

Heptacoordination in Organotin(IV) Complexes. Spectroscopic and Structural Studies of 2,6-Diacetylpyridine bis(thiosemicarbazone)di-*n*-butyltin(IV) Chloride Nitromethane Solvate, [ⁿBu₂Sn(H₂daptsc)]Cl₂·MeNO₂ and of 2,6-Diacetylpyridine bis(semicarbazone)dimethyltin(IV) trans-Tetrachlorodimethylstannate(IV), [Me₂Sn(H₂dapsc)][Me₂SnCl₄]

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Dois novos casos de heptacoordenação em complexos organoestânicos(IV) são descritos. Ambos possuem geometria pentagonal bipiramidal e mostram os grupos orgânicos nas posições axiais, com os ligantes formando cinco ligações no plano equatorial com os átomos de estanho(IV). O primeiro complexo [ⁿBu₂Sn(H₂daptsc)]Cl₂·MeNO₂ (**1**) é totalmente novo, ao passo que o segundo, [Me₂Sn(H₂dapsc)][Me₂SnCl₄] (**2**), embora anteriormente descrito na literatura, somente agora teve a sua estrutura determinada. Tanto em **1** quanto em **2** as espécies heptacoordenadas são catiônicas; ao passo que em **1** o contra-íon é um simples Cl⁻, em **2** é um ânion complexo, isto é [Me₂SnCl₄]²⁻.

Two new cases of heptacoordination in organotin(IV) complexes are described. Both possess pentagonal bipyramidal geometry and show the organic groups on the axial positions, with the ligands forming five bonds to tin(IV) on the equatorial plane. The first complex, [ⁿBu₂Sn(H₂daptsc)]Cl₂·MeNO₂ (**1**) is entirely new, whereas the second, [Me₂Sn(H₂dapsc)][Me₂SnCl₄] (**2**), although previously reported, only now had its structure determined. In both **1** and **2** the heptacoordinate species are cationic, but whereas in **1** the counterion is simply Cl⁻, in **2** it is a complex anion, namely [Me₂SnCl₄]²⁻.

Keywords: Heptacoordinate tin(IV) complexes, thiosemicarbazone complexes, semicarbazone complexes, X-ray molecular structure

Introduction

Thiosemicarbazone and semicarbazone complexes have been the subject of much interest in recent years due to the biological activity of thiosemicarbazones, in particular, and of a number of their complexes,¹ as well as to the unusual structural aspects of complexes of both types of ligands.²⁻⁴ Insofar as many organotin(IV) complexes are also noteworthy for the same reasons, a combination of the two chemistries is an interesting line to pursue.

The chelating properties of 2,6-diacetylpyridine bis(thiosemicarbazone), H₂daptsc, have been investigated

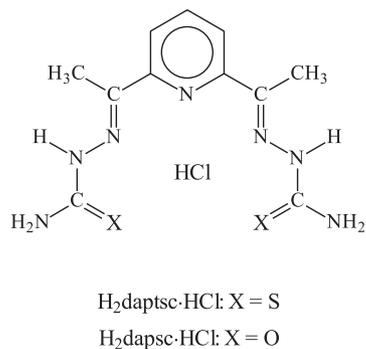
and several different coordination modes have been found.²⁻⁵ A new coordination mode is now reported for the complex [ⁿBu₂Sn(H₂daptsc)]Cl₂·MeNO₂, in which the tin(IV) atom has a pentagonal bipyramidal geometry. Both arms (thiosemicarbazide groups) of the pentadentate ligand have remained protonated. On the other hand, the oxygen analogue of H₂daptsc, 2,6-diacetylpyridine bis(semicarbazone), H₂dapsc, can form complexes with a large number of transition metal ions, as well as with tin(IV). Complexes in which the ligand is fully protonated (H₂dapsc), singly-deprotonated (Hdapsc⁻) or doubly-deprotonated (dapsc²⁻) have been reported.^{2,5-7}

Tin(IV) is remarkable in the capacity to expand its coordination number from four, which is found in most

