

Article

## New Heptacoordinated Organotin(IV) Complexes Derivatives of 2,6-diacetylpyridinebis(2-furanoylhydrazone), H<sub>2</sub>dapf, and 2,6-diacetylpyridinebis(2-thenoylhydrazone), H<sub>2</sub>dapt. Crystal and Molecular Structure of [Me<sub>2</sub>Sn(Hdapt)]Br.H<sub>2</sub>O

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As reações dos ligantes H<sub>2</sub>dapf e H<sub>2</sub>dapt, com R<sub>4-m</sub>SnX<sub>m</sub> (m = 2, 3; R = Me, Ph e X = Cl, Br) resultaram na formação de oito novos complexos organoestânicos heptacoordenados, os quais foram estudados por análise elementar, espectroscopias no IV, RMN de <sup>1</sup>H e Mössbauer, para investigar suas propriedades estruturais. O derivado metilado, [Me<sub>2</sub>Sn(Hdapt)]Br.H<sub>2</sub>O, foi também caracterizado por difração de raio X por monocristais. O complexo cristaliza no sistema monoclinico e grupo de espaço P2<sub>1</sub>/c, com a = 21.920(3), b = 7.4470(5), c = 16.805(2) Å, β = 110.18(1)° e Z = 4. A determinação estrutural revelou um complexo monocatiônico de Sn(IV), [Me<sub>2</sub>Sn(Hdapf)]<sup>+</sup>, numa geometria bipiramidal trigonal, na qual o Br<sup>-</sup> está como contra-íon e uma molécula de água ajuda o empacotamento cristalino. Os parâmetros Mössbauer para o complexo [Me<sub>2</sub>Sn(Hdapf)]<sub>2</sub>[Me<sub>2</sub>SnCl<sub>4</sub>] evidenciaram dois sítios de Sn(IV), como observado pela determinação da estrutura cristalina. Também uma correlação entre os dados de Mössbauer e de raio X, baseada no modelo carga-ponto, é discutida.

The reaction of the ligands H<sub>2</sub>dapf and H<sub>2</sub>dapt, with R<sub>4-m</sub>SnX<sub>m</sub> (m = 2, 3; R = Me, Ph and X = Cl, Br) led to the formation of eight new heptacoordinated organotin(IV) complexes, which were studied by microanalysis, IR, NMR and Mössbauer spectroscopy to investigate their structural properties. The methyl derivative [Me<sub>2</sub>Sn(Hdapt)]Br.H<sub>2</sub>O was also studied by single crystal X-ray diffraction. It crystallizes in the monoclinic system, space group P2<sub>1</sub>/c, with a = 21.920(3), b = 7.4470(5), c = 16.805(2) Å, β = 110.18(1)°, Z = 4. The structure determination revealed a monocationic complex of Sn(IV) in a distorted bipyramidal geometry [Me<sub>2</sub>Sn(Hdapf)]<sup>+</sup>, with Br<sup>-</sup> as counter ion and one molecule of water helping the crystal packing. Mössbauer parameters of the complex [Me<sub>2</sub>Sn(Hdapf)]<sub>2</sub>[Me<sub>2</sub>SnCl<sub>4</sub>] have evidenced two Sn(IV) sites, as observed in the crystal structure determination. Also a correlation between Mössbauer and X-ray data based on the point-charge model is discussed.

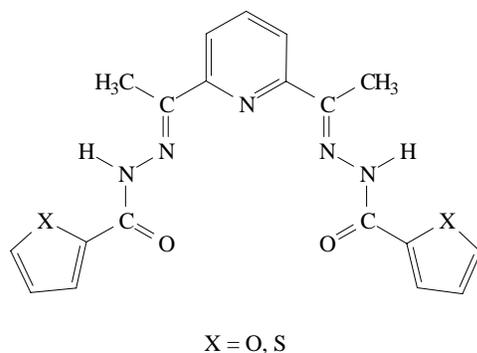
**Keywords:** *hydrazone complexes; heptacoordinated organotin(IV) complexes*

### Introduction

The chelating properties of 2,6-diacetylpyridinebis(hydrazones) have been investigated towards several organo-

tin chlorides, R<sub>4-m</sub>SnCl<sub>m</sub> (m = 2, 3). It has been found that these ligands act as pentadentate and coordinate to Sn (IV) through the two enolate oxygen atoms, the two azomethine

nitrogens and the pyridil nitrogen<sup>1,2,3</sup>. However, the nature of coordination depends on the metal ion, the pH of the medium, the reaction conditions, and also the nature of the hydrazone<sup>4</sup>. For instance, the pentadentate hydrazone can remain protonated as in the compound [MeSnCl(H<sub>2</sub>dapsc)]<sup>2+</sup>, H<sub>2</sub>dapsc = 2,6-diacetylpyridinebis(semicarbazone)<sup>2</sup>, it can be deprotonated as in the complex [Et<sub>2</sub>Sn(dapt)], H<sub>2</sub>dapt = 2,6-diacetylpyridinebis(2-thenoylhydrazone)<sup>1</sup>, or partially protonated as in the monocation [Me<sub>2</sub>Sn(Hdapf)]<sup>+</sup>, H<sub>2</sub>dapf = 2,6-diacetylpyridinebis(2-furanoylhydrazone)<sup>3</sup>. Single crystal X-ray diffraction studies have shown that in all three modes of complexation, the Sn(IV) atom exhibits a nearly pentagonal bipyramidal coordination geometry with equatorial plane defined by the ONNNO donor set of the hydrazone ligand. The present work deals with the preparation and characterization of eight new complexes with the ligands 2,6-diacetylpyridinebis(2-furanoylhydrazone), H<sub>2</sub>dapf, and 2,6-diacetylpyridinebis(2-thenoylhydrazone), H<sub>2</sub>dapt, whose structures are shown below. These two ligands were chosen since they have the potential to form pentacoordinated or higher coordinated Sn(IV) complexes. Furthermore, different possibilities of binding to the metal in the enolate or ketone forms make this study extremely interesting. The complexes formed were studied by microanalysis, IR, <sup>1</sup>H-NMR, Mössbauer spectroscopy and crystal X-ray diffraction.



