J. Braz. Chem. Soc., Vol. 12, No. 6, 722-728, 2001.
Printed in Brazil

0103 - 5053 $6.00+0.00

Article

Organotin(IV) Derivatives of 2-Acetylpyridine-N(4)-Phenylthiosemicarbazone, HAP4P, and 2-Hydroxyacetophenone-N(4)-Phenylthiosemicarbazone, H_2DAP4P. Crystal and Molecular Structure of [$SnMe_2$(DAP4P)] and [$SnBu_2$(DAP4P)]

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As reações de 2-acetilpiridina-N(4)-feniltiosemicarbazona, HAP4P, e 2-hydroxiacetofenona-N(4)-feniltiosemicarbazona, H_2DAP4P, com $R_{4-m}SnX_m$ (m = 2, 3; R = Me, ^{n}Bu, Ph e X = Cl, Br) levaram à formação de complexos organoestânicos hexa- e penta-coordenados, que foram estudados por análise elementar, espectroscopias no IV, RMN de ^{1}H e Mössbauer. As estruturas moleculares dos complexos [$SnMe_2$(DAP4P)] e [Sn^nBu_2(DAP4P)] foram determinadas por análises de difração de raios X. Nos compostos [$SnClMe_2$(AP4P)] e [$SnBrMe_2$(AP4P)], o ligante desprotonado $AP4P^-$ está N,N,S-ligado aos átomos de Sn(IV) que exibem cordenação octaédrica fortemente distorcida. As estruturas dos complexos [$SnMe_2$(DAP4P)] e [Sn^nBu_2(DAP4P)] revelaram que o ânion $DAP4P^{2-}$ age como um ligante O,N,S-tridentado. Nestes casos os átomos de Sn(IV) adotam coordenação com geometria bipiramidal trigonal fortemente distorcida, com o átomo de N e os dois átomos de C no plano equatorial, enquanto que os átomos de O e S ocupam as posições axiais.

The reactions of 2-acetylpyridine-N(4)-phenylthiosemicarbazone, HAP4P, and 2-hydroxyacetophenone-N(4)-phenylthiosemicarbazone, H_2DAP4P, with $R_{4-m}SnX_m$ (m = 2, 3; R = Me, ^{n}Bu, Ph and X = Cl, Br) led to the formation of hexa- and penta-coordinated organotin(IV) complexes, which were studied by microanalysis, IR, ^{1}H-NMR and Mössbauer spectroscopies. The molecular structures of [$SnMe_2$(DAP4P)] and [Sn^nBu_2(DAP4P)] were determined by single-crystal X-ray diffraction studies. In the compounds [$SnClMe_2$(AP4P)] and [$SnBrMe_2$(AP4P)], the deprotonated ligand $AP4P^-$ is N,N,S-bonded to the Sn(IV) atoms, which exhibit strongly distorted octahedral coordination. The structures of [$SnMe_2$(DAP4P)] and [Sn^nBu_2(DAP4P)] revealed that the $DAP4P^{2-}$ anion acts as a O,N,S-tridentate ligand. In these cases, the Sn(IV) atoms adopt a strongly distorted trigonal bipyramidal configuration where the azomethine N and the two C atoms are on the equatorial plane while the O and the S atoms occupy the axial positions.

Keywords: thiosemicarbazone complexes, organotin(VI) complexes, crystal structure analyses

Introduction

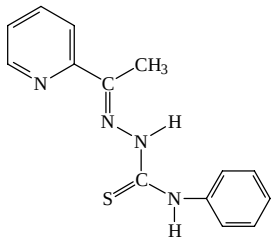
N,N,S- and O,N,S-tridentate thiosemicarbazones derived from 2-formyl- and 2-acetylpyridine form two important classes of compounds possessing biological activity[1-3]. In this context, a number of complexes of first-row transition elements have been extensively studied by X-ray structural analysis and a number of other spectroscopic techniques[2,4]. However organotin(IV) complexes of thiosemicarbazones have received less attention.