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simple organotin(IV), to five, six or seven, as we have shown in many instances previously.^{2,3,8} Indeed, even coordination number seven, once regarded as an oddity, no longer seems to be so, given the appropriate type of ligand to interact with the metal; double-armed *bis*(semicarbazone) and *bis*(thiosemicarbazone) ligands derived from pyridine belong to this class. As previous research^{2,9,10} and the present work show, these ligands tend to originate pentagonal bipyramidal complexes in which the ligand forms a pentacoordinated chelate on the equatorial plane and the organotin(IV) precursor sheds two of its ligated groups, whereas the remaining two groups now occupy the axial positions of the new complex. The latter can be either neutral^{9,10} or cationic,^{2,3} depending on whether complex formation requires HX elimination or simple loss of halide ions, respectively.

The X-ray structure determinations of [ⁿBu₂Sn(H₂daptsc)]Cl₂·MeNO₂ (**1**) and [Me₂Sn(H₂dapsc)] [Me₂SnCl₄] (**2**) revealed the occurrence of a new coordination mode to H₂daptsc·HCl, in which complex formation simply requires the loss of halide ions. Here the ligands act as pentadentate neutral molecules and coordinate to the tin(IV) atoms through two thione sulphur atoms (or two oxygens), two azomethine nitrogens and the pyridine nitrogen. The structures of H₂daptsc·HCl and H₂dapsc·HCl are shown below.



Experimental

Syntheses

H₂daptsc·HCl and H₂dapsc·HCl were prepared as previously reported.² Complexes **1** and **2** were prepared by the following procedure: 0.21 mmol of the ligand was dissolved in 15 mL of MeOH under reflux; to this was added a 5 mL solution of 0.24 mmol of the appropriate organotin halide (ⁿBu₂SnCl₂ in MeNO₂, Me₂SnCl₂ in MeOH). The resulting mixtures were refluxed for 1 h. Cooling followed by slow evaporation produced crystals in *ca.* 80% yield, which did not melt below 250 °C.

The ¹¹⁹Sn Mössbauer spectra were recorded on a Ranger Scientific Inc. MS-1200 constant-acceleration spectrometer. A standard source of CaSnO₃ was used at room temperature and the samples were analyzed at 85K. The spectra were computer-fitted assuming Lorentzian line shapes. Poor solubility properties did not allow the determination of ¹¹⁹Sn NMR spectra of the complexes in solution. IR spectra were obtained in the 4000-400 cm⁻¹ range in KBr pellets on a Nicolet 5ZDX-FT spectrophotometer. The microanalyses were carried out on a Perkin-Elmer model 240 automatic equipment, giving for C, H and N the following results. Anal. Found: C, 35.8; H, 4.0; N, 16.6. Calcd. for C₂₀H₂₇Cl₂N₈O₂S₂Sn (**1**): C, 36.1; H, 4.1; N, 16.9%. Anal. Found: C, 25.3; H, 3.7; N, 13.9. Calcd. for C₃₀H₃₄Cl₈N₁₄O₄Sn₄ (**2**): C, 25.1; H, 3.8; N, 13.7%.

X-ray crystallography

Yellow prismatic crystals of **1** and **2** were mounted in a random orientation on glass fibers. Crystal data were collected at 293(2) K using a Siemens P4/PC four-circle diffractometer with graphite monochromator MoKα (λ = 0.71073 Å) radiation. Crystal stability was monitored by measuring standard reflections every 97 reflections. Cell parameters were obtained from 35 accurately centered reflections. Data were collected using a ω-2θ scanning technique. Lorentz and polarization corrections and an absorption correction using Ψ-scans were applied. The structures were solved by direct methods, and the non-hydrogen atoms were found in difference Fourier synthesis. The structures were refined by successive full-matrix least-squares on F² and with anisotropic thermal parameters. Hydrogen atom positions were located from difference Fourier maps. The H atoms attached to carbons were allowed to ride on the C atoms and assigned a fixed isotropic temperature factor U = 0.08 Å². Only the coordinates of the H atoms attached to N atoms were refined. The weighting function applied was w⁻¹ = [σ²(Fo²) + (gP)² +] where P = (Fo² + 2Fc²)/3, with g = 0.0971 (**1**) and 0.0301 (**2**).

