 mm/s) as compared to complexes 6-11 (0.93-1.30 mm/s).

From the quadrupole splitting (Δ) value and the point-charge approach, the Eq. (1).

$$|\Delta| = -4[R](1 - 0.75\sin^2\theta)^{1/2} \tag{1}$$

gives an estimate of θ , where θ is the C–Sn–C bond angle and [R] denotes the partial quadrupole splitting (PQS) value of group R [4,10,21–23]. Considering the complexes 1 (2.33 mm/s), 3 (2.43 mm/s), **4** (2.41 mm/s), and **5** (2.62 mm/s) and using θ and Δ values (Table 4), the PQS values can be estimated. Eq. (1) yields [alkyl] = -0.81, -0.83, -0.88, and -0.83 mm/s, respectively, and allows us to evaluate an average value for [alkyl] = -0.84 mm/sin five-coordinated dialkylorganotin(IV) complexes embodying

Table 6	Ta	ble	6
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Selected observed and calculated IR absorptions bands for [Me₂SnL₁] and [Ph₂SnL₁].

Vibration mode	DZVP	3-21G(*)	$[Me_2SnL_1]$	DZVP	3-21G(*)	[Ph ₂ SnL ₁]
v(C2-C3) + v(C5-C6)	1655	1634	1628	1655	1635	
$v(C8-N2) + v(C9-C11-C12)_a$	1572	1564	1553	1574	1563	1555
$v(C8-N2) + v(C11-C9-N1)_{a}$	1539		1517	1539	1545	1528
v(C9–N1)	1476	1497	1494	1475	1498	1488
λ(C10–H) _s umbrela	1418	1462	1453	1416	1459	1450
$v(C11-C9-N1)_{a} + v(C11-C12-O1)_{a}$	1435	1442	1440	1435	1441	1428
δ (C–H) in plane; C14 to C18	1364	1389	1380	1364	1388	1377
v(C12-C13) + v(C9-C10)	1316	1309	1316	1316	1308	1300
δ (C–H); C11 + δ (C–H); C7	1269	1272	1256	1271	1274	1299
δ(C–H) in plane; C14, C15, C17, C18	1205	1246	1220	1205	1246	1238
$v(N1-N2) + \delta(C-H); C10, C11$	1091	1085	1063	1094	1085	1065
$v(S1-C8-S2)_a$	979	955	970	979	955	967
v(S1-C8-S2) _s	909	948	898	910	948	900
v(C8-S1) + v(C9-C10) + v(C12-C13)	872	894	852			
v(C7–S1)	786		775	788		768
v(C8-S2)				750	752	733
v(C7–S1)	698	705	707	698	704	707
v(C7-S1) + v(C8-S2)				683	693	695
v(Sn–O1)	544	575	543	542	572	548

Table 7

Selected observed and calculated IR absorptions bands for [Me₂SnL₂] and [Ph₂SnL₂].

Vibration mode	DZVP	3-21G(*)	[Me ₂ SnL ₂]	DZVP	3-21G(*)	[Ph ₂ SnL ₂]
$v(C1-C2) + v(C6-N2) + v(C5-N1) + v(C8-C9-O2)_a$	1607	1604	1591	1610	1607	1594
$v(C1-C2) + v(C6-N2) + v(C5-N1) + v(C8-C9-O2)_a$	1584	1575	1572	1585	1574	1573
v(C1-C2) + v(C3-C9) + v(C6-C8) + v(C5-N1) + v(C9-O2)	1564	1562	1537	1562	1559	1542
$v(C3-C4) + v(C1-C5) + \lambda(C7-H)_{s}$ umbrela	1489	1466	1455	1488	1465	1444
$v(C8-C9-O2)_{a}$	1443	1444	1433	1440	1439	1432
v(C4–S)	865	874	859	866	874	846
v(Sn–N2)	709	722	710	710	722	
v(Sn–N2)	664	683	656	665	684	656
$v(O1-Sn-O2)_a$	555	586	563	555	587	
$v(O1-Sn-O2)_s$	529	559	521	528	559	527
$\delta(\text{Sn-O2}) + \delta(\text{Sn-N2}) + \delta(\text{Sn-O1})$	451	461	445	452	460	451

Table 8

Mössbauer data and C-Sn-C angles (°) for five-coordinated Sn(IV) complexes.