The chelating behaviour of N,N,S-tridentate thiosemicarbazones has been investigated and three different complexation modes have been identified. In the most common one, the compound acts as a mononegative N,N,S-tridentate ligand and coordinates to the metal through both the nitrogen and the thiolate sulphur atoms. This coordination mode was observed in [SnX_3(FPT)] (X = Cl, Br, I and HFPT = 2-formylpyridinethiosemicarbazone)[5]. A second coordination mode was reported for a series of octahedral 1:1 adducts of the general formula [$SnCl_2R_2$(HFPT)][6], where the thiosemicarbazone molecule acts as a neutral N(azomethine),S-bidentate ligand. Finally, a third coordination mode was found in [$SnClMe_2$(FPT)][2]. In this trigonal bipyramidal 1:1 complex, the ligand acts as

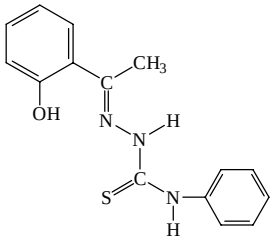
a mononegative N,S-bidentate ligand, while the pyridine nitrogen atom remains uncoordinated.

A number of organotin(IV) complexes containing O,N,S- and O,N,O-tridentate ligands and exhibiting biological or pharmacological activity have been studied, but structural features which may affect the antitumor activity and cytotoxicity of organotin(IV) are still uncertain[7].

These observations have increased our interest in the structural properties of these kinds of ligands and have motivated us to study the reactions of 2-acetylpyridine-N(4)-phenylthiosemicarbazone, HP4P, and 2-hydroxy-acetophenone-N(4)-phenylthiosemicarbazone, H_2DAP4P, with organotin(IV) compounds. The structures of these ligands are shown below.



HAP4P



H_2DAP4P

Experimental

Syntheses

HAP4P and H_2DAP4P were prepared from a 1:1 molar ratio of N(4)-phenylthiosemicabazide and the appropriate ketone (2-acetylpyridine or 2-acetylphenol) in boiling EtOH (15 mL) for 30 min. After cooling, the compounds were obtained as pale-yellow needles (HAP4P: mp 171-174 °C; H_2DAP4P: mp 120-122 ºC) which were filtered and dried under vacuum over $CaCl_2$. The organotin(IV) complexes were obtained by the following procedure: 0.20 mmol of the appropriate ligand were dissolved by refluxing in dry MeOH for 5 min. To this solution were added 0.21 mmol of one organotin(IV) species in 5 mL of MeOH, and the resulting mixture was refluxed for 1 h and filtered to give a clear solution. Cooling the solution and slowly evaporating the solvent led to crystalline products with yields on the order of 70%. Single crystals suitable for X-ray diffraction were isolated only for complexes **2**, **3**, **7** and **8**. The structures of **2** and **3** were solved and described previously[8]. The microanalyses were performed using a HERAEUS CHN rapid elemental analyzer, giving the following results for C, H and N:

[$SnCl_2Me$(AP4P)] (**1**). Anal. Calc. for $C_{15}H_{17}Cl_2N_4SSn$: C, 37.95; H, 3.61; N, 11.80. Found: C, 38.81; H, 3.56; N, 12.81%.

[$SnClPh_2$(AP4P)] (**2**). Anal. Calc. for $C_{26}H_{23}ClN_4SSn$: C, 54.06; H, 4.02; N, 9.70. Found: C, 52.48; H, 4.22; N, 11.10%.

[$SnClMe_2$(AP4P)] (**3**). Anal. Calc. for $C_{16}H_{19}ClN_4SSn$: C, 42.37; H, 4.22; N, 12.35. Found: C, 42.31; H, 4.19; N, 12.25%.

[$SnBrMe_2$(AP4P)] (**4**). Anal. Calc. for $C_{16}H_{19}BrN_4SSn$: C, 38.59; H, 3.85; N, 11.25. Found: C, 37.07; H, 3.55; N, 11.12%.

