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X-ray Crystallographic and Mössbauer Spectroscopic Applications in Dependence of Partial Quadrupole Splitting, [R], on the C–Sn–C Angle in Seven-Coordinated Diorganotin(IV) Complexes

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The synthesis and the IR, NMR (^{1}H, ^{13}C, and ^{119}Sn), and Mössbauer spectroscopies and single-crystal X-ray diffraction studies of seven-coordinated diorganotin(IV) complexes, namely, [Ph$_2$Sn(Hdapsc)]Cl·H$_2$O·DMF [**7**; H$_2$dapsc = 2,6-diacetylpyridine bis(semicarbazone)], [Me$_2$Sn(H2,6Achexim)]Br·H$_2$O [**8**; H$_2$2,6Achexim = 2,6-diacetylpyridine bis(3-hexamethyleneiminylthiosemicarbazone)], [Me$_2$Sn(dapmts)] [**9**; H$_2$dapmts = 2,6-diacetylpyridine bis(4-methythiosemicarbazone)], and [^{n}Bu$_2$Sn(dapmdtc)] [**10**; H$_2$dapmdtc = 2,6-diacetylpyridine bis(*S*-methydithiocarbazate)], were done. The determination of the structures of [Ph$_2$Sn(Hdapsc)]$^{+}$, [Me$_2$Sn(H2,6Achexim)]$^{+}$ and [Me$_2$Sn(dapmts)], [^{n}Bu$_2$Sn(dapmdtc)] revealed the presence of monocationic and neutral complexes, respectively. The structures consist of monomeric units in which the Sn^{IV} ions exhibit distorted pentagonal-bipyramidal geometries, with the X,N,N,N,X-donor (X = O, S) systems of the ligands lying in the equatorial plane and the organic groups in the apical positions. The C–Sn–C angle in the seven-coordinated diorganotin(IV) complexes was estimated using a correlation between Mössbauer and X-ray data based on the point-charge model and using new values obtained in this work for [alkyl] = –1.00 mm s^{-1} and [aryl] = –0.80 mm s^{-1} for complexes containing O,N,N,N,O-pentadentate ligands and new values for [alkyl] = –0.87 mm s^{-1} and [aryl] = –0.75 mm s^{-1} for complexes containing S,N,N,N,S-pentadentate ligands.

Introduction

Metal complexes of X,N,N,N,X-pentadentate (X = O, S) Schiff base ligands derived from semicarbazones, thiosemicarbazones, and *S*-alkyldithiosemicarbazates comprise important classes of compounds because of their interesting physicochemical properties and potential relevance in biological systems.[1−4] In this context, a number of 3d metal complexes have been extensively studied by X-ray structural analysis and a number of other spectroscopic techniques.[5,6] However, organotin(IV) complexes of these classes of compounds have received less attention.[7]

The chelating properties of 2,6-diacetylpyridine bis(semicarbazones) and 2,6-diacetylpyridine bis(thiosemicarbazones) have been investigated for a great number of transition-metal ions, as well as with main-group metal centers.[8] At least four-coordination modes were found for bis(semicarbazone)[9] derivatives and six-coordination modes

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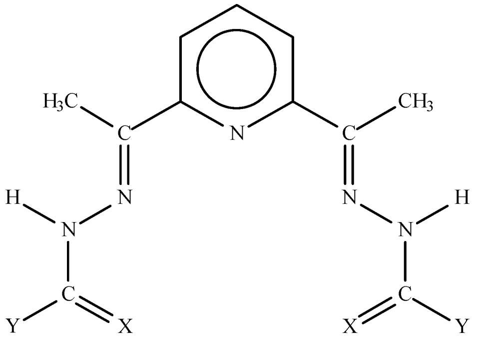
were observed with bis(thiosemicarbazone)[10] derivatives. Metal complexes of 2,6-diacetylpyridine bis(*S*-alkyldithiocarbazate) ligands have not received much attention, so the present work allows us to say that seven-coordinated diorganotin(IV) complexes containing pentadentate bis(dithiocarbazate) ligands have not yet been reported.

This paper is an extension of research programs devoted to the investigation of the coordination modes of bis(semicarbazones) and bis(thiosemicarbazones) with organotin(IV) compounds as well as to the chemistry and structures of five-, six-, and seven-coordinated organotin(IV).[7,10] The ligands shown below were chosen because they have the potential to form four-, five-, and six-coordinated or higher tin(IV) compounds. Furthermore, different possibilities of binding to the metal in the keto−enol and thioketo−thioenol tautomerisms make a comparison between the ligands even more interesting.



$H_22,6Achexim$; X = S, Y = –$N(CH_2)_6$
$H_2dapmts$; X = S, Y = –$NHCH_3$
$H_2dapmdtc$; X = S, Y = –SCH_3
H_2dapsc; X = O, Y = –NH_2

The C−Sn−C angle (θ) in seven-coordinated diorganotin(IV) complexes containing O,N,N,N,O-pentadentate ligands was first estimated by Carini et al.[11] using established point-charge procedures. Carini's team found partial quadrupole splitting (PQS) values of [R] of −0.97 and −0.78 mm s^{-1} for dialkyl- and diaryltin(IV) complexes, respectively. So, this work allows us to calculate new refined values for [alkyl] and [Ph] in seven-coordinated complexes embodying X,N,N,N,X-pentadentate (X = O, S) ligands using crystallographic data (θ) and observed quadrupole splitting (Δ) values.

Experimental Section

General Details. Solvents were purified and dried according to standard procedures. Semicarbazide, 4-methyl-3-thiosemicarbazide, 2,6-diacetylpyridine, dimethyltin(IV) dichloride, dimethyltin(IV) dibromide, di-*n*-butyltin(IV) dichloride, and diphenyltin(IV) dichloride were of the highest commercially available grade. IR spectra were recorded on a Nicolet 5ZDX-FT spectrophotometer in the 4000−400-cm^{-1} range using KBr pellets. NMR spectra were recorded in $CDCl_3$ ($SiMe_4$) using a Varian Mercury Plus 300-MHz spectrophotometer. ^{119}Sn Mössbauer spectra were collected at 90 K in the transmission geometry on a constant-acceleration conventional spectrometer by using a $CaSnO_3$ 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^{-1}. Elemental analyses (C, H, and N) were carried out using a Carlo Erba 1104 elemental analyzer.