## Experimental

### Synthesis

The ligands H<sub>2</sub>dapf and H<sub>2</sub>dapt were prepared according to the literature<sup>5</sup>, using EtOH as solvent. The Sn(IV) complexes were prepared by the following method. The methanol solution of the organotin(IV) derivative was added to the hot methanol solution of appropriate hydrazone in a 1/1 mol ratio. The resulting mixture was refluxed for 1 h and filtered to form a clear solution and allowed to stand at room temperature. After cooling and slow evaporation of the solvent, crystalline products were formed with yields about 60%, which did not melt below 250 °C. Crystals, which were suitable for X-ray analysis, were

isolated only for the complexes **2** and **7**. The structure of **2** was determined previously<sup>3</sup>. The microanalysis were performed with a Perkin Elmer 2400C analyser, giving for C, H and N the following results.

1. [MeSnCl(dapf)]. Anal. Calcd. for (C<sub>20</sub>H<sub>18</sub>ClN<sub>5</sub>O<sub>2</sub>Sn): C, 43.90; H, 3.32; N, 12.81. Found: C, 43.40; H, 2.90; N, 12.72%.
2. [Me<sub>2</sub>Sn(Hdapf)]<sub>2</sub>[Me<sub>2</sub>SnCl<sub>4</sub>]. Anal. Calcd. for (C<sub>23</sub>H<sub>28</sub>Cl<sub>4</sub>N<sub>5</sub>O<sub>2</sub>Sn<sub>2</sub>): C, 39.31; H, 3.67; N, 10.41. Found: C, 38.72; H, 3.39; N, 10.62%.
3. [Me<sub>2</sub>Sn(Hdapf)]Br. Anal. Calcd. for (C<sub>21</sub>H<sub>22</sub>BrN<sub>5</sub>O<sub>2</sub>Sn): C, 41.53; H, 3.62; N, 11.54. Found: C, 40.25; H, 3.87; N, 11.40%.
4. [Ph<sub>2</sub>Sn(dapf)]. Anal. Calcd. for (C<sub>31</sub>H<sub>25</sub>N<sub>5</sub>O<sub>2</sub>Sn): C, 57.26; H, 3.11; N, 10.77. Found: C, 58.57; H, 2.93; N, 10.50%.
5. [MeSnCl(dapt)]. Anal. Calcd. for (C<sub>20</sub>H<sub>18</sub>ClN<sub>5</sub>O<sub>2</sub>Sn): C, 41.52; H, 3.11; N, 12.10. Found: C, 40.73; H, 2.93; N, 12.11%.
6. [Me<sub>2</sub>Sn(Hdapt)]<sub>2</sub>[Me<sub>2</sub>SnCl<sub>4</sub>]. Anal. Calcd. for (C<sub>23</sub>H<sub>28</sub>Cl<sub>4</sub>N<sub>5</sub>S<sub>2</sub>Sn<sub>2</sub>): C, 37.51; H, 3.58; N, 9.94%. Found: C, 37.07; H, 3.44; N, 9.77%.
7. [Me<sub>2</sub>Sn(Hdapt)]Br.H<sub>2</sub>O. Anal. Calcd. for (C<sub>21</sub>H<sub>22</sub>BrN<sub>5</sub>S<sub>2</sub>Sn): C, 38.25; H, 3.61; N, 10.62%. Found: C, 38.55; H, 3.41; N, 10.33%.
8. [Ph<sub>2</sub>Sn(dapt)]. Anal. Calcd. for (C<sub>31</sub>H<sub>25</sub>N<sub>5</sub>S<sub>2</sub>Sn): C, 54.55; H, 3.66; N, 10.26. Found: C, 53.81; H, 3.49; N, 9.87%.

Infrared spectra were recorded on a Nicolet 5ZDX-FT spectrophotometer in the 4000-400 cm<sup>-1</sup> range using KBr pellets. Due to poor solubility of the complexes, it was possible to perform <sup>1</sup>H NMR spectra only for the complexes **2**, **3**, **6** and **7** in CDCl<sub>3</sub>, using a 250 MHz Bruker spectrometer. Chemical shifts are relative to internal tetramethylsilane. <sup>119</sup>Sn Mössbauer spectra were measured using a constant acceleration spectrometer moving a CaSnO<sub>3</sub> source at room temperature. The isomer shift values are given with respect to this source. The samples were measured at liquid nitrogen temperature and all spectra were computer fitted assuming Lorentzian line shapes. X-ray diffraction data were collected at room temperature using an Enraf-Nonius CAD-4 automatic diffractometer, with a graphite monochromated MoK<sub>α</sub> radiation (λ = 0.71073 Å), obtained in a fine focus sealed tube.

### X-ray structure determination of [Me<sub>2</sub>Sn(Hdapt)]Br.H<sub>2</sub>O

The unit cell of the complex **7** was determined by a least-squares fit of settings for 25 strong reflections, with 10° ≤ θ ≤ 18°. Intensity measurements were carried out up to 27°, using ω/2θ scan mode. A yellow, prismatic, single-crystal with dimensions: 0.2 x 0.15 x 0.3 mm was used. During the data collection the intensity decay was checked through the measurement of 3 standard reflections every

120 min and a correction factor was applied (average value = 0.9976). Absorption corrections were also taken into account according to an empirical method,  $\psi$  scan<sup>6</sup>. The maximum and minimum transmission factors were respectively 0.9964 and 0.7905. The crystal data and structure refinement parameters are given in Table 1.