[$SnCl^nBu_2$(AP4P)] (**5**). Anal. Calc. for $C_{22}H_{31}ClN_4SSn$: C, 49.14; H, 5.81; N, 10.42. Found: C, 48.82; H, 5.75; N, 10.36%.

[$SnCl_2Me$(HDAP4P)] (**6**). Anal. Calc. for $C_{16}H_{17}Cl_2N_3SSn$: C, 39.29; H, 3.48; N, 8.59. Found: C, 41.89; H, 4.00; N, 8.69%.

[$SnPh_2$(DAP4P)] (**7**). Anal. Calc. for $C_{27}H_{23}N_3OSSn$: C, 58.30; H, 4.17; N, 7.55. Found: C, 59.56; H, 4.40; N, 7.75%.

[$SnMe_2$(DAP4P)] (**8**). Anal. Calc. for $C_{17}H_{19}N_3OSSn$: C, 47.25; H, 4.43; N, 9.72. Found: C, 47.13; H, 4.29; N, 9.71%.

[Sn^nBu_2(DAP4P)] (**9**). Anal. Calc. for $C_{23}H_{31}N_3OSSn$: C, 53.51; H, 6.05; N, 8.14. Found: C, 53.38; H, 5.82; N, 8.13%.

Infrared spectra were recorded on a Nicolet 5ZDX-FT spectrophotometer in the 4000-400 cm^{-1} range using KBr pellets. Due to the poor solubility of some of the complexes, it was possible to obtain ^1H NMR spectra only for **3**, **4** and **8**, in $CDCl_3$, using a 250 MHz Bruker spectrometer. Chemical shifts are relative to internal tetramethylsilane. ^{119}Sn Mössbauer spectra were measured using a Model AM-1 Mössbauer efect spectrometer, moving a 15-mCi $BaSnO_3$ 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.

Crystal structure determinations

Single-crystal X-ray diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer, with a graphite monochromated $K_\alpha Mo$ radiation (λ = 0.71073 Å), obtained in a fine focus sealed tube[9].

Experimental parameters and crystallographic data for both complexes are shown in Table 1. In both cases, the data reductions were carried out with the XCAD-4 software[10]. The structures were solved using the heavy-atom method[11]. The SHEL97 software[12] was used for refinement by full-matrix least-squares calculations.

Table 1. Crystallographic data and experimental parameters.

	[$SnMe_2$(DAP4P)] (**8**)	[Sn^nBu_2(DAP4P)] (**9**)
Molecular Formula	$C_{17}H_{19}N_3OSSn$	$C_{23}H_{31}N_3OSSn$
Molecular Weight	432.10	516.26
Crystal System	orthorhombic, Pbca	Trigonal, R3
a (Å)	8.0260(5)	31.694(5)
b (Å)	18.5789(19)	31.694(5)
c (Å)	24.0779(15)	12.488(2)
V (Å)^3	3590.4(5)	10864(3)
Z	8	18
D_{calc} (g cm^{-3})	1.599	1.420
Data Collection		
h	-1 → 11	0 → 38
k	-1 → 26	0 → 38
l	-1 → 33	0 → 17
μ (mm^{-1})	1.547	1.163
T (K)	298	283
F(000)	1728.0	4752.0
No. measured reflections	5890	3708
No. of independent reflections	5245	3641
No. of reflections with I ³ 4σ(I)	4060	1926
R_{int}	0.019	0.033
Refinement		
No. of refined parameters	211	262
$R[F^2 > 4s(F)^2]$	0.031	0.048
S	1.05	1.03

Results and Discussion

*Crystal structures of [$SnMe_2$(DAP4P)](**8**) and [Sn^nBu_2(DAP4P)]* (**9**).

The structure determinations of compounds **8** and **9** revealed similar molecular structures with the occurrence of pentacordinated Sn(IV) complexes, with a trigonal bipyramidal (TBP) geometry. In the coordination polyhedron of the two compounds, two carbons (from alkyl groups) and the N(1) atom (from the thiosemicarbazone) occupy the equatorial plane. Atoms S and O occupy axial positions. Figures 1 and 2 show the molecules along with the labeled atoms.