Preparation of the Quinquedentate Ligands. The ligands H_2dapsc,[12] $H_22,6Achexim\cdot H_2O$,[13] H_2dpmts,[14] and $H_2dapmdtc$[15] were prepared as described previously.

Preparation of the Organotin(IV) Complexes. R_2SnCl_2 (R = Me, ^{n}Bu, Ph; 1.4 mmol) in 15 mL of MeOH was added to a warmed MeOH solution (20 mL) of the appropriate ligand (1.3 mmol). The mixture was refluxed for about 1 h. After filtration, a clear solution was obtained, and slow evaporation of the solvent led to the appearance of a crystalline product. Crystals suitable for X-ray diffraction studies for complex **7** were grown by a slow-evaporation technique from a MeOH/dimethylformamide (DMF) (1:1, v/v) solution. The yields were found in the 49−60% range, and not one of the complexes melted below 250 °C. $[Ph_2Sn(Hdapsc)]Cl\cdot H_2O\cdot DMF$ (**7**). Anal. Calcd for $C_{26}H_{33}ClN_8O_4Sn$ (675.74): C, 46.17; H, 4.88; N, 16.57. Found: C, 45.95; H, 4.76; N, 16.48. $[Me_2Sn(H2,6Achecim)]Br\cdot H_2O$ (**8**). Anal. Calcd for $C_{25}H_{42}BrN_7OS_2Sn$ (719.38): C, 41.70; H, 5.84; N, 13.62; S, 8.89. Found: C, 41.64; H, 5.81; N, 13.58; S, 8.83. $[Me_2(dapmts)]$ (**9**). Anal. Calcd for $C_{15}H_{24}N_7S_2Sn$ (485.22): C, 37.10; H, 4.95; N, 20.10; S, 13.19. Found: C, 36.89; H, 4.91; N, 19.78; S, 13.12. $[^nBu_2(dapmdtc)]$ (**10**). Anal. Calcd for $C_{21}H_{33}N_5S_4Sn$ (602.45): C, 41.86; H, 5.48; N, 11.63; S, 21.26. Found: C, 40.17; H, 5.33; N, 10.34; S, 20.58.

X-ray Structure Determination. Single crystals for X-ray data collection[16] were obtained as reported in the syntheses section. Experimental parameters and crystallographic data are given in Table 1. The data reduction was carried out with the XCAD-4 software[17] for complex **9** and with HELENA[18] for complexes **7**, **8**, and **10**. The structures were solved using the heavy-atom method[19] and refined by full-matrix least-squares calculations[20] on F^2, after absorption correction. The data collected from crystals of complexes **7** and **10** were corrected using DELABS.[18] The Ψ scan method[21] was applied to crystals of **8** and **9**. The positions of the H atoms were calculated using the riding model except for the crystal water molecules in the structures of **7** and **8**, whose coordinates were

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Table 1. Crystallographic Data for Complexes **7**−**10**

	7	**8**	**9**	**10**
formula	$C_{26}H_{33}ClN_8O_4Sn$	$C_{25}H_{42}BrN_7OS_2Sn$	$C_{15}H_{23}N_7S_2Sn$	$C_{21}H_{33}N_5S_4Sn$
fw	675.74	719.38	484.21	602.45
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
cryst color	yellow	yellow	orange	orange
Z	4	2	4	4
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
T (K)	293(2)	213(2)	293(2)	298(2)
a (Å)	9.9825(14)	8.7028(8)	8.8640(9)	11.260(3)
b (Å)	31.177(4)	10.750(2)	15.208(4)	17.070(8)
c (Å)	9.436(2)	17.027(5)	14.540(3)	14.207(4)
β (deg)	96.78(3)	80.533(15)	92.268(12)	94.20(4)
V (Å^3)	2916.2(8)	1526.7(5)	1958.5(6)	2723.5(17)
ρ_{calcd} (g cm^{-3})	1.539	1.565	1.642	1.469
index ranges	$-12 \leq h \leq 12$	$-1 \leq h \leq 10$	$0 \leq h \leq 12$	$-1 \leq h \leq 12$
	$-39 \leq k \leq 0$	$-12 \leq k \leq 12$	$0 \leq k \leq 21$	$0 \leq k \leq 21$
	$-1 \leq l \leq 12$	$-19 \leq l \leq 19$	$-20 \leq l \leq 20$	$-18 \leq l \leq 18$
F(000)	1376	732	976	1232
μ (mm^{-1})	1.014	9.711	1.531	1.263
refinement method	a	a	a	a
reflns collected	7496	6311	6042	6580
data/param	6348/388	5182/346	5709/233	5675/280
GOF on F^2	1.029	1.036	0.973	0.999
R1 [$I > 2\sigma(I)$]^b	0.0484	0.0494	0.0503	0.0529
wR2 [$I > 2\sigma(I)$]^c	0.1146	0.1181	0.833	0.905

[a] Full-matrix least squares. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o{}^2|^2]^{1/2}$.

found in a Fourier map and refined with isotopic displacement parameters. The C atoms of a DMF solvate molecule were refined disordered into two positions, assigned as *a* and *b*, with occupation factors of 52 and 48%, respectively.

Results and Discussion

X-ray Structures. Single crystals for complexes **7**−**10**, suitable for X-ray data collection, were obtained as reported in the syntheses section. The structure determinations for all of the compounds revealed similar molecular structures with the occurrence of seven-coordinated Sn^{IV} complexes, with a pentagonal-bipyramidal (PBP) geometry. The ORTEP drawings for four compounds are depicted in Figure 1. Experimental parameters and crystallographic data of complexes are shown in Table 1 and selected bond distances and angles in Table 2.

[Ph_2Sn(Hdapsc)]Cl·H_2O·DMF (7). During the formation of **7**, the ligand loses a proton and Ph_2SnCl_2 loses two Cl ions, one as HCl and the other as a counterion. One molecule of water and another of DMF help the packing mode. The single-deprotonated complexed ligand (Hdasc$^-$) has the O1 atom in the ketone form and the O2 as an enolate. The monocation complex adopts a distorted PBP geometry, with the larger ligand as a pentadentate species occupying the equatorial plane and two phenyl groups in the axial positions forming an angle of 66.7(2)° between the planes defined by C1−C21−C31−C41−C51−C61 and C2−C22−C32−C42−C52−C62 atoms, as shown in Figure 1a.