The structure was solved by heavy-atom method. The refinement on  $(F(hkl))^2$  through iterative full-matrix least-squares calculations including all data was done, and weights  $\omega = 1/[S^2(F^2_{\text{obs}}) + (0.0817P)^2 + 10.9505P]$  where  $P = (F^2_{\text{obs}} + 2F^2_{\text{calc}})/3$  were assigned to them<sup>7</sup>. The observed criterion was used only for calculating R factor for observed reflections. The refinement process was applied until convergence (mean value of shift/esd = 0.000) and the maximum, minimum and average peaks of electronic density residues were 2.80, -2.34 and 0.14 e Å<sup>-3</sup>, respectively. These peaks are high. The most positive is 0.44 Å from C132 and the negative is 0.50 Å from S135. Anisotropic displacement parameters were assigned to non-H atoms, with exception of one of the thiophene rings (C131, C132, C133, C134, S135). The rings have different behaviors during the refinement process, one of them is close to the bromide and the water molecule. The other one has a greater volume to occupy in the crystal structure. Due to this, the model was refined with isotropic temperature parameters for the atoms of this thiophene ring. Consequently, the highest peak and the deepest hole in the resi-

dual electronic density are close to these atoms. Several attempts to refine them anisotropically and/or including disorder effects were done, without any success.

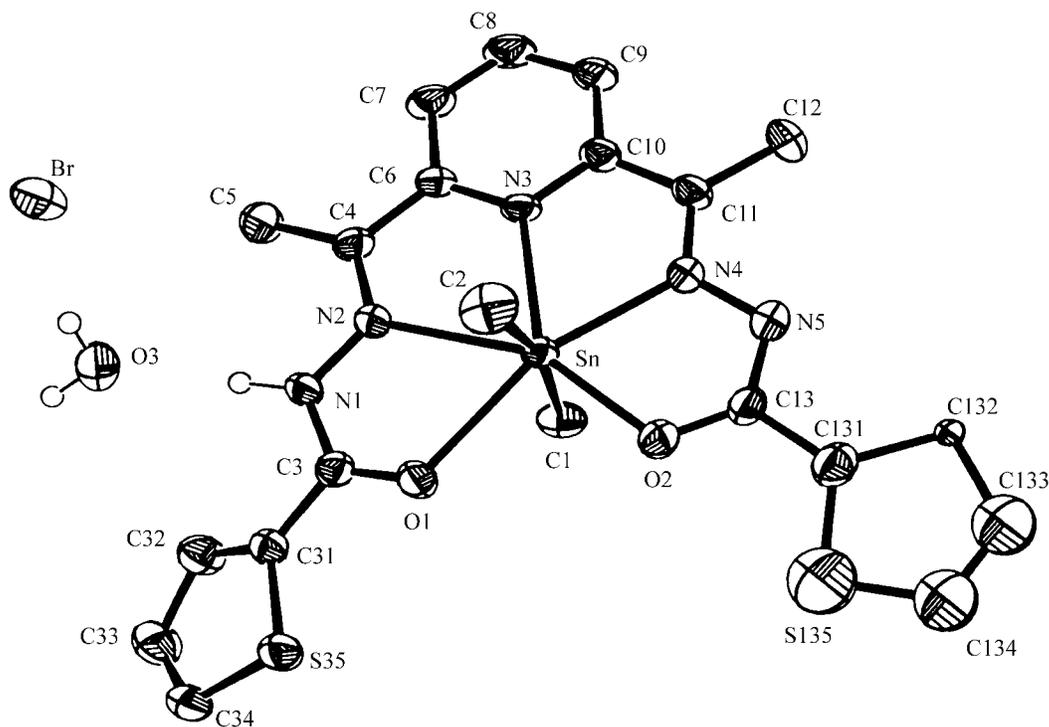
The H-atom positions were calculated and refined as riding atoms, except HN1, HO3A and HO3B, whose fractional atomic coordinates were determined in a difference Fourier map, calculated after convergence of the model with all other atoms and refined. An isotropic displacement parameter was applied to all H-atoms, using values 20% greater than the equivalent temperature factor of the corresponding C-atom.

## Results and Discussion

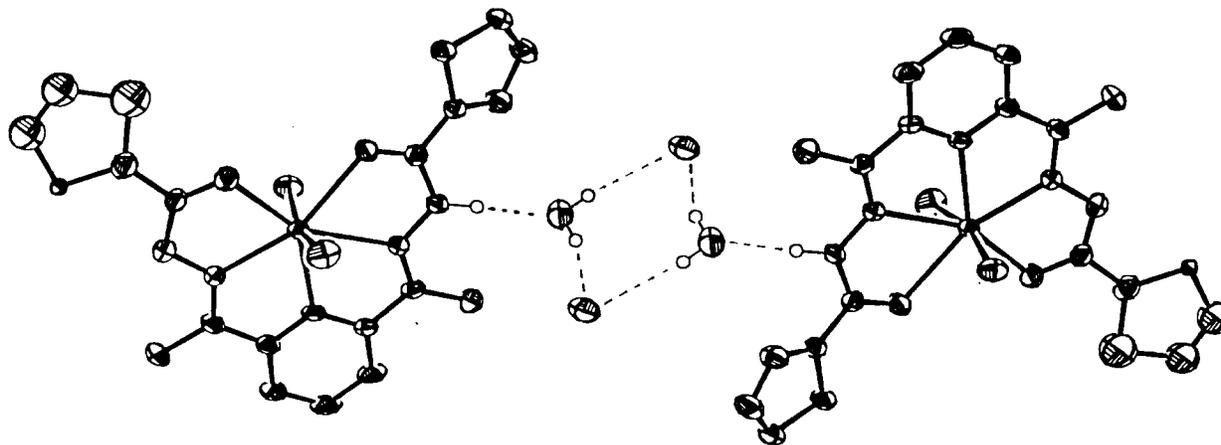
### Crystal structure of $[Me_2Sn(Hdapt)]Br \cdot H_2O$

The structure determination revealed the presence of a complex cation of tin(IV), *trans*-dimethyl[2,6-diacetylpyridinebis(2-thenoylhydrazone)]tin(IV), with bromide as counter ion. A water molecule helps the packing mode.