One of the butyl groups in **1** displays conformational disorder, such that C(18), C(19) and C(20) split in two alternative positions with complementary occupancy factors of 0.70 and 0.30. Scattering factors taken from the International Tables¹¹ for X-ray crystallography package were used for data reduction. The structures were solved by direct methods¹² which revealed the position of all non-hydrogen atoms and SHELXL-97 was used for structure refinement.¹³ Table 1 contains a summary of the crystallographic data. Atomic coordinates, positional parameters, a complete list of bond distances and angles are included in the deposited material (see Supplementary Material for CCDC).

Table 1. Crystal data, data collection and structure refinement parameters for [ⁿBu₂Sn(H₂daptsc)]Cl₂·MeNO₂ (**1**) and [Me₂Sn(H₂dapsc)][Me₂SnCl₄] (**2**)

	1	2
Empirical formula	C ₂₀ H ₂₇ Cl ₂ N ₈ O ₂ S ₂ Sn	C ₃₀ H ₅₄ Cl ₈ N ₁₄ O ₄ Sn ₄
Formula weight (g mol ⁻¹)	665.2	1433.2
Crystal system	monoclinic	triclinic
Crystal size (mm ³)	0.70 x 0.34 x 0.16	0.26 x 0.16 x 0.08
Space group	P2 ₁ /n	P $\bar{1}$
<i>a</i> (Å)	13.582(2)	13.615(1)
<i>b</i> (Å)	12.487(2)	14.357(1)
<i>c</i> (Å)	18.237(3)	15.128(2)
α (°)		74.56(1)
β (°)	102.63(1)	89.79(1)
γ (°)		65.27(1)
<i>V</i> (Å ³)	3018.1(8)	2569.3(4)
<i>Z</i>	4	2
<i>D</i> _{calc} (g cm ⁻³)	1.417	1.853
μ (mm ⁻¹)	1.187	2.386
<i>F</i> (000)	1312	1400
θ range for data collection	1.50 to 27.50 deg.	1.50 to 25.00 deg.
Limiting indices	0 ≤ <i>h</i> ≤ 17 0 ≤ <i>k</i> ≤ 16 -23 ≤ <i>l</i> ≤ 23	0 ≤ <i>h</i> ≤ 15 -14 ≤ <i>k</i> ≤ 16 -17 ≤ <i>l</i> ≤ 17
Reflections collected / unique	7206 / 6921 [R(int) = 0.0278]	9260 / 8855 [R(int) = 0.0534]
Max. and min. transmission	0.4693 and 0.3592	0.9542 and 0.7607
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	6921 / 1 / 314	8855 / 3 / 581
Goodness-of-fit on F ²	1.057	1.005
Final R indices [I > 2σ(I)]	R1 = 0.0581, wR2 = 0.1546	R1 = 0.0530, wR2 = 0.0960
R indices (all data)	R1 = 0.0947, wR2 = 0.1793	R1 = 0.0995, wR2 = 0.1127
Extinction coefficient	0.0017(4)	0.0037(1)
Largest diff. peak and hole e.Å ⁻³	1.187 and -0.617	0.845 and -0.710

Results and Discussion

Molecular structure of [ⁿBu₂Sn(H₂daptsc)]Cl₂·MeNO₂ (**1**)

Figure 1 shows the pentagonal bipyramidal coordination of complex **1**. Table 1 contains the crystal data and structure refinement parameters and Table 2 shows selected bond distances and angles. The structure determination revealed the presence of a dication complex of tin(IV), 2,6-diacetylpyridine *bis*(thiosemicarbazone)di-*n*-butyltin(IV) chloride, with two chlorides as counter ions. A nitromethane molecule helps the packing mode.

The metal is heptacoordinated, showing a distorted pentagonal bipyramidal geometry, with the pentahapto ligand, H₂daptsc, on the equatorial plane and two *n*-butyl groups on the axial positions. This is strikingly different from other cases already reported in the literature. When the H₂daptsc ligand reacted with Ph₂SnCl₂ elimination of one HCl molecule took place, originating the [Ph₂Sn(Hdaptsc)]Cl cation complex.³ Reaction with Me₂SnO led to H₂O elimination and formation of [Ph₂Sn(daptsc)]·2DMF.¹⁰ This work relates the first tin(IV) complex of *bis*(thiosemicarbazone) in which during the reaction the N(3)-H and N(6)-H protons remained in the structure.

