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Diorganotin(IV) complexes with acetone N(4)-phenylthiosemicarbazone (Haptsc) as ligand. The crystallographic structures of $[Sn(CH_3)_2(aptsc)X]$ ($X = Cl$ and Br)

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Abstract

The reaction of Haptsc with $SnMe_2Cl_2$ and $SnMe_2Br_2$ yielded $[Sn(CH_3)_2(aptsc)Cl]$ (**1**) and $[Sn(CH_3)_2(aptsc)Br]$ (**2**), respectively. The complexes were characterized by IR and NMR (^1H, ^{119}Sn) spectroscopic methods, elemental analysis and X-ray crystal structure determination. The X-ray study revealed that both complexes possess a trigonal bipyramidal geometry. (**1**) crystallizes in the orthorhombic crystal system, space group $P2_12_12_1$, with $a = 10.5157(6)$, $b = 12.2085(15)$, $c = 12.496(3)$ Å, $V = 1604.2$ Å^3 and $Z = 4$. (**2**) crystallizes in the monoclinic crystal system, space group $P2_1/c$, with $a = 17.3253(17)$, $b = 7.2323(6)$, $c = 13.3527(15)$ Å, $\beta = 108.560(10)°$, $V = 1586.1$ Å^3 and $Z = 4$.
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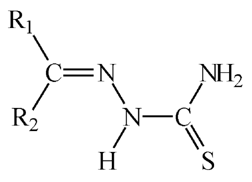
Keywords: Organotin(IV) complexes; Thiosemicarbazone complexes; Crystal and molecular structures

1. Introduction

Thiosemicarbazones have attracted a crescent interest in recent years due to their biological properties, such as antiviral, antibacterial, antimalarial, antifungal and antitumoral activities [1–3]. As ligands, they can behave as bi-, tri-, tetra- and penta-coordinate chelating agents towards a wide range of metallic ions, forming many structurally different complexes [3]. The research on coordination chemistry, analytical applications and biological activities of thiosemicarbazones and its metallic derivatives has increased considerably. A search on the Cambridge Structure Database (CSD) showed more than thousand papers published in the last decade [3,4].



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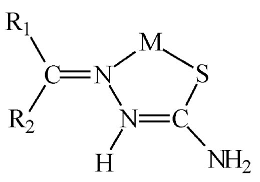

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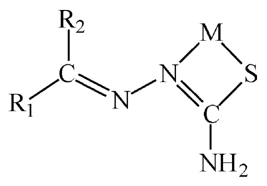

III

The uniqueness of thiosemicarbazone (**I**) relates not only to the presence of many electron donor centers in the structure but also to the bonding scheme. Ten different coordination fashion were already observed [3]. As a bidentate ligand, it can coordinate anionically, either bonding to the metal ion through the imine nitrogen and the sulfur atoms (**II**), or via the hydrazinic nitrogen and the sulfur atoms (**III**), forming five- and four-membered chelate rings, respectively, [5,6]. The different coordination modes (**II and III**) of (**I**) are related to the level of steric hindrance caused by the bulk group R_1 located in the *trans* position to the hydrazinic nitrogen [5,6].

The complexes (**1**) and (**2**) were synthesized as part of a research program dedicated to the investigation of the coordination modes of multidentate thiosemicarbazones towards organotin(IV) compounds, namely $SnMe_2Cl_2$, $SnMe_2Br_2$, $Sn^nBu_2Cl_2$, $SnPh_2Cl_2$ [7–10].

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2. Experimental

2.1. Material and procedures

All starting compounds and reagents of highest grade were used without further purification. IR spectra were recorded in KBr pellets on a Bomen BM100 FT-IR spectrometer in the 4000–400 cm^{-1} region. ^1H NMR spectra were recorded in CD_2Cl_2 ($SiMe_4$) and ^{119}Sn NMR spectra in $CHCl_3$ ($SnMe_4$) using a Bruker AC250 MHz and a Varian Mercury Plus 300 MHz spectrophotometers, respectively. A Carlo Erba 1104 elemental analyzer was used for the microanalyses. X-ray data for structure determination were collected on an Enraf-Nonius CAD-4 diffractometer.