The metal is heptacoordinated, showing a distorted pentagonal bipyramidal geometry, with the pentahapto ligand, Hdapt<sup>+</sup>, at the equatorial plane and two methyl groups at the axial positions. The major ligand is planar, except for the thiophene rings, which make dihedral angles of 27.4(1)° and 11.4(3)°, respectively, with the equatorial plane. Table 2 contains the fractional atomic coordinates and the equivalent isotropic displacement parameters. Table 3 contains



**Figure 1.** View of the asymmetric unit of  $[Me_2Sn(Hdapt)]Br \cdot H_2O$ , with labelled atoms and 50% probability ellipsoids.



**Figure 2.** View of one pair of [Me<sub>2</sub>Sn(Hdapt)]Br.H<sub>2</sub>O, to show Br<sup>-</sup> and water molecule roles in the crystal packing.

selected bond distances and angles. Figure 1 shows the molecule with labeled atoms.

During the reaction the proton from one of the azomethine groups leaves the molecule. The other, HN1, remains in the structure. As a consequence, differences between bond distances and angles around the metal can be observed, O1 atom is in a keto form and O2 is an enolate, which has greater basicity (Table 3).

This fact was also observed in the structures of other complexes, in which a similar ligand loses one proton, such as in [Ph<sub>2</sub>Sn(Hdaptsc)]Cl<sup>8</sup> [H<sub>2</sub>daptsc = 2,6-diacetylpyridinebis(thiosemicarbazone)] with distances Sn-S: 2.592(1) and 2.703(1) Å; Sn-N: 2.348(4), 2.353(4) and 2.491(4) Å; [Me<sub>2</sub>Sn(Hdapf)]<sub>2</sub>[Me<sub>2</sub>SnCl<sub>4</sub>]<sup>3</sup> [H<sub>2</sub>dapf = 2,6-diacetylpyridinebis(furanoylhydrazone)] with distances Sn-O: 2.227(4) and 2.474(4) Å; Sn-N: 2.246(4), 2.263(5), and 2.314(4) Å; and [MeSnCl(Hdaptsc)]Cl.MeOH<sup>2</sup> with distances Sn-S: 2.527(2) and 2.633(2) Å, Sn-N: 2.288(6), 2.328(6), and 2.430(6) Å. On the other hand, when both protons, from the two arms of the molecule remain attached or leave it, the observed values of the homologue bond distances and angles are similar, reflecting a higher symmetry for these complexes. Two examples of the first case are: [MeSnCl(H<sub>2</sub>dapsc)]Cl<sub>2</sub>.2H<sub>2</sub>O<sup>2</sup>, with distances Sn-O: 2.177(6) and 2.180(6) Å; Sn-N: 2.252(7), 2.262(6) and 2.284(7) Å; [ClSnCl(H<sub>2</sub>dapsc)]Cl<sub>2</sub>.2H<sub>2</sub>O<sup>9</sup> with distances Sn-O: 2.127(5) and 2.123(6) Å; Sn-N: 2.259(6), 2.260(7), and 2.272(7) Å. Examples of the second case are: [PhSnPh(daptsc)].2DMF<sup>10</sup>, with distances Sn-S: 2.593(1) and 2.603(1) Å, Sn-N: 2.368(3), 2.421(4) and 2.427(4) Å; [EtSnEt(dapt)]<sup>1</sup> with distances: Sn-O: 2.251(13) and 2.285(14) Å, Sn-N: 2.300(16), 2.306(17) and 2.356(16) Å.

In the crystal packing, pairs of [Me<sub>2</sub>Sn(Hdapt)]Br.H<sub>2</sub>O are observed. These pairs are built by H-interactions through the proton from the azomethine groups, the water molecules and the bromide. This can be seen in

**Table 1.** Crystal data and structure refinement parameters of [Me<sub>2</sub>Sn(Hdapt)]Br.H<sub>2</sub>O.

Molecular Formula	C <sub>21</sub> H <sub>24</sub> N <sub>5</sub> O <sub>3</sub> S <sub>2</sub> SnBr
Molecular Weight	657.18
Crystal System	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	21.920(3)
<i>b</i> (Å)	7.4470(5)
<i>c</i> (Å)	16.805(2)
β (°)	110.178(10)
<i>V</i> (Å <sup>3</sup> )	2574.8(5)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g.cm <sup>-3</sup> )	1.696
μ (mm <sup>-1</sup> )	2.738
<i>T</i> (K)	298
Range of <i>h, k, l</i>	-25 → 27, -9 → 0, -20 → 0
No. measured reflections	5831
No. of observed reflections ( <i>F</i> > 4σ( <i>F</i> ))	4218
<i>F</i> (000)	1304
No. of refined parameters	289
<i>R</i> <sub>obs</sub>	0.0472
<i>R</i> <sub>all</sub>	0.0659
<i>R</i> <sub>w</sub>	0.1351
<i>S</i>	1.051

**Fig. 2.** The H-bond distances and angles are N1-O3: 2.889(8), HN1-O3: 2.24(7), N1-HN1-O3: 166(9)°, O3-Br: 3.294(7), O3-HO3A: 0.58(10), O3-HO3B: 0.78(9), Br-HO3A: 2.86(12) Å, HO3-O3-HO3B: 109(9)°, O3-HO3A-Br: 134(14)°.