In both complexes, the largest bond angle involving the Sn(IV) atom was O–Sn–S: 151.32(6) and 156.96(15)°, respectively, indicating strong deviations from the ideal value of 180°. Dihedral angles of 88 and 87° were observed between the planes through Sn, C(16), C(17), N(1) and Sn, O, S (**8**) and Sn, C(16), C(20), N(1) and Sn, O, S (**9**), respectively. Selected bond distances and angles of the two complexes are shown in Table 2.

The structures of the complexes [$SnPh_2$(Hdaptsc)]Cl[13] (**A**), H_2daptsc = 2,6-diacetylpyridine*bis*(thiosemicarbazone), [$SnMe_2$(Hdapf)]$_2$[$SnCl_4Me_2$][14] (**B**), H_2dapf = 2,6-diacetylpyridine*bis*(2-furoylhydrazone) and [$SnMe_2$(Hdapt)]Br.H_2O[15] (**C**), H_2dapt = 2,6-diacetylpyridine*bis*(2-tenoylhidrazone) showed that one proton from the azomethine group of the ligand molecules has been eliminated upon coordination. The proton on the other azomethine group remained bonded to the nitrogen after coordination and the ligand showed one S atom as a thione (or O as keto) and the other S atom as a thiolate (or O as enolate), as evidenced by the differences observed in bond distances between the sulfur (or oxygen) and Sn(IV) atoms and between the sulfur (or oxygen) and the carbon atoms. Thus, the following bond distances were observed in the compounds mentioned: **A**[13], Sn–S(1)

Table 2. Selected bond distances (Å) and angles (°) for [$SnMe_2$(DAP4P)] (**8**) and [Sn^nBu_2(DAP4P)] (**9**).

	8	**9**
Sn–O	2.095(2)	2.120(4)
Sn–N(1)	2.233(2)	2.194(6)
Sn–S	2.5296(8)	2.547(2)
S–C(1)	1.734(3)	1.754(8)
N(1)–N(2)	1.390(3)	1.382(8)
C(1)–N(2)	1.291(3)	1.292(8)
C(1)–N(3)	1.375(3)	1.365(9)
N(3)–C(10)	1.417(4)	1.396(9)
N(1)–C(2)	1.307(3)	1.311(8)
O–C(9)	1.336(3)	1.338(8)
Sn–C(16)	2.117(3)	2.129(7)
Sn–C(17)	2.123(3)	2.165(8)[a]
O–Sn–S	151.32(6)	156.69(15)
O–Sn–N(1)	79.50(7)	80.7(2)
O– Sn–C(16)	88.80(11)	94.1(2)
O–Sn–C(17)	98.55(12)	85.5(3)[b]
S – Sn – N(1)	76.71(6)	76.24(15)
S–Sn–C(16)	95.54(11)	97.6(2)
S–Sn–C(17)	102.82(11)	100.2(3)[c]
N(1)–Sn–C(16)	132.48(11)	100.2(3)
N(1)–Sn–C(17)	104.81(11)	112.6(3)[d]
O–C(9)–C(4)	122.7(2)	121.5(6)
C(16)–Sn–C(17)	122.50(13)	134.4(4)[e]

[a] Sn–C(20), [b] O-Sn-C(20), [c] S-Sn-C(20), [d] S-Sn-C(20), [e] C(16)-Sn-C(20)