2.1.1. Preparation of Haptsc

The thiosemicarbazone Haptsc was prepared by reacting equimolar amounts of N(4)-phenylthiosemicarbazide (1 g, 6 mmol) and acetone (0.4 g, 7 mmol) in 20 ml of a 1:1 ethanol–water mixture under reflux for 30 min. After cooling, 0.8 g of the ligand was obtained as a white solid, which was filtered off and dried under vacuum over $CaCl_2$. Yield 64% (0.8 g, 3.8 mmol). Mp 125–127 °C.

*2.1.2. Preparation of [$Sn(CH_3)_2$(aptsc)Cl] (**1**) and [$Sn(CH_3)_2$(aptsc)Br] (**2**)*

The halogen complexes were synthesized by refluxing Haptsc (0.2 g, 0.97 mmol) and the appropriate $SnMe_2X_2$ (0.97 mmol) in 15 ml of EtOH for 1 h. The reaction mixture was then filtered to give a clear solution. The products were isolated as white solids by slow evaporation of the mother solution. Anal. Calcd for $C_{12}H_{18}ClN_3SSn$ (**1**): C 36.81, H 4.86, N 10.74, S 8.19. Found C 36.84, H 4.07, N 10.89, S 7.89. ^1H NMR δ 1.1 [s, 6H, $Sn(CH_3)_2$], 2.2 and 2.1 [s, 6H, $N{=}C(CH_3)_2$] and 7.4, 7.2, 7.0, 6.6 (m, 5H, C_6H_5). ^{119}Sn NMR δ −80. Yield 63% (1.2 g, 3.1 mmol). Mp 175 °C (d). Anal. Calcd for $C_{12}H_{18}BrN_3SSn$ (**2**): C 33.05, H 4.36, N 9.64, S 7.34. Found C 33.10, H 4.46, N 9.74, S 7.19. ^1H NMR δ 1.2 [s, 6H, $Sn(CH_3)_2$], 2.2 and 2.1 [s, 6H, $N{=}C(CH_3)_2$] and 7.4, 7.2, 7.0, 6.6 (m, 5H, C_6H_5). ^{119}Sn NMR δ −79. Yield 76% (1.6 g, 3.7 mmol). Mp 195–197 °C.

2.2. Crystal structure determinations

Suitable crystals for structural analysis for both complexes were obtained by slow evaporation of the refluxed solutions. The cell constants were calculated from 25 reflections measured with a wide range of 2θ. The program HELENA [11] was used for data reduction. The structures were solved using the heavy atom method, with the program SHELXS-97 [12]. All non-hydrogen atoms were refined anisotropycally with SHELXL-97 [13] and the hydrogen atoms were found in the Fourier-Map for both complex structures. A semi-empirical ψ-scans absorption was performed for corrections [11]. More detailed information about the crystal structure determination is given in Table 1. Table 2 presents selected bond lengths and angles. Labeled diagrams of (**1**) and (**2**) are shown in Figs. 1 and 2, respectively.

Table 1
Crystal data collection and structure refinement data for **1** and **2**

	1	**2**
Empirical formula	$C_{12}H_{18}ClN_3SSn$	$C_{12}H_{18}BrN_3SSn$
Formula weight	390.49	434.95
Temperature (K)	208(2)	208(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Crystal color	Colorless	Colorless
Crystal size (mm)	0.60 × 0.25 × 0.15	0.45 × 0.35 × 0.20
Space group	$P2_12_12_1$	$P2_1/c$
Z, calculated density (g cm^{-3})	4, 1.617	4, 1.821
Absorption coefficient (mm^{-1})	1.877	4.249
a (Å)	10.5157(6)	17.3253(17)
b (Å)	12.2085(15)	7.2323(6)
c (Å)	12.496(3)	13.3527(15)
β (°)	90.000	108.560(10)
V ($Å^3$)	1604.2(4)	1586.1(3)
F(000)	776	848
Theta range for data collection (°)	3.03–28.00	3.06–27.97
Limiting indices	$-13 \leq h \leq 13$ $-1 \leq k \leq 16$ $-1 \leq l \leq 16$	$-22 \leq h \leq 22$ $-9 \leq k \leq 1$ $-1 \leq l \leq 17$
Reflections collected/unique	4940/3858 [R(int) = 0.0202]	4935/3807 [R(int) = 0.0256]
Completeness to theta	28.00(99.8%)	27.97(99.9%)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3858/0/235	3807/0/236
Goodness-of-fit on F^2	1.087	1.046
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0208$, $wR2 = 0.0533$	$R1 = 0.0252$, $wR2 = 0.0548$
R índices (all data)	$R1 = 0.0218$, $wR2 = 0.0538$	$R1 = 0.0386$, $wR2 = 0.0588$
Largest diff. Peak and hole (e$Å^{-3}$)	0.321 and −0.885	0.490 and −0.537