Differences can be observed between the bond parameters in both arms of the ligand. The differences in the distances were found in the pairs Sn−O1 = 2.294(3) Å, Sn−O2 = 2.170(3) Å and Sn−N3 = 2.378(4) Å, Sn−N5 = 2.255(4) Å. The pairs of different angles are O1−Sn−N3 = 67.92(13)°, O2−Sn−N5 = 70.87(14)° and N3−Sn−N4 = 66.51(14)°, N5−Sn−N4 = 69.86(15)°. These differences occur because, during the complexation process, the azomethine H−N6 atom loses its proton and the azomethine H−N2 atom remains protonated. So, the O2 atom coordinates in the enolate form, while O1 is in the ketone form. The former has its basicity enhanced with the O2 atom, and the Sn−O1 distance is shortened. This complex seems to be the fourth case in a series of diorganotin(IV) bis(semicarbazone) complexes in which the ligand suffers a partial deprotonation. These results are in good agreement with analogous bond and angle parameters found in the reported complex [Me_2Sn(Hdapf)]$_2$[Me_2SnCl_4][22] [H_2dapt = 2,6-diacetylpyridine bis(2-furoylhydrazone)].

The bond distances Sn−C1 = 2.159(5) Å and Sn−C2 = 2.189(5) Å and the angle C1−Sn−C2 = 174.50(17)° are higher than the analogous bond distances and angles found in [Me_2Sn(Hdapf)]$_2$[Me_2SnCl_4]. The reported compounds [UO_2(dapsc)H_2O]·2DMSO[9] and [Me_2Sn(H_2dapsc)][Me_2SnCl_4][23] are instances of eigth- and seven-coordinated complexes in which the bis(semicarbazone) ligand is fully deprotonated and doubly protonated, respectively. X-ray crystallographic data is available in CIF format for the following CCDC numbers: 242639, **7**; 242640, **8**; 279132, **9**; 242641, **10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or 12 Union Road, Cambridge CB2 1EK, U.K., tel +44 1223 336408.

[Me_2Sn(H2,6Achexim)]Br·H_2O (8). This complex has an approximately PBP stereochemistry, with the bis(thiosemicarbazone) ligand lying in the equatorial plane and the two methyl groups in the axial positions, as shown in Figure 1b. A water molecule helps the packing mode. During the reaction, the H−N6 proton leaves the molecule whereas the

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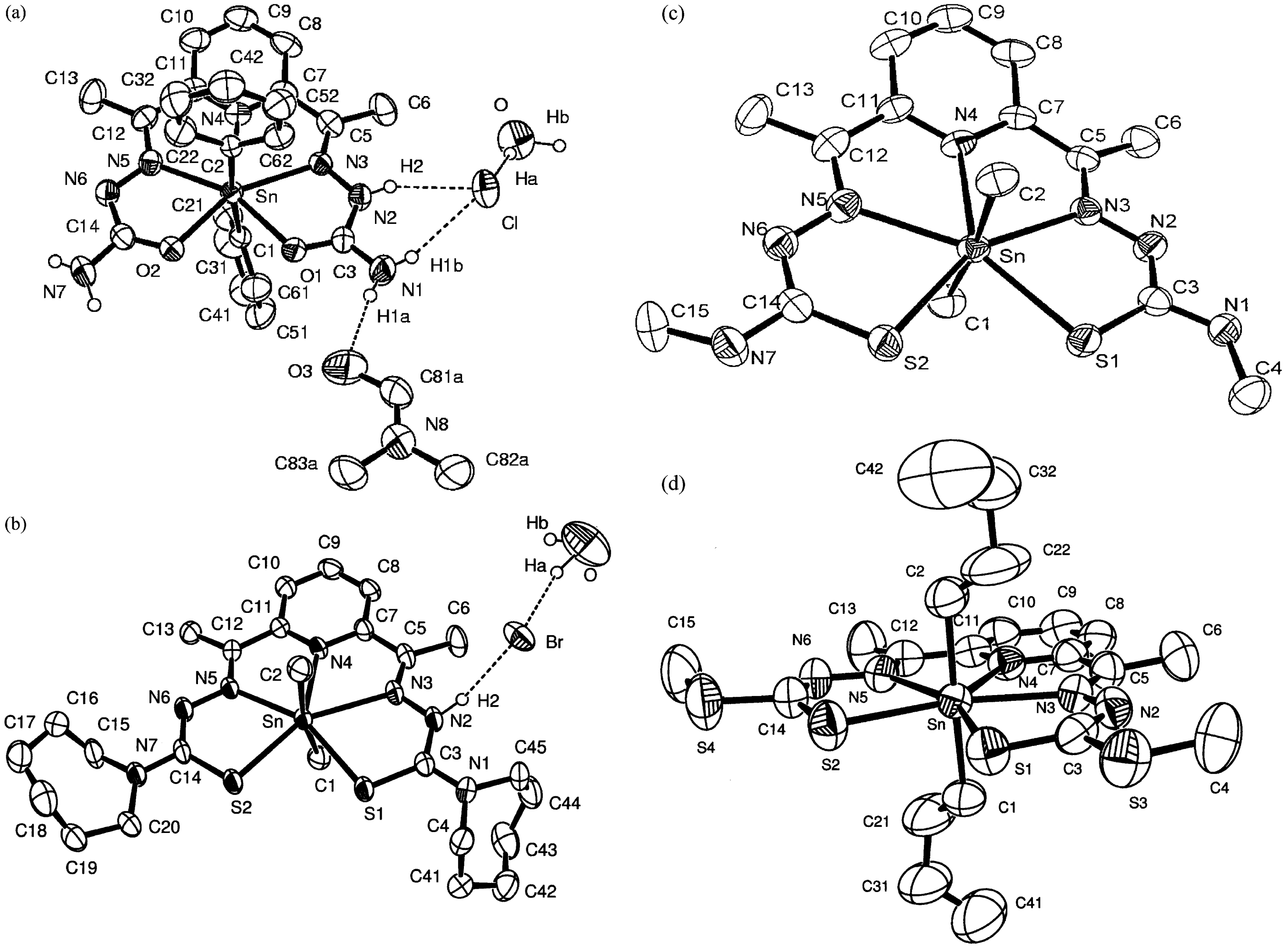

Figure 1. ORTEP drawing with the numbering scheme for the non-H atoms of complexes (a) **7** (for clarity reasons, only the positions with greater occupation factors, assigned with *a*, are shown), (b) **8**, (c) **9**, and (d) **10**.

other H−N2 proton remains in the structure. As a consequence, differences between bond distances and angles around the metal can be observed; the S1 atom is in a thioenolate form, which has greater basicity, while the S2 atom is in a thioketone form.