**Table 2.** Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for  $[\text{Me}_2\text{Sn}(\text{Hdapt})]\text{Br}\cdot\text{H}_2\text{O}$ .

Atom	x	y	z	U
Sn	0.207648(17)	-0.03068(5)	0.19223(2)	0.03021(14)
Br	0.43929(4)	0.64998(11)	0.35530(4)	0.0567(2)
C1	0.2356(3)	-0.2973(9)	0.2287(4)	0.0469(15)
C2	0.1867(4)	0.2452(9)	0.1891(4)	0.0490(15)
O1	0.24297(19)	0.0069(7)	0.3490(3)	0.0439(11)
C3	0.3017(3)	0.0305(8)	0.3888(3)	0.0336(12)
C31	0.3296(3)	0.0118(8)	0.4807(4)	0.0335(12)
C32	0.3910(3)	-0.0279(10)	0.5304(4)	0.0482(15)
C33	0.3971(4)	-0.0434(12)	0.6162(4)	0.0592(19)
C34	0.3413(3)	-0.0142(11)	0.6296(4)	0.0541(18)
S35	0.27854(7)	0.0287(3)	0.53857(10)	0.0444(4)
N1	0.3444(2)	0.0678(8)	0.3490(3)	0.0378(12)
HN1	0.374(4)	0.096(10)	0.372(5)	0.045
N2	0.3230(2)	0.0504(7)	0.2628(3)	0.0333(10)
C4	0.3616(3)	0.0671(8)	0.2210(4)	0.0354(12)
C5	0.4321(3)	0.1109(12)	0.2581(4)	0.0532(18)
C6	0.3307(3)	0.0337(8)	0.1286(4)	0.0352(12)
C7	0.3645(3)	0.0393(9)	0.0723(4)	0.0453(15)
C8	0.3328(4)	0.0041(10)	-0.0113(5)	0.0533(18)
C9	0.2661(3)	-0.0337(10)	-0.0397(4)	0.0476(15)
C10	0.2351(3)	-0.0432(8)	0.0190(4)	0.0371(12)
N3	0.2666(2)	-0.0094(6)	0.1009(3)	0.0325(10)
C11	0.1657(3)	-0.0961(9)	-0.0038(3)	0.0386(13)
C12	0.1256(4)	-0.1434(11)	-0.0933(4)	0.0559(19)
N4	0.1449(2)	-0.1017(7)	0.0585(3)	0.0361(10)
N5	0.0830(2)	-0.1621(8)	0.0459(3)	0.0427(12)
C13	0.0705(3)	-0.1573(9)	0.1174(4)	0.0411(13)
C131	0.0077(3)	-0.2312(10)	0.1135(4)	0.0485(15)
C132	-0.0455(2)	-0.3020(7)	0.0296(3)	0.0230(9)
C133	-0.0953(5)	-0.3664(14)	0.0663(6)	0.079(3)
C134	-0.0814(5)	-0.3511(14)	0.1470(6)	0.080(3)
S135	-0.01130(15)	-0.2609(4)	0.1990(2)	0.0954(8)
O2	0.1088(2)	-0.0990(7)	0.1893(3)	0.0468(11)
O3	0.4614(3)	0.2544(9)	0.4486(4)	0.0652(17)
HO3A	0.474(6)	0.306(16)	0.433(7)	0.078
HO3B	0.477(5)	0.258(14)	0.498(6)	0.078

### Infrared spectroscopy

The main vibrational bands of the ligands  $\text{H}_2\text{dapf}$  and  $\text{H}_2\text{dapt}$ , and their complexes are shown in Table 4. The disappearance of the  $\nu(\text{NH})$  and  $\nu(\text{CO})$  bands in complexes **1**, **4**, **5** and **8**, derived from the most acidic organotin precursors, namely  $\text{MeSnCl}_3$  and  $\text{Ph}_2\text{SnCl}_2$ , is a conse-

**Table 3.** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[\text{Me}_2\text{Sn}(\text{Hdapt})]\text{Br}\cdot\text{H}_2\text{O}$ .

Sn-C1	2.106(7)	C1-Sn-C2	165.5(3)
Sn-C2	2.102(6)	C1-Sn-O1	81.1(2)
Sn-O1	2.493(4)	C1-Sn-O2	88.5(2)
Sn-O2	2.209(4)	C1-Sn-N2	86.8(2)
Sn-N2	2.469(4)	C1-Sn-N3	94.8(2)
Sn-N3	2.327(4)	C1-Sn-N4	94.9(2)
Sn-N4	2.255(5)	C2-Sn-O1	84.4(2)
O1-C3	1.241(7)	C2-Sn-O2	91.2(2)
O2-C13	1.286(7)	C2-Sn-N2	87.2(2)
C3-N1	1.355(7)	C2-Sn-N3	94.8(2)
C13-N5	1.322(8)	C2-Sn-N4	89.7(2)
N1-N2	1.366(7)	O1-Sn-O2	89.64(14)
N4-N5	1.375(6)	O1-Sn-N2	64.66(14)
N1-HN1	0.67(7)	O2-Sn-N4	70.62(16)
		N2-Sn-N3	65.81(15)
		N3-Sn-N4	69.22(16)