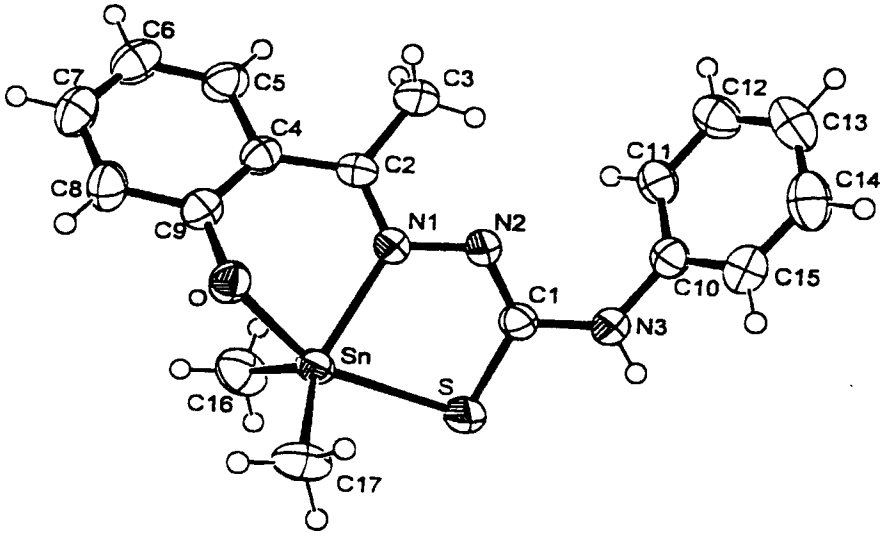


Figure 1. Perspective view of [$SnMe_2$(DAP4P] (**8**) showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

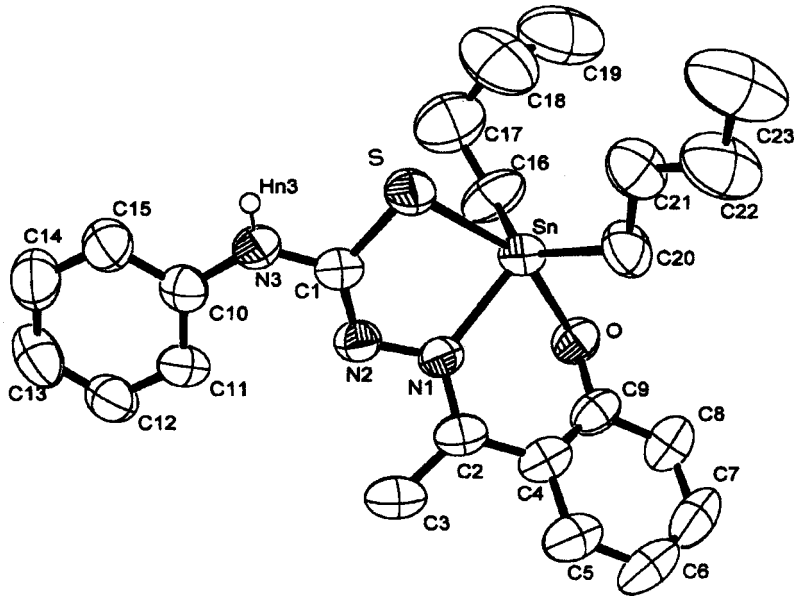


Figure 2. Perspective view of [Sn^nBu_2(DAP4P] (**9**) showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

(thiolate form) 2.592(1), S(1)–C(13) 1.731(5), Sn–S(2) (thione form) 2.703(1), and S(2)–C(23) 1.694(6) Å; in complex **B**[14], the distances are: Sn(2)–O(1) (enolate form) 2.227(4), O(1)–C(4) 1.276(8), Sn(2)–O(2) (keto form) 2.474(4) and O(2)–C(14) 1.242(7) Å; for **C**[15] the values are: Sn–O(1) (keto) 2.493(4), O(1)–C(3) 1.241(7), Sn–O(2) (enolate) 2.209(4) and O(2)–C(13) 1.286(7) Å.

In the cases, of compounds **8** and **9**, part of the thiosemicarbazone derivative molecule is planar. The observed dihedral angle between the phenyl rings was 51° for complex **8** and 57° for complex **9.** The packing mode is determined by the nature of the alkyl ligands. The presence of butyl groups in **9**, larger and with larger displacement parameters, prevents the orthorhombic symmetry once the average distances between the thiosemicarbazones are not very different. In both structures there are intermolecular interactions involving N(3)–HΛO. The geometric features of these interactions are respectively: N(3)–H 0.85 Å, N(3)–HΛO (1/2 + x, 1/2 - y, 1 - z) 3.033 Å, N(3)–HΛO 179.1º for compound **8** and N(3)–H 0.86 Å, N(3)–HΛO 174.6º for compound **9**.