The bond distances Sn−S1 = 2.7318(13) Å, Sn−S2 = 2.5814(13) Å, Sn−N3 = 2.537(4) Å, Sn−$\mathrm{N_{py}}$4 = 2.349(4) Å, and Sn−N5 = 2.327(4) Å and bond angles S1−Sn−N3 = 67.87(14)°, N3−Sn−$\mathrm{N_{py}}$4 = 65.32(13)°, $\mathrm{N_{py}}$4−Sn−N5 = 69.77(13)°, and N5−Sn−S2 = 74.36(10)° are in good agreement with the analogous bond distances observed in [$\mathrm{Ph_2}$(Hdaptsc)]Cl [$\mathrm{H_2}$daptsc = 2,6-diacetylpyridine bis(thiosemicarbazone)].[24] The Sn−C1 = 2.136(5) Å and Sn−C2 = 2.138(5) Å distances are slightly shorter than the Sn−C1 = 2.163(4) Å and Sn−C7 = 2.170(4) Å distances found in [$\mathrm{Ph_2Sn}$(Hdaptsc)]Cl.[24] However, the C1−Sn−C2 = 168.8(2)° angle is very similar to the C1−Sn−C7 angle reported as 167.9(2)°. The reported complex [$^n\mathrm{Bu_2Sn(H_2daptsc)]Cl_2}$·$\mathrm{MeNO_2}$[23] is an example of a seven-coordinated PBP diorganotin(IV) compound in which the ligand is doubly protonated.

[$\mathrm{Me_2Sn}$(dapmts)] (9). The reaction of $\mathrm{H_2}$dapmt with $\mathrm{Me_2SnCl_2}$ in MeOH yields crystals of the neutral complex **9**, in which the S,N,N,N,S-pentahapto ligand is fully deprotonated, as shown in Figure 1c. The metal is six-coordinated, showing distorted PBP geometry, with the organic ligand on the equatorial plane and the two methyl groups at the axial positions. Because of the structural requirements of the bis(thiosemicarbazone) moieties, the pentagonal geometry is not regular around the $\mathrm{Sn^{IV}}$ atom. The angle subtended by the two S atoms is significantly greater than the others, which are closer to the internal ideal angle (72°), as shown in Table 2. The axial methyl groups also contribute to the observed distortion because they have an angle C1−Sn−C2 of 174.0(2)°.

The equatorial coordination bond distances Sn−S1 = 2.6487(16) Å, Sn−S2 = 2.6946(16) Å, Sn−N3 = 2.405(4) Å, Sn−$\mathrm{N_{py}}$4 = 2.367(5) Å, and Sn−N5 = 2.428(5) Å are shorter than the analogous bonds found in [$^n\mathrm{Bu_2Sn(H_2daptsc)]Cl_2}$·$\mathrm{MeNO_2}$.[23] Coordination to the $\mathrm{Sn^{IV}}$ center by the imine N atom and the thiolate S atom shortens the bond distances around the metal because of the strong attraction of the negatively charged $\mathrm{dapmt^{2-}}$ by the metal atom. The equatorial bond distances Sn−C1 = 2.154(6) Å and Sn−C2 = 2.134(6) Å are very similar to the axial bond lengths Sn−

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **7**−**10**

	7[a]	**8**[a]	**9**	**10**
	Bond Distances			
Sn−X1[b]	2.294(3)	2.7318(13)	2.6487(16)	2.656(2)
Sn−X2[b]	2.170(3)	2.5814(13)	2.6946(16)	2.680(2)
Sn−C1	2.159(5)	2.136(5)	2.154(6)	2.157(6)
Sn−C2	2.189(5)	2.138(5)	2.134(6)	2.137(7)
Sn−N3	2.378(4)	2.537(4)	2.405(4)	2.423(5)
Sn−N4	2.315(4)	2.349(4)	2.367(5)	2.382(5)
Sn−N5	2.255(4)	2.327(4)	2.428(5)	2.429(5)
C3−X1	1.237(6)	1.701(5)	1.725(5)	1.705(7)
C14−X2	1.287(6)	1.739(5)	1.735(7)	1.705(7)
C3−N2	1.374(6)	1.365(6)	1.335(7)	1.312(7)
C14−N6	1.344(7)	1.333(6)	1.319(7)	1.304(8)
N2−N3	1.363(6)	1.380(6)	1.359(6)	1.376(7)
N5−N6	1.353(6)	1.372(5)	1.371(6)	1.384(7)
C5−N3	1.272(6)	1.288(6)	1.298(7)	1.279(7)
C12−N5	1.288(6)	1.307(6)	1.302(7)	1.294(7)
	Bond Angles			
C1−Sn−C2	174.50(17)	168.8(2)	174.0(2)	174.5(3)
X1−Sn−X2	84.86(13)	81.44(4)	81.47(5)	82.20(6)
X1−Sn−N3	67.92(13)	69.11(30)	72.19(12)	72.13(13)
X2−Sn−N5	70.87(14)	74.36(10)	71.49(12)	71.92(13)
X1−Sn−N4	134.35(14)	134.28(9)	140.00(12)	138.77(14)
X2−Sn−N4	140.72(15)	144.11(10)	138.50(12)	139.00(14)
N3−Sn−N5	136.36(15)	135.09(13)	134.85(16)	133.80(17)
N3−Sn−N4	66.51(14)	65.32(13)	67.95(16)	66.76(18)
N4−Sn−N5	69.86(15)	69.77(13)	67.02(16)	67.08(18)

[a] The arms of the ligands in **7** and **8** are not equivalent. [b] X = O for complex **7** and X = S for complexes **8**−**10**.