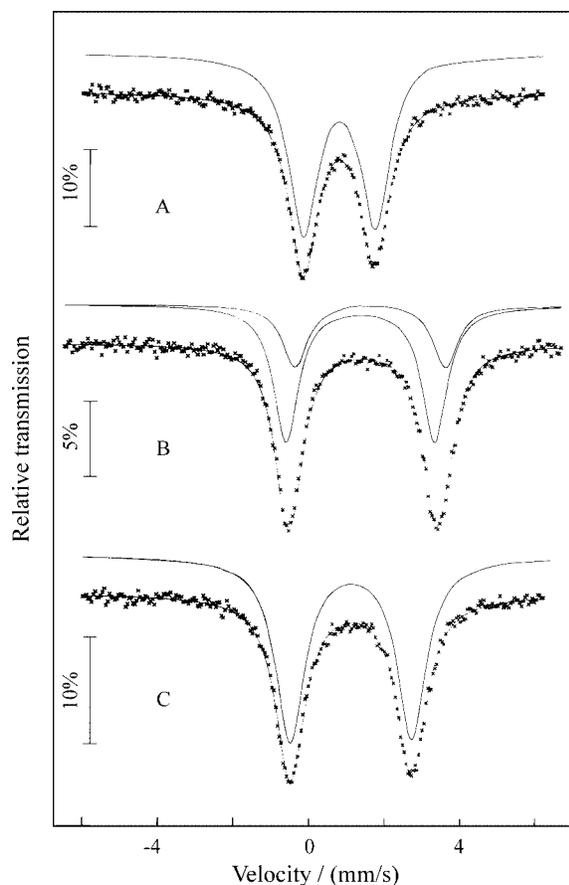
quence of the double deprotonation of the ligands, indicating that these groups are involved in the formation of deprotonated complexes via enolisation. On the other hand, the IR spectra of complexes **2**, **3**, **6** and **7**, obtained with the same ligands and the less acidic precursors  $\text{Me}_2\text{SnCl}_2$  and  $\text{Me}_2\text{SnBr}_2$  in this region are different, showing that the  $\nu(\text{CO})$  band shifts to lower frequencies, which is indicative of bonding of the carbonyl oxygen to the metal atom.

The position of the  $\nu(\text{NH})$  absorption shifted to smaller frequencies in complexes **2** and **3**, is probably due to the hydrogen bond in which the N-H group is involved being weaker than in free ligands. The N5-HN5 distance<sup>3</sup> of  $0.82(6)^\circ$  found in complex **2** is longer than the N1-HN1 distance of  $0.67(7)^\circ$  found here in complex **7**. The IR results suggest that deprotonation may not occur upon complexation with  $\text{Me}_2\text{SnX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ). However, the structure determined by X-ray diffraction of the complexes **2** and **7**, shows that partial deprotonation of the ligands indeed take place.

It is seen from Table 4 that  $[\nu(\text{CO}) + \nu(\text{CN})]$ ,  $\delta(\text{CH})_{\text{aryl}}$  and  $\delta(\text{CH})_{\text{alkyl}}$  absorption bands have shifted to higher frequencies in all the complexes. This is due to a greater rigidity shown by these groups. Similar results can be found in the literature<sup>1,3,11</sup>.

### <sup>1</sup>H-NMR spectroscopy

Table 5 shows the  $^2\text{J}(^{117,119}\text{Sn}, ^1\text{H})$  coupling constants only for the ionic complexes **2**, **3**, **6** and **7**, obtained from the partial deprotonation of  $\text{H}_2\text{dapf}$  and  $\text{H}_2\text{dapt}$ . The neutral complexes **1**, **4**, **5** and **8**, resulting from the double depro-



**Figure 3.** Experimental, partial and fitted Mössbauer spectra at liquid nitrogen temperature of A: [MeSnCl(dapf)], B: [Me<sub>2</sub>Sn(Hdapt)]<sub>2</sub> [Me<sub>2</sub>SnCl<sub>4</sub>] and C: [Ph<sub>2</sub>Sn(dapt)].

tonation showed poor solubility in CDCl<sub>3</sub> and in other usual solvents. The observed Sn-H coupling constants are in the range characteristic of heptacoordinated organotin(IV) complexes<sup>11</sup>. <sup>2</sup>J values are very close for the heptacoordinated complexes **2**, **3**, **6** and **7**, suggesting similar structures for these species. The same can be concluded for the anionic hexacoordinated counter ions in **2**, **6** and **9**.

### Mössbauer spectroscopy

<sup>119</sup>Sn Mössbauer spectroscopy was performed on all eight complexes, giving the results in Table 5, which includes parameters from the literature for comparison. Some of the spectra are shown in Fig. 3.

All the complexes present one heptacoordinated Sn(IV) site, except **2** and **6** which show the presence of two different Sn(IV) sites in a 2:1 ratio. The most abundant site corresponds to a monocationic complex with heptacoordinated Sn(IV), in a distorted pentagonal bipyramidal geometry, and the other site corresponds to the hexacoordinated Sn(IV) which is a dianionic complex acting as counter ion. This conclusion is in accordance with single crystal X-ray analysis<sup>3</sup> of the complex **2**.

The isomer shift ( $\delta$ ) of the complex **1** (0.68 mm/s) and **5** (0.65 mm/s) are lower than that of the parent acid MeSnCl<sub>3</sub><sup>14</sup> (1.20 mm/s). The same is true for the heptacoordinated site of **2** (1.29 mm/s) and **6** (1.25 mm/s), **3** (1.31 mm/s) and **7** (1.25 mm/s), and **4** (1.01 mm/s) and **8** (1.03 mm/s) compared to their parent acids Me<sub>2</sub>SnCl<sub>2</sub><sup>14</sup> (1.49 mm/s), Me<sub>2</sub>SnBr<sub>2</sub><sup>15</sup> (1.59 mm/s) and Ph<sub>2</sub>SnCl<sub>2</sub><sup>14</sup> (1.32 mm/s), respectively.

Isomer shifts decrease on complexation, as a result of rehybridization to higher coordination for Sn atoms in the complexes, indicating lower s-electron density at the Sn nucleus in the complexes as compared to the parents acids. This can be attributed to a greater involvement of d-orbitals, which now take part in the Sn(IV) hybridization scheme, thus reducing the weight of s-orbitals in the overall hybridization of the metal<sup>16,17</sup>. This conclusion is consistent with that observed for the Sn-H coupling constants, *i.e.*, an increase in the coordination number produces an increase in <sup>2</sup>J values<sup>1,11</sup> (Table 5). Similar results have been reported for a great variety of other Sn(IV) compounds<sup>1,18,19</sup>.