Compound	$\delta(mm/s)$	⊿ (mm/s)	PQS (mm/s)	C-Sn-C (exptl)	C-Sn-C (calcd)
1. $[Me_2Sn(L_1)]^a$	1.14	2.33	-0.81	127.1	123.7
2. $[Me_2Sn(L_2)]^a$	1.12	2.78		122.3	180.0
3. [Me ₂ Sn(HBT)] ^b	1.27	2.43	-0.83	127.5	127.1
4. $[Me_2Sn(DAP4P)]^c$	1.18	2.41	-0.88	122.5	126.4
5. $[Bu_2Sn(DAP4P)]$	1.31	2.62	-0.83	134.4	133.7
6. $[Ph_2Sn(L_1)]^a$	1.08	2.03	-0.82	115.1	119.7
7. $[Ph_2Sn(L_2)]^a$	0.93	2.16			124.6
8. [Ph ₂ Sn(HBT)] ^b	1.30	2.30	-0.79	127.0	129.8
9. [Ph ₂ Sn(hacm)] ^c	1.10	1.88	-0.72	119.4	113.8
10. [Ph ₂ Sn(hacmm)] ^c	1.10	1.93	-0.74	118.9	115.9
11. $[Ph_2Sn(DAP4P)]^c$	1.09	2.03			119.8

Abbreviations: PQS = partial quadrupole splitting, $H_2L_1 = 4$ -phenyl-2,4-butanedione-1-(*S*-benzyldithiocarbazate), H_2L = salicylaldehydethiosemicarbazone, $H_2DAP4P = 2$ -hydroxyacetophenone- N^4 -phenylthiosemicarbazone, $H_2hacm = 2$ -hydroxyacetophenone- N^4 -morpholylthiosemicarbazone, $H_2hacm = 2$ -hydroxyacetophenone- N^4 -2,6-dimethylmorpholylthiosemicarbazone.

^b Ref. [18].

^c Ref. [22].

ONS-tridentate ligands. Similarly, from complexes **6**, **8**, **9** and **10** we obtain a value for [Ph] = -0.77 mm/s (average of -0.82, -0.79, -0.72, and -0.74 mm/s, respectively) in similar five-coordinated diorganotin(IV) derivatives containing ONS-tridentate dibasic ligands. Now, using our alternative values for [Me] = -0.84 mm/s and for [Ph] = -0.77 mm/s, we predict Me–Sn–Me and Ph–Sn–Ph angles of 123.7° and 119.7° for complexes **1** and **6**, respectively. The average value of -0.77 mm/s is very far from

the value for [Ph] = -0.98 mm/s previously reported [10] by Bancroft's team, but it is in good agreement with calculated value of [Ph] = -0.75 mm/s reported recently by us [24].

3.6. Theoretical calculations

The B3LYP hybrid density functional method [25] with all electron basis sets DZVP [26,27] and the smaller 3-21G(*) [28], were

^a This work.



Fig. 4. ¹¹⁹Sn Mössbauer effect spectra obtained at 80 K to complexes [Ph₂Sn(L₁)] (a), [Me₂Sn(L₁)] (b), [Ph₂Sn(L₂)] (c) and [Me₂Sn(L₂)] (d).