C13 = 2.143(7) Å and Sn−C17 = 2.126(8) Å, observed in $[^{n}\text{Bu}_2\text{Sn}(\text{H}_2\text{daptsc})]\text{Cl}_2\cdot\text{MeNO}_2$.[23]

These two complexes also differ with respect to the bond distances in both arms of the ligand. Thus, the S1−C1 = 1.731(5) Å, S2−C9 = 1.729(5) Å, N2−C1 = 1.331(7) Å, N6−C9 = 1.333(6) Å, N2−N3 = 1.365(5) Å, N5−N6 = 1.381(5) Å, N3−C2 = 1.307(6) Å, and N5−C8 = 1.306(7) Å bond distances observed in $[^{n}\text{Bu}_2\text{Sn}(\text{H}_2\text{daptsc})]\text{Cl}_2\cdot\text{MeNO}_2$ are different from those found in **9**. These differences occur because the double deprotonation of the N−H groups allows the delocalization of the π electrons in the deprotonated arms of dapmt^{2-}, lengthening the C═S and N═C double bonds and shortening the C−N and N−N single bonds (see Table 2). The reported complex $[^{n}\text{Bu}_2\text{Sn}(2,6\text{Achexim})]$[13] is a seven-coordinated diorganotin(IV) compound in which the ligand is doubly deprotonated.

$[^{n}\text{Bu}_2\text{Sn}(\text{dapmdtc})]$ (10). The structure determination of **10** revealed the presence of a neutral complex of Sn$^{\text{IV}}$, in which the metal is seven-coordinated, showing a distorted PBP geometry, with the pentahapto ligand, H_2dapmdc, on the equatorial plane and the two *n*-butyl groups on the axial positions, as shown in Figure 1d.

The chelating bond distances Sn−S1 = 2.656(2) Å, Sn−S2 = 2.680(2) Å, Sn−N3 = 2.423(5) Å, Sn−N$_{\text{py}}$4 = 2.382(5) Å, and Sn−N5 = 2.429(5) Å are significantly shorter than the equivalent values found in $[^{n}\text{Bu}_2\text{Sn}(\text{H}_2\text{daptsc})]\text{Cl}_2\cdot\text{MeNO}_2$,[23] indicating a stronger interaction in dapmdtc^{2-}/^{n}Bu$_2$Sn^{2+} than in H$_2$daptsc/^{n}Bu$_2$Sn^{2+}. On the other hand, the bond lengths and angles observed along the bis(thiosemicarbazone) moieties in **10** are nearly identical with those found in **9** (see Table 2). The complexes $[^{n}\text{Bu}_2\text{Sn}(2,6\text{Achexim})]$[13] and $[^{n}\text{Bu}_2\text{Sn}(\text{dappt})]\cdot(\text{Me}_2\text{CO})_{0.5}$ [H$_2$dappt = 2,6-diacetylpyridine bis(4-phenylthiosemicarbazone)][10] are examples of seven-coordinated dibutyltin(IV) derivatives containing fully deprotonated bis(thiosemicarbazone) ligands in the pentagonal girdle.

IR Spectroscopy. Table 3 shows the assignments of the main IR absorption bands for the ligands and their complexes. The free ligand H$_2$dapsc shows IR bands at ca. 3383−3082, 1677, and 1599−1549 cm^{-1}, which may be assigned to ν(N−H), amide I [ν(C═O)], and amide II [ν(C═N) + δ(N−H)] stretching vibrations, respectively. The IR spectrum of **7** shows several bands in the 3438−3129-cm^{-1} range assigned to ν(O−H) and ν(N−H) absorptions. The amide I and amide II absorptions are shifted to lower wavenumbers and are found at 1635 and 1592, 1520 cm^{-1}, respectively, indicating that one of the amide O atoms takes part in the ketone form coordination, in agreement with the X-ray structural data. The amide I band was previously observed at 1655 cm^{-1} in $[\text{Me}_2\text{Sn}(\text{Hdapsc})][\text{MeSnCl}_4]$,[23] a similar seven-coordinated diorganotin(IV) complex. The IR spectrum also exhibits a very strong band at 1670 cm^{-1} attributed to ν(C═O) stretching vibration due to DMF of crystallization.

The IR spectrum of **8** differs in several aspects from that of the free ligand, which exhibits a ν(N−H) absorption band at 3221 cm^{-1}, but no ν(S−H) at ca. 2570 cm^{-1} is observed. Hence, in the solid state, the ligand exists in the thione form.[13] As a consequence of the presence of the water of crystallization and the single deprotonation (H2,6Achexim^{-}) of the ligand, the spectrum of the complex shows bands at 3418 and 3330 cm^{-1}, which are likely due to ν(O−H) and δ(N−H), respectively. The spectrum of H$_2$2,6Achexim·H$_2$O has bands in the 1615−1519-cm^{-1} range, and the spectrum of **8** has bands at 1605, 1588, and 1544 cm^{-1}, which we suggest are due to ν(C═N) for N3−C5/N5−C12, N6−C14, and N2−C3, respectively. When two bands are present in the spectrum of a coordinated anionic bis(thiosemicarbazone) that are assignable to ν(C═N), one is usually at lower energy, e.g., N2−C3, and the other at higher energy, e.g., N6−C14, compared to ν(C═N) of the free ligand.[13] The bands at ca. 1272 and 836 cm^{-1} in the spectrum of H$_2$2,6Achexim·H$_2$O, which have a significant contribution from the ν(C═S) stretching vibrations, are shifted to lower frequencies at 1213, 802, and 771 cm^{-1}, suggesting coordination through the S atoms.[10,13]

The IR spectrum of **9** shows several bands in the 3381−3124-cm^{-1} range due to ν(N−H) vibrations and strong bands at 1619, 1543, 1519, and 1429 cm^{-1}, which are assigned to the combination of ν(C═N) + ν(C═C) modes. The bands around 1235 and 819 cm^{-1} observed in the free ligand, assigned to ν(C═S) stretching vibrations, are shifted to lower frequencies, suggesting removal of both −NH− azomethine protons via thioenolization. The coordination of the azomethine N atoms to the Sn$^{\text{IV}}$ ions is supported by displacement to higher wavenumbers of the ν(N−N) band of the free ligand at 1047−1095 cm^{-1} upon complexation.