The complexes of the same Sn(IV) precursor with different ligands, *i.e.*, **1** and **5**, **2** and **6**, **3** and **7**, and **4** and **8**, have very similar isomer shifts. This is in accordance to the fact that the only difference between the ligands is in the 5-member ring, which has oxygen in H<sub>2</sub>dapf and sulfur in H<sub>2</sub>dapt. Since this difference is outside of the coordination sphere of the Sn atom, no sensible change in the s-electron density of Sn(IV) nucleus is expected.

From Table 5 it can be seen that, except for the complex **7**, the same conclusion is true for the quadrupole splittings. The difference between complex **3** ( $\Delta = 4.01$  mm/s) and **7** ( $\Delta = 3.80$  mm/s) may be related to the presence of a H<sub>2</sub>O molecule in **7**.

On the other hand, the complexes of the same ligand with different Sn(IV) precursors show that the inverse dependence of the isomer shift values with the electronegativity of the substituents is quite reasonable<sup>18-21</sup>. This behavior can be seen either for the complexes of H<sub>2</sub>dapf or H<sub>2</sub>dapt. Complexes **1**, **2** (monocationic), **3** and **4** have the same ligand H<sub>2</sub>dapf in the equatorial plane and different axial groups. Going from **1** to **2**, chloride was replaced by a less electronegative Me group, which accounts for higher  $\delta$  of **2** compared to **1**. Complexes **2** and **3** have the same axial groups, therefore the same  $\delta$  is observed. Now going from **3** to **4**, Me is replaced by a more electronegative group Ph, leading to a decrease in  $\delta$ .

The Mössbauer parameters  $\delta$  and  $\Delta$  obtained for the dianionic complexes **2** and **6** are in agreement with similar species, complexes **10**, **11** and **12** (Table 5).

Quadrupole splitting ( $\Delta$ ) values, presented in Table 5, are not sufficient to characterize a Sn(IV) complex as either tetra-, penta-, hexa-, or heptacoordinated<sup>1</sup>. However, a

**Table 4.** Main IR bands (cm<sup>-1</sup>) of the ligands H<sub>2</sub>dapf and H<sub>2</sub>dapt, and their complexes.

Compound	$\nu(\text{NH})$	$\nu(\text{CO})$	$\nu(\text{CO}) + \nu(\text{CN})$	$\delta(\text{CH})_{\text{aryl}}$	$\delta(\text{CH})_{\text{alkyl}}$
H <sub>2</sub> dapf	3224m	1682vs	1522s	1470s	1450s
1. [MeSnCl(dapf)]	-	-	1553m	1506m	1474s
2. [Me <sub>2</sub> Sn(Hdapf)] <sub>2</sub> [Me <sub>2</sub> SnCl <sub>4</sub> ]	3189w	1641m	1552m	1519m	1466m
3. [Me <sub>2</sub> Sn(Hdapf)]Br	3215w	1639m	1552m	1497m	1462m
4. [Ph <sub>2</sub> Sn(dapf)]	-	-	1549m	1498m	1475m
H <sub>2</sub> dapt	3166m	1698vs	1518s	1447s	1422m
5. [MeSnCl(dapt)]	-	-	1528m	1492m	1438m
6. [Me <sub>2</sub> Sn(Hdapt)] <sub>2</sub> [Me <sub>2</sub> SnCl <sub>4</sub> ]	3167w	1606m	1530m	1480m	1423m
7. [Me <sub>2</sub> Sn(Hdapt)]Br.H <sub>2</sub> O	3184w	1614m	1528s	1483m	1430m
8. [Ph <sub>2</sub> Sn(dapt)]	-	-	1526m	1484m	1427m

successful correlation between quadrupole splitting and the structure of different coordinated Sn(IV) using, either simple point-charge approach<sup>10,22-24</sup> or a more elaborate hybridization treatment<sup>25</sup>, has been reported. According to these models, one assumes that L, a parameter [L], is assigned to each ligand, which makes a fixed and independent contribution to the quadrupole splitting.

For Sn(IV) complexes containing SnR<sub>2</sub> moiety, such a quadrupole splitting is dominated by highly covalent Sn-C bonds, and one can show by ignoring the contribution of the other ligands, that  $\Delta$  is given by<sup>22,23</sup>,

$$|\Delta| = 4 [R] \left(1 - \frac{3}{4} \sin^2\theta\right)^{1/2} \quad (1)$$

where [R] denotes the partial quadrupole splitting of the group R and  $\theta$  is the R-Sn-R angle. Eq. (1) has been satisfactorily applied to four-, five- and six-coordinated Sn(IV) compounds, using appropriate values of [R] for each coordination number<sup>21,22,24</sup>. Although little Mössbauer and structural data are available in the literature for heptacoordinated Sn(IV) compounds, the existing data have shown a reasonable and consistent behavior for Eq. (1)<sup>1,9,23</sup>.

Considering the complexes **2** and **7** whose structure were determined by single crystal X-ray diffraction, the [Me] can be estimated. Inserting the values  $\Delta = 3.96$  mm/s and  $\theta = 166^\circ$ <sup>3</sup> for the heptacoordinate site of complex **2** and  $\Delta = 3.80$  mm/s and  $\theta = 164.9^\circ$  of **7** into Eq. (1) we get [Me] = -1.01 mm/s and [Me] = -0.98 mm/s, respectively. These values agree within 4% with [alkyl] = -0.97 mm/s reported for heptacoordinate Sn(IV) complexes embodying pentacoordinate ligands<sup>1</sup>. Now using the value [Me] = 1.00 mm/s (average of -1.01 and -0.98 mm/s) and  $\Delta = 4.01$  mm/s

of complex **3** and  $\Delta = 3.94$  mm/s for the heptacoordinate Sn(IV) of complex **6**, Eq. (1) allows us to predict for the Me-Sn-Me angle  $\theta = 180^\circ$  and  $\theta = 169^\circ$  for the complexes **3** and **6**, respectively. The later value is in excellent agreement with  $\theta = 166^\circ$  found for complex **2**.