Due to the geometric requirements of the thiosemicarbazone moieties, the pentagon is not regular; the angle subtended at tin(IV) by the two sulfur atoms is significantly enlarged to 84.42(6)° from that in an idealized pentagonal bipyramidal (72°), while the other equatorial angles are: S(2)-Sn-N(5) = 71.2(1), N(5)-Sn-N(1) = 66.1(2), N(1)-Sn-N(2) = 66.7(2), N(2)-Sn-S(1) = 71.8(1)°. The axial *n*-butyl groups also contribute to the observed distortion since they have an C(13)-Sn-C(17) angle of 176.2(3)°.

The equatorial bond distances Sn-S(1) = 2.708(2), Sn-S(2) = 2.736(2), Sn-N_{py}(1) = 2.384(5), Sn-N(2) = 2.455(5) and Sn-N(5) = 2.470(5) Å are significantly longer than the equivalent bond distances Sn-S(1) = 2.593(1), Sn-S(2) = 2.603(1), Sn-N_{py}(4) = 2.368(3), Sn-N(3) = 2.427(4) and Sn-N(5) = 2.421(4) Å, found in [Ph₂Sn(daptsc)]·2DMF.¹⁰ However, the axial bond lengths Sn-C(13) = 2.143(7) and Sn-C(17) = 2.126(8) Å are shorter than the axial bond lengths Sn-C(11) = 2.178(4) and Sn-C(21) = 2.179(4) Å, observed in [Ph₂Sn(daptsc)]·2DMF.¹⁰ Coordination to the tin(IV) center by the imine nitrogen and thiolate sulfur atoms, shorten the bonds distances around the metal due to the strong attraction of the negatively charged ligand, daptsc²⁻, with the metal atom.

These two complexes also differ with respect to the

bond distances in both arms of the ligand. Thus, the S(1)-C(1) = 1.731(5), S(2)-C(9) = 1.729(5), N(2)-C(1) = 1.331(7), N(6)-C(9) = 1.333(6), N(2)-N(3) = 1.365(5), N(5)-N(6) = 1.381(5), N(3)-C(2) = 1.307(6) and N(5)-C(8) = 1.306(7) Å bond distances observed in $[\text{Ph}_2\text{Sn}(\text{daptsc})] \cdot 2\text{DMF}^{10}$ are different from those found in complex **1**. These differences occur because the double deprotonation of the N-H groups allows the delocalization of the π electrons in the deprotonated arms of daptsc^{2-} , lengthen the C=S, and N=C double bonds and shorten the C-N and N-N single bonds.

The $[(^n\text{Bu})_2\text{Sn}(2,6\text{Achexim})]$ complex,¹⁴ $[\text{H}_2, 2,6\text{Achexim} = 2,6\text{-diacetylpyridine bis}(3\text{-hexamethyleneiminylthiosemicarbazone})]$, is also a heptacoordinated pentagonal bipyramidal diorganotin(IV) derivative containing a double deprotonated *bis*(thiosemicarbazone) ligand in the pentagonal girdle.