The IR spectrum of **10**, when compared with that of the ligand, shows that the ν(N−H) bands at 3320 and 3182 cm^{-1} of the free ligand disappear in the spectrum of the complex, supporting the double deprotonation of the ligand upon

Table 3. Important IR Spectral Bands (cm^{-1}) and Their Assignments for Ligands and Their Complexes

compound	ν(N−H)	ν(C═N) + ν(C═C)	ν(C−N)	ν(N−N)	ν(C═S)
H_2dapsc[a]	3383, 3206, 3082	1655, 1599, 1577, 1549	1347	1070	
[Ph_2Sn(Hdapsc)]Cl·H_2O·DMF[b] (**7**)	3335, 3196, 3129	1593, 1520, 1429	1386	1096	
$H_2$2,6Achexim·H_2O[c]	3221	1615, 1580, 1561, 1519	1366, 1335	1017	1272, 836
[Me_2Sn(H2,6Achexim)]Br·H_2O[d] (**8**)	3330	1605, 1588, 1544, 1486	1368	1078	1213, 802, 771
H_2dapmts	3370, 3329	1606, 1550, 1514, 1451	1335	1047	1335, 819
[Me_2Sn(dapmts)] (**9**)	3381, 3333, 3201	1619, 1543, 1519, 1429	1385	1095	1200, 810, 741
H_2dapmdtc	3182	1629, 1567, 1487, 1445	1361, 1338	1066	1272, 811, 749
[^{n}Bu_2Sn(dapmdtc)] (**10**)		1592, 1561, 1543, 1455	1394, 1304	1047	1136, 807, 795

[a] ν(C═O) = 1677 cm^{-1}. [b] ν(C═O) = 1670 cm^{-1} (DMF), ν(C═O) = 1635 cm^{-1}, and ν(O−H) = 3438 cm^{-1}. [c] ν(O−H) = 3435 cm^{-1}. [d] ν(O−H) = 3418 cm^{-1}.

complex formation. Significant changes in the ligand bonds upon complexation include variations in the azomethine ν(C═N) absorptions at 1629 and 1567 cm^{-1}, which shift to lower wavenumbers in the spectrum of the complex, indicating coordination via azomethine N atoms.[25,26] The bands around 1272 and 811, 749 cm^{-1} observed in the free ligand that may be assigned to ν(C═S) vibrations are shifted to lower frequencies upon complexation. This behavior is typical for this ligand when it is S,N,N,N,S-coordinated.[7] In the spectrum of the free ligand, a band at ca. 960 cm^{-1} is assigned to ν(C−S−S) of the dithiocarbazate moiety, and in the spectrum of the complex, this band appears as a well-defined peak shifted to slightly lower frequencies at 946 cm^{-1}. Metal complexes of N,N,S-chelating agents derived from *S*-alkyldithiocarbazates have been extensively investigated, and their IR spectra show that the ν(C−S−S) absorption either is split into two components or has well-defined shoulders, indicating that the ligands coordinate to the metal ions through one of the S donors of the CSS group.[27,28]

NMR Spectroscopy. Only complex **10** was soluble in $CDCl_3$, and its ^1H NMR spectrum showed three singlets in the methyl region occurring at 1.61 [^2J(Sn−CH_2−) = 132 Hz], 2.61, and 2.72 ppm, due to magnetically and chemically nonequivalent protons assigned to Sn−CH_2−, S−CH_3, and N═C−CH_3, respectively. The Sn−C−CH_2−CH_2− protons appear as two complicated multiplets centered at about 1.02 and 1.16 ppm, while the ^{n}Bu-C−C−C−CH_3 protons appear as a triplet centered at 0.65 ppm. The spectrum of **10** also shows no peaks assignable to N2−H or N6−H but shows a triplet centered at 8.16 ppm and a doublet at 7.93 ppm for the pyridine ring H atoms.

The ^{13}C NMR spectrum of **10** shows 11 separate signals: 7 peaks for ligand C atoms, C9 141.0, C8,C10 123.9, C7,C11 152.8, C5,C12 149.5, C3,C14 188.9, C6,C13 14.7, C4,C15 16.5 ppm and four peaks for ^{n}Bu_2Sn^{2+} C atoms, C1,C2 42.4 [^2J(Sn−CH_2−) = 1096 Hz], C21,C22 28.5, C31,C32 26.2, C41,C42 13.6 ppm.

The ^{119}Sn NMR δ value in diorganotin(IV) derivatives is very sensitive to complexation and is usually greatly shifted dowfield or upfield upon bonding to a Lewis base. The upfield chemical δ value of −370 ppm observed for complex **10** is indicative of considerable shielding of the Sn^{IV} nucleus and a high coordination number, consistent with literature data for seven-coordinated diorganotin(IV) complexes.[29] The complex [Me_2Sn(DPTSC)] [H_2DPTSC = 2,6-diacetylpyridine bis(thiosemicarbazone)][30] showed a singlet at −393 ppm. On the other hand, the complex [^{n}Bu_2Sn(dib)][29] [H_2-dib = 2,6-diacetylpyridine bis(benzoylhydrazone)] showed a singlet at −441 ppm, indicating that S,N,N,N,S-donor ligands have a smaller shielding effect on the Sn^{IV} nucleus than O,N,N,N,O-donor ligands. The complex [Ph_2Sn(DPTSC)]·2DMF[30] showed a chemical shift at −453 ppm (−60 ppm higher than the value found in the dimethyl analogue), indicating that high acidity on the Lewis diorganotin(IV) precursor produces an increase in the shielding of the Sn^{IV} nucleus.

Mössbauer Spectroscopy. ^{119}Sn Mössbauer spectral parameters of all of the compounds are reported in Table 4, which includes parameters from the literature for comparison. The spectra of the diorganotin(IV) complexes **7**−**10** shown in Figure 2 indicated the presence of two overlapping quadrupole doublets (two lines); the areas under principal lines determined by computer evaluation indicated 90, 82, 90, and 87% of complexes **7**−**10**, respectively. These doublets were associated with the pure compounds and a small doublet with $\delta = 0.30$ mm s^{-1} and $\Delta = 2.20$ mm s^{-1} was added in order to take into account a small contribution from Sn^{IV} phases.