In complexes **3** and **4**, whose structures are nearly identical, except for the presence of a chloride ligand in **3** and a bromide ligand in **4**, the ligand molecule bears only one substituent on the pyridine ring[8]. The observed distances were: Sn–S 2.4728(8), S–C(10) 1.750(3) Å for the chloride complex and Sn–S 2.4743(12), S–C(10)

1.739(5) Å for the bromide complex, indicating that the S atom is coordinated in the thiolate form.

^{1}H NMR spectroscopy

The ^{1}H NMR spectrum of complex **8** showed two singlets at δ 2.7 and 0.7 [$^2J(^{119}Sn–CH_3)$ 73 Hz], due to two magnetically non-equivalent methyl groups assigned to N=C–CH_3 and Sn–CH_3, respectively. According to the literature, the use of the Lockhart-Manders[16] equation shown below and of the observed coupling constant of 73 Hz yields a C–Sn–C angle of 123º , in excellent agreement with the angle of 122.50(13)º observed in the solid state. This data suggests that the basic structural features of the solid-state phase remain in solution.

$$\theta = 0.0161\{^2J(^{119}Sn–CH_3)\}^2 - \\ - 1.32\{^2J(^{119}Sn–CH_3)] + 133.4$$

A similar result has been reported for a trigonal bipyramidal (TBP) complex with an analogous coordination geometry, [$SnMe_2$(L)][17] (H_2L = salicylaldeydethiosemicarbazone). In this case, the $^2J(^{119}Sn–CH_3)$ was 70 Hz.

Infrared spectroscopy

Table 3 shows the assignment of the main IR absorption bands for the ligands and their complexes. In the 3463-1168 cm^{-1} region the HAP4P and H_2DAP4P ligands show bands attributed to hydrogen-bonded O–H and N–H overlapping with the C–H stretching absorptions of phenyl and pyridyl rings. As a result of the monodeprotonation of the HAP4P ligand and double deprotonation of the H_2DAP4P ligand (except in complex **6**), the spectra of compounds **1**-**5** and **7**-**9** lack bands located at 3241 and 3168 cm^{-1}, attributed to ν(NN–H), and retain the absorption bands found in the free ligands at 3301 and 3305 cm^{-1}, attributed to ν(PhN–H) vibrations, which are shifted to lower frequencies. Thus, the bands in the 3426-3237 cm^{-1} range are assigned to the ν(NN–H) stretching frequencies.

The ν(C=N) absorptions at 1523 and 1521 cm^{-1} for HAP4P and H_2DAP4P, respectively, are shifted to higher frequencies by *ca*. 15-30 cm^{-1} in the spectra of the complexes, indicating coordination of the azomethine nitrogen N(2) to the metal ion[18]. The same trend is exhibited by the bands at 1360 cm^{-1} for HAP4P and at 1366 cm^{-1} for H_2DAP4P.

The bands at 1189 and 782 cm^{-1} in HAP4P and at 1197 and 757 cm^{-1} in H_2DAP4P, which have a significant contribution from ν(C=S) stretching vibrations, are shifted to lower frequencies in the spectra of the complexes, suggesting coordination through the sulfur atom[18,19]. The far IR bands observed in the 509-504 cm^{-1} range were tentatively assigned to the ν(Sn–O) mode.

Mössbauer spectroscopy

^{119}Sn Mössbauer spectroscopy was performed on all nine complexes, giving the results shown in Table 4, which include parameters from the literature for comparison.

Complexes **1**-**6** exhibit octahedral coordination while complexes **7**-**9** adopt a strongly distorted trigonal bipyramidal (TBP) configuration where the anions AP4P$^-$ and HDAP4P$^-$ act as N,N,S- and O,N,S-tridentate ligands, respectively. Their isomer shifts (δ) are lower than those of the parent acids[15] [$SnCl_3Me$] (1.20 mm s^{-1}), [$SnCl_2Ph_2$] (1.32 mm s^{-1}), [$SnCl_2Me_2$] (1.49 mm s^{-1}), [$SnBr_2Me_2$] (1.59 mm s^{-1}) and [$SnCl_2{}^nBu_2$] (1.75 mm s^{-1}).