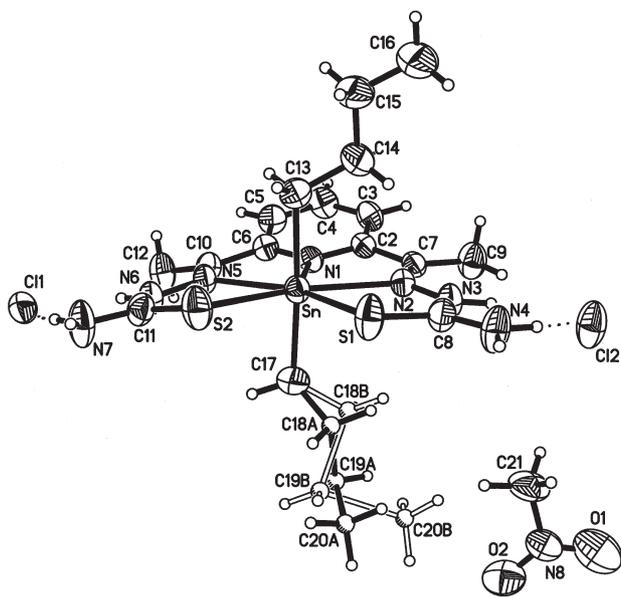


Figure 1. Perspective view of $[(^n\text{Bu})_2\text{Sn}(\text{H}_2\text{daptsc})]\text{Cl}_2 \cdot \text{MeNO}_2$ (**1**) showing the atom numbering scheme.

Molecular structure of $[\text{Me}_2\text{Sn}(\text{H}_2\text{daps})][\text{Me}_2\text{SnCl}_4]$ (**2**)

Complex **2** was described in a previous paper,² but at that time it had not been possible to obtain single crystals of **2** suitable for crystallographic work. Single crystals have since then been obtained and the results of the X-ray diffraction study are given in Figure 2 and Table 2. The structure determination revealed the occurrence of two independent cationic molecules per unit cell, 2,6-diacetylpyridine *bis*(semicarbazone)dimethyltin(IV), with hydrogen-bonding interactions between these cations and the counter ion, *trans*-tetrachlorodimethylstannate(IV), as shown in Figure 3.

In $[\text{Me}_2\text{Sn}(\text{H}_2\text{daptsc})]^{2+}$, the tin(IV) is heptacoordinate in a distorted pentagonal bipyramidal configuration, with the O,N,N,N,O-donor atoms in the pentagonal plane and the two methyl groups in the axial positions. The geometry about the tin(IV) in $[\text{Me}_2\text{SnCl}_4]^{2-}$ is a distorted octahedron with the methyl groups arranged in a *trans* fashion.

The chelating bond distances Sn(1)-O(1) = 2.314(6), Sn(1)-O(2) = 2.330(6), Sn(1)-N_{py}(1) = 2.365(7), Sn(1)-N(2) = 2.378(7) and Sn(1)-N(5) = 2.383(8) Å are significantly longer than the equivalent bond distances Sn-O(1) = 2.177(6), Sn-O(2) = 2.180(6), Sn-N_{py}(1) = 2.262(6), Sn-N(2) = 2.284(7) and Sn-N(5) = 2.252(7) Å, found in $[\text{MeSnCl}(\text{H}_2\text{daps})]_2\text{Cl} \cdot 2\text{H}_2\text{O}^2$, indicating a weaker interaction among H_2daps and the less acidic organotin(IV) derivative (Me_2SnCl_2). On the other hand, the bond lengths O(1)-C(8) = 1.266(10), O(2)-C(11) = 1.266(10), N(3)-C(8) = 1.360(11), N(6)-C(11) = 1.378(11), N(2)-N(3) = 1.378(10), N(5)-N(6) = 1.355(9), N(2)-C(6) = 1.293(11), and N(5)-C(9) = 1.295(11) Å, observed along the *bis*(semicarbazone) moieties in $[\text{MeSnCl}(\text{H}_2\text{daps})]_2\text{Cl} \cdot 2\text{H}_2\text{O}^2$ are nearly identical to those found in complex **2**.

Other reports on a similar tin(IV) heptacoordinate complex with O,N,N,N,O-pentadentate ligand include $[\text{Me}_2\text{Sn}(\text{Hdapf})]_2[\text{Me}_2\text{SnCl}_4]^{15}$ ($\text{H}_2\text{dapf} = 2,6\text{-diacetylpyridine bis}(2\text{-furoylhydrazone})$), containing a single-deprotonated ligand at the equatorial plane. The $[\text{ClSnCl}(\text{H}_2\text{daps})]_2\text{Cl} \cdot 2\text{H}_2\text{O}^6$ complex is another heptacoordinated tin(IV) derivative containing a fully-protonated ligand in the pentagonal girdle.