The isomer shifts (δ) of the complexes presented in Table 4 are lower than those of the parent acids (80 K) Me_2SnCl_2 (1.52 mm s^{-1}),[31] Me_2SnBr_2 (1.59 mm s^{-1}),[31] Et_2SnCl_2 (1.66 mm s^{-1}),[32] ^{n}Pr_2SnCl_2 (1.67 mm s^{-1}), ^{n}Bu_2SnCl_2 (1.62 mm s^{-1})[32] and Ph_2SnCl_2 (1.34 mm s^{-1}).[31] Isomer shifts decrease upon complexation, as a result of rehybridization to higher coordination for Sn^{IV} atoms in the complexes, indicating lower s electron density of the Sn^{IV} nucleus in the complexes compared to those of the parent 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 the s orbitals in the overall hybridization of the metal.[33,34]

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Table 4. Mössbauer Data and C−Sn−C Angles (deg) for Seven-Coordinated Sn^{IV} Complexes[a]

compound	δ (mm s^{-1})	Δ (mm s^{-1})	PQS (mm s^{-1})	C−Sn−C(θ, exptl)	C−Sn−C(θ, calcd)	$\Delta\theta$
1. [Me_2Sn((Hdapt)]Br·H_2O[g]	1.25	3.80	−0.97	165.5	158.9[b]	6.6
2. [Me_2Sn(Hdapf)]$_2$[Me_2SnCl_4][h]	1.29	3.96	−1.01	166.0	170.6[b]	−4.6
3. [Me_2Sn(H_2dapsc)][Me_2SnCl_4][i]	1.29	4.36	−1.10	169.5	180.0[b]	−10.5
4. [Et_2Sn(dapt)][j]	1.31	3.72	−0.94	172.4	154.9[b]	17.5
5. [$^nPr_2Sn$(daps)][j]	1.31	3.82	−0.96	170.4	160.0[b]	10.4
6. [Ph_2Sn(dapa)][j]	0.89	3.12	−0.78	176.4	169.5[c]	6.9
7. [Ph_2Sn(Hdapsc)]Cl·H_2O·DMF[k]	1.05	3.32	−0.83	174.5	180.0[c]	−5.3
8. [Me_2Sn(H2,6Achexim)]Br·H_2O[k]	1.29	3.45	−0.87	168.8	171.3[d]	−2.5
9. [Me_2Sn(dapmts)][k]	1.03	3.38	−0.85	174.0	164.0[d]	10.0
10. [$^nBu_2Sn$(dapmdtc)][k]	1.46	3.53	−0.88	174.5	180.0[d]	−5.5
11. [$^nBu_2Sn$(2,6Achexim)][l]	1.38	3.40	−0.86	171.6	165.7[d]	5.9
12. [$^nBu_2Sn$(dappt)]·$(Me_2CO)_{0.5}$[m]	1.43	3.51	−0.89	168.1	180.0[d]	−11.9
13. [Ph_2Sn(daptsc)]·2DMF[n]	1.22	2.84	−0.72	166.9	158.2[e]	8.7
14. [Ph_2Sn(Hdaptsc)]Cl[o]	1.21	3.13	−0.79	167.9	159.9[e]	8.0
15. [$Me_2Sn(NCS)_2$(terp)][j]		4.29	−1.08	173.7	172.2[f]	1.5
16. [Et_2SnCl_2(oxphen)][j]		3.94	−1.09	150.4	151.7[f]	−1.3
17. [$^nBu_2SnCl_2$(aip)][j]	1.69	4.19	−1.10	158.3	163.7[f]	−5.4
18. [$^nBu_2Sn$(picolinate)$_2$]$_n$[p]	1.45	4.26	−1.08	169.0	168.9[f]	0.1
19. [$^nBu_2Sn$(dipicolinate)][p]	1.47	4.17	−1.08	162.5	162.4[f]	0.1
20. [$Ph_2Sn(NO_3)_2(Ph_3AsO)$][j]	1.32	4.03	−1.07	156.0	155.4[f]	0.6
21. [$Ph_2Sn(NO_3)_2(Ph_3PO)$][j]	1.36	4.28	−1.07	178.0	171.0[f]	−7.0
22. [Ph_2Sn(NCS)][Ni(3MeO-salpd)(NCS)(MeCN)][q]	1.19	4.31	−1.10	166.7	175.5[f]	−8.8

[a] Abbreviations: PQS = partial quadrupole splitting, H_2dapt = 2,6-diacetylpyridine bis(2-thionylhydrazone), H_2dapf = 2,6-diacetylpyridine bis(2-furanoylhydrazone),[24] H_2dapsc = 2,6-diacetylpyridine bis(semicarbazone), H_2daps = 2,6-diacetylpyridine bis(salicyloylhydrazone), H_2dapa = 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone), $H_2$26Achexim = 2,6-diacetylpyridine bis(3-hexamethyleneiminylthiosemicarbazone), H_2dapmts = 2,6-diacetylpyridine bis(4-methylthiosemicarbazone), H_2dapmdtc = 2,6-diacetylpyridine bis(*S*-methyldithiocarbazate), H_2dappt = 2,6-diacetylpyridine bis(4-phenylthiosemicarbazone), terpy = 2,2′:6′,2′′-terpyridyl, DMF = dimethylformamide, 3MeOH_2salpd = *N*′,*N*′-bis(3-methoxysalicylidene)propane-1,3-diamine, oxphen = 2-(5-methyl-1,2,4-oxadiazol-3-yl)-1,10-phenanthroline, aip = 2-phenyl[*N*-(2′-pyridylmethyl)imino]-4-oxo-1,2,3,4-tetrahydroquinazoline, picolinate = anion of pyridine-2-carboxylic acid, dipicolinate = anion of pyridine-2,6-dicarboxylic acid. [b] Calculated using [alkyl] = −1.00 mm s^{-1}. [c] Calculated using [Ph] = −0.80 mm s^{-1}. [d] Calculated using [alkyl] = −0.87 mm s^{-1}. [e] Calculated using [Ph] = −0.75 mm s^{-1}. [f] Calculated using [R] = −1.08 mm s^{-1}. [g] Reference 35. [h] Reference 22. [i] Reference 23. [j] Reference 11. [k] This work. [l] Reference 13. [m] Reference 10. [n] Reference 30. [o] Reference 24. [p] Reference 40. [q] Reference 41.

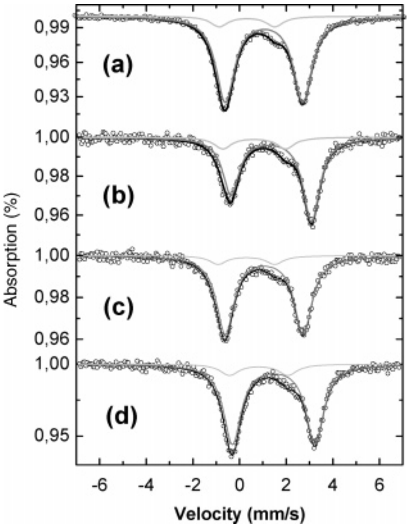

Figure 2. ^{119}Sn Mössbauer effect spectra obtained at 90 K to complexes (a) **7**, (b) **8**, (c) **9**, and (d) **10**.