applied to obtain the global minimum energy geometry and IR harmonic frequencies for all molecules presented here. All calculations were done with the software Gaussian G03W D01, using a fine integration grid, tight energy minimization and verified for the absence of imaginary frequencies. The B3LYP method was chosen because it gives good accuracy for single molecule geometries and reasonably accurate IR frequencies for a wide variety of molecular systems [29] as well as for Sn(IV) compounds [30-32]. Geometries were compared only for the three complexes for which X-ray data was available. Since calculations were done in vacuum and zero Kelvin it would be expected that theoretical bond lengths should be shorter than experimental ones. However, larger bond lengths were observed with mean signed differences (MSD) of +0.026 Å for both basis sets. This particular behavior can be due to deficiencies such as an inadequate treatment of electron correlation effects, leading to stronger electron repulsion, and lack of relativistic effects [30]. Even with this bias the B3LYP method performs quite well as a practical option for predicting molecular geometries in our systems, with mean absolute differences (MAD) of 0.029 Å (3-21G(*)) and 0.031 Å (DZVP). Maximum differences were smaller than 0.099 Å for both basis sets, i.e., less than 8% differences to the crystal X-ray bond lengths. Surprisingly although 3-21G(*) has about 73% of DZVP's basis functions, it performed a little better for all complexes. This difference was more striking when only the 15 Sn(IV) bonds were included on statistics, MADs of 0.034 Å (3–21G(*)) and 0.049Å (DZVP), the latter showing a more pronounced bias in overestimating Sn(IV) bond lengths. Smaller bias were observed for bond angles, MSD of -0.08° (3-21G(*)) and $+0.34^{\circ}$ (DZVP). In absolute values both basis sets had similar results, MADs of 1.95° and 1.74° respectively. It is well known from the literature that IR absorption frequencies are usually overestimated by ab initio methods, requiring correction with general purpose scaling factors or functional groups specific ones. General and specific average scaling factors were calculated for both basis sets from all 75 (four complexes and two ligands) and 10 (involving Sn(IV) atom) harmonic frequency values respectively. While general MADs were 19 cm^{-1} (3–21G(*)) and 17 cm⁻¹ (DZVP), suggesting that both basis sets might have similar quality, specific Sn(IV) MADs of 24 cm⁻¹ and 5 cm⁻¹ were found respectively, proving the superior quality of DZVP predicted Sn(IV) harmonic frequencies. The calculated general average scaling factors were 0.9866 (3-21G(*)) and 0.9929 (DZVP), when using all 75 frequencies, and 0.9587 (3-21G(*)) and 0.9967 (DZVP) for Sn(IV) specific frequencies. The larger difference between 3 and 21G(*) general and specific factors is due to it's poorer performance on Sn(IV) specific frequencies.

4. Conclusions

The $\delta(^{119}Sn)$ chemical shifts values found for $[Me_2Sn(L_1)]$ and $[Me_2Sn(L_2)]$ are -149.4 and -147.2 ppm, respectively. These chemical shifts are comparable with reported values of -146.8 and -151.5 ppm for Me_2Sn[Ph(O)C=CH-C(Me)=N-N=C(O)Ph] and Ph_2Sn[Ph(O)C=CH-C(Me)=N-N=C(O)Ph], respectively. From the similarity among $\delta(^{119}Sn)$ values of these diorganotin(IV) compounds and the undeniable more acidic behavior of Ph_2Sn²⁺ compared to Me_2Sn²⁺, it is clear that our diphenyltin(IV) five-coordinate complexes would not suffer dissociation in CDCl₃ solution. The correlation between Mössbauer and X-ray structural data, using a simple point-charge model, gave values of -0.84 mm/s for [alkyl] and -0.77 mm/s for [Ph] in five-coordinate diorganotin(IV) complexes embodying ONS-tridentate ligands.

Theoretical B3LYP calculations employing 3–21G(*) and DZVP basis sets for the ligands and complexes agree quite well with experimental data, maximum differences in bond lengths and angles were not larger than 8%. Comparison between calculated and X-ray bond lengths and internal angles of three complexes showed MADs of approximately 0.03 Å and 2°. However, DZVP basis set calculations have a stronger tendency to overestimate Sn(IV) bond lengths than 3-21G(*). Although 3-21G(*) showed better geometries than DZVP for the complexes, the later was clearly superior for IR harmonic frequencies specially the ones involving the Sn(IV) atom. While general MADs were smaller than 20 cm⁻¹ for both basis sets, a MAD of 5 cm⁻¹ was found for DZVP on frequencies involving Sn(IV). Average frequency scaling factors of 0.9866 (3-21(*)) and 0.9929 (DZVP) were obtained from a group of 75 experimental selected frequencies, as well as specific Sn scaling factors of 0.9587 (3-21(*)) and 0.9967 (DZVP) from 10 frequencies of the original group.

5. Supplementary information

Crystallographic data for the structural analysis of the complexes have been deposited at the Cambridge Crystallographic Data Center with the deposition numbers CCDC 697620 for $[Me_2Sn(L_1)]$, CCDC 697621 for $[Ph_2Sn(L_2)]$ and CCDC 742944 for $[Me_2Sn(L_2)]$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

The authors are grateful to CNPq, FAPESP and FINEP (CT INFRA 0970/01) for financial support. GFS also gratefully acknowledges the financial support of the CNPq (Edital Universal-2007, Processo 307412/2008-3).

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