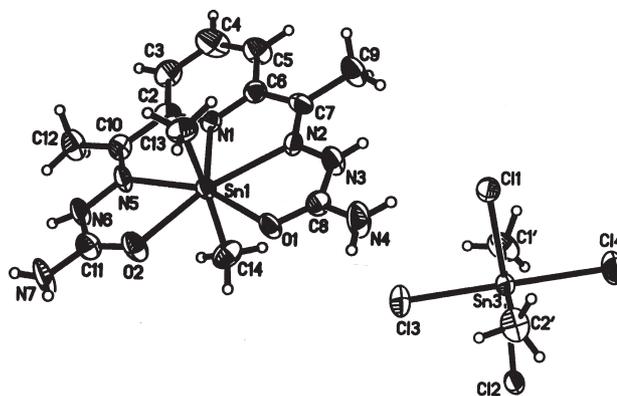


Figure 2. Perspective view of $[\text{Me}_2\text{Sn}(\text{H}_2\text{daps})][\text{Me}_2\text{SnCl}_4]$ (**2**) showing the atom numbering scheme.

Mössbauer spectroscopy

Since the ^{119}Sn Mössbauer spectrum of complex **2** had not originally shown more than one site,² a careful second measurement was undertaken, revealing two different tin(IV) atoms absorbing not far from each other, with isomer

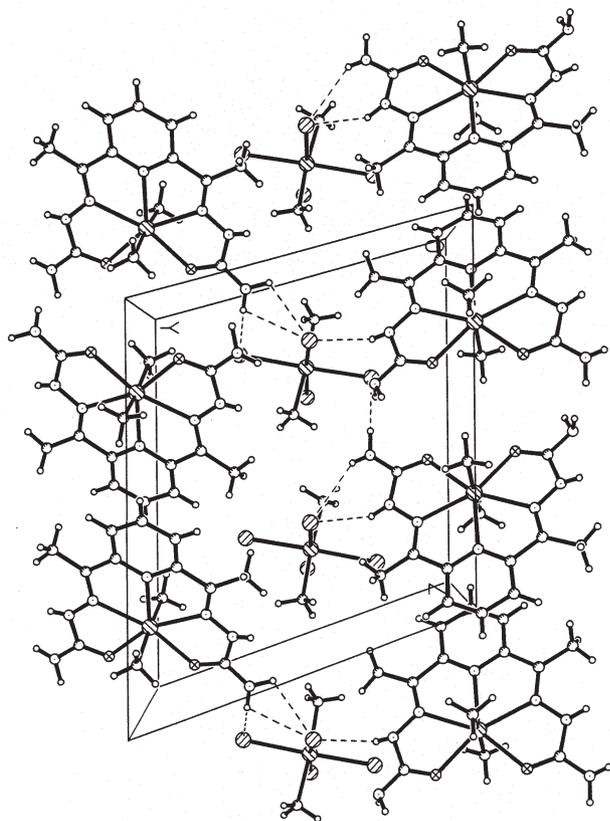


Figure 3. Packing of molecules in $[\text{Me}_2\text{Sn}(\text{H}_2\text{dapsc})][\text{Me}_2\text{SnCl}_4]$ (**2**). The N-H...Cl bonds are indicated.

shifts of $\delta = 1.29$ and 1.59 mm s^{-1} and quadrupole splitting of $\Delta = 4.24$ and 4.36 mm s^{-1} , respectively. Similar results were reported in the literature for $[\text{Me}_2\text{Sn}(\text{Hdapf})_2][\text{Me}_2\text{SnCl}_4]$,¹⁵ where the most abundant site, with isomer shift $\delta = 1.29 \text{ mm s}^{-1}$ and quadrupole splitting $\Delta = 3.96 \text{ mm s}^{-1}$, was assigned to the heptacoordinated tin(IV) atom of the $[\text{Me}_2\text{Sn}(\text{Hdapf})]^+$ cation. The other site, having $\delta = 1.56 \text{ mm s}^{-1}$ and $\Delta = 4.11 \text{ mm s}^{-1}$, corresponds to the hexacoordinated tin(IV) atom of the anion, $[\text{Me}_2\text{SnCl}_4]^{2-}$.