Isomer shifts always decrease upon adduct formation, as a result of rehybridization to higher coordination for the Sn(IV) atoms in the complexes in which s orbital participation is less than 25%. The reduction in the isomer shift in complex **6** (0.90 mm s^{-1}), compared to **1** (0.98 mm s^{-1}), is due to the structural differences between AP4P$^-$ and HDAP4P$^-$. The former ligand has one ligating pyridine N atom, whereas the latter one has a phenol O atom. Therefore, AP4P$^-$ is a much less electronegative ligand than HDAP4P$^-$, which accounts for the lower value of the isomer shift in complex **6**.

Table 3. Main IR bands (cm^{-1}) for the ligands HAP4P and H_2DAP4P and their complexes

Compound	ν(N–H)	ν(C=N, C=C)	ν(C–S) + ν(C–N)	ν(C=S)	ν(Sn–O)
HAP4P	3301, 3241	1598, 1523, 1468, 1444	1360	1189, 782	
[$SnCl_2Me$(AP4P)] (**1**)	3280	1597, 1544, 1497, 1453	1428	1163, 761	-
[$SnClPh_2$(AP4P)] (**2**)	3237, 3178	1596, 1535, 1498, 1457	1433	1160, 762	-
[$SnClMe_2$(AP4P)] (**3**)	3276	1596, 1532, 1497, 1458	1435	1160, 766	-
[$SnBrMe_2$(AP4P)] (**4**)	3243	1596, 1548, 1499, 1459	1433	1152, 761	-
[$SnBr{}^nBu_2$(AP4P)] (**5**)	3426, 3335	1601, 1520, 1493, 1480	1401	1159, 767	-
H_2DAP4P*	3305, 3168	1593, 1521, 1444	1366	1197, 757	-
[$SnCl_2$Me(HDAP4P)] (**6**)	3407, 3388	1599, 1574, 1501	1434	1178, 757	505
[$SnPh_2$(DAP4P)] (**7**)	3325	1599, 1543, 1494	1436	1183, 745	504
[$SnMe_2$(DAP4P)] (**8**)	3241	1595, 1570, 1537, 1494	1438	1190, 756	509
[$Sn{}^nBu_2$(DAP4P)] (**9**)	3245	1596, 1567, 1540, 1494	1434	1191, 744	509

* ν(O-H): 3463 cm^{-1}

Table 4. ^{119}Sn Mössbauer spectroscpy data for Sn(IV) complexes.

Complex	C.N.	δ (mm s^{-1})	Δ (mm s^{-1})	θ (C–Sn–C)$_{(exp.)}$
[$SnCl_2Me$(AP4P)] (**1**)	6	0.98(1)	1.96(1)	-
[$SnClPh_2$(AP4P)] (**2**)	6	1.26(1)	2.92(1)	-
[$SnClMe_2$(AP4P)] (**3**)	6	1.38(1)	3.35(1)	145º
[$SnBrMe_2$(AP4P)] (**4**)	6	1.42(1)	3.40(1)	144º
[$SnBr^nBu_2$(AP4P)] (**5**)	6	1.54(1)	3.50(1)	-
[$SnCl_2Me$(HDAP4P)] (**6**)	6	0.90(1)	2.02(1)	-
[$SnPh_2$(DAP4P)] (**7**)	5	1.09(1)	2.03(1)	-
[$SnMe_2$(DAP4P)] (**8**)	5	1.18(1)	2.41(1)	122º
[Sn^nBu_2(DAP4P)] (**9**)	5	1.31(1)	2.62(1)	134º
[$ClSnCl_2$(FPT)][a] (**10**)	6	0.58	0.00	-
[$MeSnCl_3$(BtSOMe)][b] (**11**)	6	0.98(1)	2.07(1)	-
[Ph_2SnCl(of)][c] (**12**)	6	1.10	2.61	-
[$Ph_2Sn(L_1)$][d] (**13**)	5	1.30	2.30	127º
[$Me_2Sn(L_1)$][d] (**14**)	5	1.27	2.43	127º
[$Bu_2Sn(L_2)$][e] (**15**)	5	1.28	2.85	-