The Ph-Sn-Ph angle for the phenyl derivatives, complexes **4** and **8**, can be also predicted through Eq. (1) and appropriate values of [Ph].

Combining Mössbauer and structural data for the heptacoordinate complex [Ph<sub>2</sub>Sn(Hdaptsc)]Cl<sup>8</sup> [H<sub>2</sub>dapstc = 2,6-acetylpyridinebis(thiosemicarbazone)], *i.e.*,  $\Delta = 3.13$  mm/s) and  $\theta = 167.9^\circ$ , we found [Ph] = -0.80 mm/s, which agrees very well with a previous reported<sup>1</sup> value [Ph] = -0.78 mm/s. Inserting  $\Delta = 3.22$  mm/s **4** and  $\Delta = 3.24$  mm/s **8** and [Ph] = -0.80 mm/s into Eq. (1) we get  $\theta = 180^\circ$  for both complexes.

Finally the predicted Me-Sn-Me angles for the hexacoordinate Sn(IV) sites of complexes **2** and **6**, namely [Me<sub>2</sub>SnCl<sub>4</sub>]<sup>2-</sup> can be estimated using [Me] = -1.03 mm/s for hexacoordinate species<sup>21,22</sup>. Inserting  $\Delta = 4.11$  mm/s **2** and  $\Delta = 3.99$  mm/s **6** together with [Me] = -1.03 mm/s into Eq. (1) we obtained  $\theta = 175^\circ$  (X-ray diffraction:  $180^\circ$ ) and  $\theta = 163^\circ$ , respectively for Me-Sn-Me angle of complexes **2** and **6**.

The correlation between Mössbauer and X-ray structural data, using a simple point-charge model, gave values for [Me] and [Ph] in excellent agreement with earlier reported values. We think that this correlation is important considering the poor number of published structural data for heptacoordinate complexes as compared to penta- and hexacoordinate species.

**Table 5.** <sup>1</sup>H-NMR and Mössbauer spectroscopy data for the complexes.

Complex	C.N	<sup>2</sup> J( <sup>117</sup> Sn, <sup>1</sup> H) (Hz)	<sup>2</sup> J( <sup>119</sup> Sn, <sup>1</sup> H) (Hz)	δ (mm/s)	Δ (mm/s)
1. [MeSnCl(dapf)] <sup>a</sup>	7	-	-	0.68	1.89
2. [Me <sub>2</sub> Sn(Hdapf)] <sub>2</sub>	7	107	110	1.29	3.96
[Me <sub>2</sub> SnCl <sub>4</sub> ] <sup>a</sup>	6	70	81	1.56	4.11
3. [Me <sub>2</sub> Sn(Hdapf)]Br <sup>a</sup>	7	99	109	1.31	4.01
4. [Ph <sub>2</sub> Sn(dapf)] <sup>a</sup>	7	-	-	1.01	3.22
5. [MeSnCl(dapt)] <sup>a</sup>	7	-	-	0.65	1.83
6. [Me <sub>2</sub> Sn(Hdapt)] <sub>2</sub>	7	106	113	1.25	3.94
[Me <sub>2</sub> SnCl <sub>4</sub> ] <sup>a</sup>	6	78	81	1.49	3.99
7. [Me <sub>2</sub> Sn(Hdapt)]Br.H <sub>2</sub> O <sup>a</sup>	7	106	111	1.25	3.80
8. [Ph <sub>2</sub> Sn(dapt)] <sup>a</sup>	7	-	-	1.03	3.24
9. [C <sub>5</sub> H <sub>7</sub> N <sub>2</sub> ] <sub>2</sub> [Me <sub>2</sub> SnCl <sub>4</sub> ] <sup>b</sup>	6	79	83	-	-
10. (Cs) <sub>2</sub> [Me <sub>2</sub> SnCl <sub>4</sub> ] <sup>c</sup>	6	-	-	1.63	4.32
11. [2-H <sub>3</sub> NC <sub>6</sub> H <sub>4</sub> C(O)NH <sub>2</sub> ] <sub>2</sub> [Me <sub>2</sub> SnCl <sub>4</sub> ] <sup>c</sup>	6	92	-	1.19	4.09
12. (C <sub>5</sub> H <sub>5</sub> NH) <sub>2</sub> [Me <sub>2</sub> SnCl <sub>4</sub> ] <sup>c</sup>	6	-	-	1.59	4.32

Abbreviations: C.N = coordination number, C<sub>5</sub>H<sub>7</sub>N<sub>2</sub> = 2 aminopyridine, H<sub>2</sub>dapf = 2,6-diacetylpyridinebis(2-furanoylhydrazone), H<sub>2</sub>dapt = 2,6-diacetylpyridinebis(2-thenoylhydrazone), δ = isomer shift (±0.01 mm/s) relative to CaSnO<sub>3</sub> at room temperature, Δ = quadrupole splitting (±0.02 mm/s), <sup>a</sup>this work, <sup>b</sup>Ref. 12, <sup>c</sup>Ref. 13.

Concluding, eight new heptacoordinated organotin(IV) complexes of the ligands H<sub>2</sub>dapf and H<sub>2</sub>dapt were obtained, which were investigated by means of microanalysis, IR, <sup>1</sup>H-NMR, Mössbauer spectroscopy and X-ray diffraction.

The crystallographic data were deposited at the Cambridge Crystallographic Data Centre under the number CCDC114597.

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