In the heptacoordinate species the s character shown by the tin(IV) atom is $1/7$, or 13% (presuming its hybridization to be sp^3d^3), whereas in the hexacoordinate counterion the s character is $1/6$, or 17% (corresponding to an sp^3d^2 hybridized atom). Therefore the higher isomer shift value corresponds to the hexacoordinate tin(IV) atom, given the direct relationship between isomer shift and s character.

Complex **1**, on the other hand, with only one tin(IV) atom per unit formula, showed just one ^{119}Sn Mössbauer absorption, with $\delta = 1.63 \text{ mm s}^{-1}$ and quadrupole splitting $\Delta = 4.05 \text{ mm s}^{-1}$. The isomer shift value is quite consistent with a lower ligand electronegativity, which causes an increase in δ .

The quadrupole splittings of the two heptacoordinate species are very close, reflecting similar electron density

Table 2. Selected bond lengths (Å) and angles (°) for $[\text{t}^n\text{Bu}_2\text{Sn}(\text{H}_2\text{dapsc})]\text{Cl}_2 \cdot \text{MeNO}_2$ (**1**) and for $[\text{Me}_2\text{Sn}(\text{H}_2\text{dapsc})][\text{Me}_2\text{SnCl}_4]$ (**2**)

		1	2
Bond lengths			
Sn-N(1)	2.384(5)	Sn(1)-N(1)	2.365(7)
Sn-N(2)	2.455(5)	Sn(1)-N(2)	2.378(7)
Sn-N(5)	2.470(5)	Sn(1)-N(5)	2.383(8)
Sn-S(1)	2.708(2)	Sn(1)-O(1)	2.314(6)
Sn-S(2)	2.736(2)	Sn(1)-O(2)	2.330(6)
Sn-C(13)	2.143(7)	Sn(1)-C(13)	2.11(1)
Sn-C(17)	2.126(8)	Sn(1)-C(14)	2.09(1)
S(1)-C(8)	1.703(7)	O(1)-C(8)	1.25(1)
S(2)-C(11)	1.700(8)	O(2)-C(11)	1.26(1)
N(3)-C(8)	1.356(9)	N(3)-C(8)	1.36(1)
N(6)-C(11)	1.341(10)	N(6)-C(11)	1.38(1)
N(2)-N(3)	1.364(8)	N(2)-N(3)	1.36(1)
N(5)-N(6)	1.370(7)	N(5)-N(6)	1.36(1)
N(2)-C(7)	1.295(9)	N(2)-C(7)	1.29(1)
N(5)-C(10)	1.279(9)	N(5)-C(10)	1.29(1)
		Sn(2)-C(1')	2.11(1)
		Sn(2)-Cl(1)	2.586(3)
		Sn(2)-Cl(3)	2.609(3)
Bond angles			
C(13)-Sn-C(17)	176.2(3)	C(13)-Sn(1)-C(14)	169.5(4)
C(13)-Sn-N(1)	88.0(3)	C(13)-Sn(1)-N(1)	94.5(3)
C(13)-Sn-N(2)	91.7(2)	C(13)-Sn(1)-N(2)	89.6(4)
C(13)-Sn-N(5)	91.3(3)	C(13)-Sn(1)-N(5)	93.9(4)
C(13)-Sn-S(1)	90.6(2)	C(13)-Sn(1)-O(1)	87.6(4)
C(13)-Sn-S(2)	87.8(2)	C(13)-Sn(1)-O(2)	86.3(4)
N(1)-Sn-N(2)	66.7(2)	N(1)-Sn(1)-N(2)	66.4(3)
N(1)-Sn-N(5)	66.1(2)	N(1)-Sn(1)-N(5)	67.0(3)
N(2)-Sn-S(1)	71.8(1)	N(2)-Sn(1)-O(1)	67.9(2)
N(5)-Sn-S(2)	71.2(1)	N(5)-Sn(1)-O(2)	67.4(2)
S(1)-Sn-S(2)	84.42(6)	O(1)-Sn(1)-O(2)	91.4(2)
N(1)-Sn-S(1)	138.5(1)	N(1)-Sn(1)-O(1)	134.2(2)
N(1)-Sn-S(2)	136.9(1)	N(1)-Sn(1)-O(2)	134.3(2)
		C(1')-Sn(2)-C(2')	175.0(5)
		Cl(1)-Sn(2)-Cl(2)	173.59(9)
		Cl(3)-Sn(2)-Cl(4)	178.2(1)

symmetries about the metal in both complexes. In the hexacoordinate counterion present in **2**, however, the quadrupole splitting of tin(IV) is noticeably different from that of its heptacoordinate cation, evidencing the difference in electron distribution in the two species.