The increase in the isomer shift (δ) in complex **10** (1.46 mm s^{-1}) compared to that in **7** (1.05 mm s^{-1}) is due to the differences in σ donation of S atoms and *n*-butyl groups in **10** compared to O atoms and phenyl groups in **7**. Other similar effects are observed, as indicated in Table 4, and isomer shifts decrease in the sequence $Ph_2Sn < Me_2Sn < {}^nBu_2Sn$.

Quadrupole splitting (Δ) values are not sufficient to characterize Sn^{IV} complexes as being four-, five-, six-, or seven-coordinated.[11] However, a successful correlation between Δ and the angle θ has been reported[10,11,35] for a series of distorted seven-coordinated diorganotin(IV) derivatives by eq 1, where θ is the C−Sn−C angle and [R] is the PQS

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

of the R group arising from either the alkyl or aryl groups. Equation 1 has also been satisfactorily applied to the characterization of four-, five-, and six-coordinated Sn^{IV} complexes using appropriate values of [R] for each coordination number.[36−39] The model assumes that quadrupole splitting (Δ) arises from point-charge hydrocarbon groups separated by a C−Sn−C angle of (180 − 2θ)°, with contributions from other coordinated ligands being ignored. The quadrupole splitting has been used to estimate the C−Sn−C angle, and the accuracy of the predicted angle is shown in Table 4.

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Considering the complexes **1** (3.80 mm s^{-1}), **2** (3.96 mm s^{-1}), **3** (4.36 mm s^{-1}), **4** (3.72 mm s^{-1}), and **5** (3.82 mm s^{-1}) and using θ and Δ values (Table 4), the PQS can be estimated. Equation 1 yields [alkyl] = −1.01, −1.10, −0.97, −0.94, and −0.96 mm s^{-1}, respectively, and allows us to evaluate an average value for [alkyl] = −1.00 mm s^{-1} in seven-coordinated dialkylorganotin(IV) systems. Similarly, from complexes **6** and **7**, we obtain a value for [Ph] = −0.80 mm s^{-1} (average of −0.78 and −0.83 mm s^{-1}, respectively) in similar seven-coordinated diarylorganotin(IV) derivatives containing O,N,N,N,O-pentadentate ligands lying in the pentagonal girdle. Following the same reasoning, eq 1 allows us to calculate working values for [alkyl] = −0.87 mm s^{-1} (complexes **8**−**12**) and for [Ph] = −0.75 mm s^{-}1 (complexes **13** and **14**) in dialkyl- and diarylorganotin(IV) derivatives containing single S,N,N,N,S-pentadentate ligands in the equatorial plane, respectively.

The PQS values for [alkyl] = −0.97 mm s^{-1} and [Ph] = −0.78 mm s^{-1}, obtained from the complexes **4**−**6**, were reported by Carini et al.[11] and used by Casas et al.[30] to quantify the deviation of the C−Sn−C bond angle from the ideal 180°. The angle calculated for the dimethyl derivative [Me_2Sn(daptsc)][30] (154°) is approximately 26° narrower than the value of 180° obtained by our new PQS value for [alkyl] = −0.87 mm s^{-1}. A similar value of 152° was obtained for the diphenyl derivative [Ph_2Sn(daptsc)]•2DMF[30] (complex **13**), and an angle approximately 15° smaller than the value of 166.9° was observed by X-ray diffraction. Now, using our alternative value for [Ph] = −0.75 mm s^{-1}, we predict a Ph−Sn−Ph angle of 160°, only approximately 8° lower than the experimental value (168°). These results show us that the PQS values found by Carini et al. are not satisfactorily applicable for similar complexes containing S,N,N,N,S-pentadentate bis(thiosemicarbazones).

The concept of PQS is best applied to seven-coordinated diorganotin(IV) systems that involve coordination between the metal and ligands of low denticity. Compounds **15**−**22** form a group that allows one to calculate a consistent value of [R] = −1.10 mm s^{-1} (R = alkyl and Ph; average of −1.08, −1.09, −1.10, −1.08, −1.08 −1.07, and −1.07 mm s^{-1}, respectively) in other analogous seven-coordinated Sn^{IV} complexes containing ligands of low denticity.

The PQS values of the individual R groups shown in Table 4 depend on the nature of the other ligands in the complex. These data indicate that the exchange of O by S donor atoms in analogous complexes results in an increase of the isomer shift values, indicating an increased electron density at the site of the Sn^{IV} nucleus, and in a decrease of the quadrupole splitting values, reflecting the increased symmetry of the electronic shell around the Sn^{IV} atom[30] (compare complex **1** with **8** and compounds **6** and **7** with **13** and **14**, respectively). An interesting feature shown in Table 4 is the fact that the PQS values found in diarylorganotin(IV) complexes are lower than those observed in dialkylorganotin(IV) derivatives containing X,N,N,N,X-pentadentate (X = O, S) ligands.

As a diagnostic of the Sn^{IV} coordination number, coupling constants $^{1}J(^{119}Sn,^{13}C)$ and ^{119}Sn NMR chemical shifts are potentially more accurate and more easily obtainable than Mössbauer quadrupole splittings (PQS model) because of the greater range and sensitivity of the NMR technique. However, our attempts to evaluate this supposition in seven-coordinated diorganotin(IV) complexes have been hindered by the considerably low solubility of most of the reported compounds in uncoordinating solvents.

Conclusions

The correlation between Mössbauer and X-ray structural data, using a simple point-charge model, gave working values for [alkyl] = −1.00 mm s^{-1} and [Ph] = −0.80 mm s^{-1} for seven-coordinated diorganotin(IV) complexes containing O,N,N,N,O-pentadentate ligands lying in the pentagonal plane. On the other hand, this same correlation gave different values for similar complexes containing S,N,N,N,S-pentadentate ligands, namely, [alkyl] = −0.87 mm s^{-1} and [Ph] = −0.75 mm s^{-1}. For a seven-coordinated derivative involving low-denticity ligands, [R] = −1.10 mm s^{-1} (R = alkyl and Ph) seems more appropriate. The PQS [Ph] values of −0.80 and −0.75 mm s^{-1} found by us for seven-coordinated diphenyltin(IV) complexes were obtained from limited crystallographic data, so we are sure that these values will be subject to refinement as more crystallographic data become available.

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