Abreviations: C.N. = coordination number, HAP4P = 2-acetylpiridine-N(4)-phenylthiosemicarbazone, H_2DAP4P = 2-hydroxyacetophenone-N(4)-phenylthiosemicarbazone, BtSOMe = (2-methylsulphinyl)benzothiazole, Hof = 3-hydroxyflavone, H_2L_1 = salicilaldehydethiosemicarbazone, H_2L_2 = salicilaldehyde-2-furanthiosemicarbazone, [a]Ref. 5, [b]Ref. 23, [c]Ref. 22, [d]Ref. 18, [e]Ref. 24.

In complexes **2** to **5**, the ligand remains unchanged, but the phenyl groups in complex **2** (1.26 mm s^{-1}) were replaced by methyl groups in **3** (1.38 mm s^{-1}), the chloride in complex **3** was replaced by bromide in **4** (1.42 mm s^{-1}) and the methyl groups in complex **4** were replaced by *n*-butyl groups in **5** (1.54 mm s^{-1}). Again, a similar effect is observed as before, and the isomer shifts decrease on going from complex **5** to **2**. Similar results were observed for complexes **7** (1.09 mm s^{-1}), **8** (1.18 mm s^{-1}) and **9** (1.31 mm s^{-1}).

A somewhat analogous trend can be seen in literature examples, as shown in Table 4. Although the ligands are not the same in all cases, they are related, and one can see that lower δ values correspond to the complexes containing electronegative groups (Cl ou Ph), whereas alkyl groups (Me, ^{n}Bu), of low electronegativity, lead to higher δ values.

Quadrupole splitting (Δ) values, presented in Table 4, are not sufficient in themselves to characterize a Sn(IV) complex as either tetra-, penta-, hexa-, or hepta-coordinated[20]. However, Δ has been useful in distinguishing between *cis*-, *trans*-[SnX_4R_2] and [SnX_3R_2] configurations in complexes with octahedral and trigonal bipyramidal geometries, respectively. Thus, a complex with a *trans*-[SnX_4R_2] configuration usually has Δ values of *ca.* 4 mm s^{-1}, while a value of *ca.* 2 mm s^{-1} would be expected for a complex with a *cis*-SnX_4R_2 configuration. Sham and Bancroft[21], also using point charge calculations, have shown that the quadrupole splittings (Δ) for *trans*-[SnX_4R_2] compounds decrease smoothly from the value (4 mm s^{-1}) for a regular octahedral geometry (θ = 180º) as the structure becomes more distorted, *i.e.* the q angle (R-Sn-R) becomes less than 180º.

The quadrupole splitting (Δ) values, shown in Table 4, indicate that complexes **2**-**5** adopt a *trans*-[SnX_4R_2] arrangement and the octahedral diphenyl compound (complex **2**) is the most distorted among all of them. The values between 2.03-2.85 mm s^{-1} for complexes **7**-**9** and **13**-**15** are typical of diorganotin(IV) complexes in a distorted trigonal bipyramidal (TBP)[17,22] environment. The lower quadrupole splitting (Δ) value for complex **10** (0.0 mm s^{-1}) indicates that the charge distribution around the Sn(IV) nucleus is highly symmetrical[5] and the geometry is considerably non distorted.

Acknowledgments

The authors are grateful for financial support from CNPq, CAPES, FINEP, FAPEMIG and FAPESP in Brazil. The authors are grateful also to Dr. Julio Zukerman-Schpector for data collection, carried out on a CAD-4 at the Instituto de Química-USP.

Supplementary Information

Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. 149653 and 149654. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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Received: November 6, 2000
Published on the web: July 29, 2001
FAPESP helped in meeting the publication costs of this article.