A semiquantitative relationship of the Mössbauer quadrupole splitting (Δ) and the R-Sn-R angle has been reported¹⁶⁻¹⁹ for a series of distorted heptacoordinated diorganotin(IV) derivatives. The equation is $|\Delta| = 4[\text{R}](1 - 3/4\sin^2\theta)^{1/2}$, where [R] is the partial quadrupole splitting of the group R. Inserting the values $\Delta = 4.05 \text{ mm s}^{-1}$ and $\theta = 176.3(3)^\circ$ for complex **1** and $\Delta = 4.24 \text{ mm s}^{-1}$ and $\theta = 169.4(6)^\circ$ for complex **2** we predict $[\text{t}^n\text{Bu}] = -1.01 \text{ mm s}^{-1}$ and $[\text{Me}] = -1.07 \text{ mm s}^{-1}$, respectively. Similar values have been reported for heptacoordinate tin(IV) complexes embodying pentadentate ligands, namely $[\text{t}^n\text{Bu}_2\text{Sn}(\text{dappt})][\text{Me}_2\text{CO}]_{0.5}$,²⁰ $[\text{t}^n\text{Bu}] = -0.89 \text{ mm s}^{-1}$, $[\text{t}^n\text{Bu}_2\text{Sn}(2,6\text{Achexim})]$,¹⁴ $[\text{t}^n\text{Bu}] = -0.86 \text{ mm s}^{-1}$ and

$[\text{Me}_2\text{Sn}(\text{Hdapf})]_2[\text{Me}_2\text{SnCl}_2]^{15}$ $[\text{Me}] = -1.01 \text{ mm s}^{-1}$, where $\text{H}_2\text{dappt} = 2,6$ -diacetylpyridine *bis*(4-phenylthiosemicarbazone), $\text{H}_22,6\text{Achexim} = 2,6$ -diacetylpyridine *bis*(3-hexamethyleneiminylthiosemicarbazone) and $\text{H}_2\text{dapf} = 2,6$ -diacetylpyridine *bis*(2-furanoylhydrazone).

Infrared spectroscopy

The IR spectrum of $\text{H}_2\text{daptsc}\cdot\text{HCl}$ shows three bands at 3423, 3270 and 3161 cm^{-1} attributed to $\nu(\text{N-H})$ of the hydrogen bonded NH and NH_2 groups.¹⁰ The spectrum of complex **1** is different, showing one very broad band at 3067 cm^{-1} shifted to smaller wavenumbers. These shifts are probably due to the hydrogen bond in which the NH and NH_2 groups are involved with MeNO_2 and Cl. These hydrogen bonding interactions are indicated in Figure 1. Similar observations are supported by literature data.¹⁹ The $\nu(\text{C=N}, \text{C=C})$ absorption bands, at 1612, 1568 and 1464 cm^{-1} , are shifted to higher frequencies relative to those of the free ligand, at 1602, 1504 and 1441 cm^{-1} and the $\nu(\text{C=S})$ bands, at 1245, 1104 and 812 cm^{-1} , are shifted to lower frequencies, at 1196, 1012 and 792 cm^{-1} , in complex **1**. This behavior is typical for this ligand when it is S,N,N,N,S-coordinated.²⁰

The IR spectrum of $\text{H}_2\text{daps}\cdot\text{HCl}$ shows several bands in the 3500-3171 cm^{-1} range and a strong absorption at 1668 cm^{-1} attributed to $\nu(\text{N-H})$ and $\nu(\text{C=O})$, respectively. These bands in the spectrum of complex **2** are shifted to lower wavenumbers and are found at 3127 and 1655 cm^{-1} , respectively, in agreement with the structural data.

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Supplementary Material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 157339 (**1**) and CCDC 157340 (**2**). 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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