3. Results and discussion

3.1. Infrared spectroscopy

The main stretching bands for Haptsc and their complexes are shown in Table 3. The two high frequency bands of the free ligand, centered at 3249 and 3170 cm^{-1},

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

	1	2
Sn–C(9)	2.123(3)	2.116(3)
Sn–C(10)	2.117(3)	2.121(3)
Sn–N(1)	2.328(2)	2.359(2)
Sn–S	2.4192(8)	2.4467(7)
Sn–X[a]	2.5242(8)	2.6559(4)
C(2)–S	1.771(2)	1.764(3)
C(1)–N(1)	1.293(3)	1.287(3)
C(2)–N(2)	1.295(3)	1.293(3)
C(2)–N(3)	1.360(3)	1.374(3)
N(1)–N(2)	1.391(3)	1.397(3)
N(3)···Cl[b]	3.292(2)	
H(3)···Cl[b]	2.43(4)	
C(9)–Sn–C(10)	129.26(16)	135.59(16)
C(9)–Sn–N(1)	93.87(11)	93.73(13)
C(10)–Sn–N(1)	92.68(11)	89.41(11)
C(9)–Sn–X[a]	92.31(10)	95.00(11)
C(10)–Sn–X[a]	93.55((10)	93.56(10)
N(1)–Sn–X[a]	165.50(5)	164.14(5)
C(9)–Sn–S	115.67(12)	110.12(12)
C(10)–Sn–S	114.92(11)	113.70(9)
N(1)–Sn–S	78.13(5)	76.83(5)
S–Sn–X[a]	87.38(3)	87.729(19)
N(2)–C(2)–S	128.17(19)	128.8(2)
C(2)–N(3)–C(3)	128.8(2)	127.5(2)
N(3)–H(3)–Cl[b]	178(3)	

[a] X = Cl in **1** and Br in **2**.

[b] Symmetry operation: $-x + 3/2, -y + 2, z - 1/2$.

were attributed to ν(N–H) stretching. The spectra of both complexes lack bands located at about 3170 cm^{-1}, as a result of the ligand deprotonation, indicating that this absorption refer to the ν(N$_{\text{hydrazinic}}$–H) vibration. The lower position of the ν(N$_{\text{aminic}}$–H) absorption in (**1**) (3307 cm^{-1}) compared to (**2**) (3374 cm^{-1}), might be a consequence of the intermolecular hydrogen bond N(3)–H(3)···Cl observed in (**1**). This situation is not realized in (**2**), although similar results can be found in the literature [7–10, 14–17].

Significant changes in the ligand bonds upon complexation include variations in the ν(C=C) + ν(C=N) and ν(C–S) + ν(C–N) vibrational frequencies to lower values. These data has been a good indication of coordination through the azomethine nitrogen and the sulfur atoms [7,8,10].

3.2. NMR spectroscopy

The ^{1}H NMR spectrum of (**1**) has showed an isolated singlet at δ 1.1 [$^2J(^{119}\text{Sn–CH}_3) = 81$ Hz] and a pair of singlets at δ 2.2 and 2.1, which suggest that the methyl groups N=C(CH$_3$)$_2$ are magnetically non-equivalent. The spectrum of (**2**) showed similar signals at δ 1.2 [$^2J(^{119}\text{Sn–CH}_3) = 75$ Hz] and δ 2.2 and 2.1. The use of Lockhart-Manders equation $\{\theta = 0.0161\ [^2J(^{119}\text{Sn–CH}_3)]^2 - 1.32\ [^2J(^{119}\text{Sn–CH}_3)] + 133.4\}$ [18] with the observed coupling constants of 81 and 75 Hz results in CH$_3$–Sn–CH$_3$ bond angles of 125° in (**1**) and 132° in (**2**). These values fairly accurate to the angles observed in their crystal structures, 129.26(16)° in (**1**) and 135.59(16)° in (**2**), indicating that the structural arrangement of the complexes in the solid state are retained in solution. A similar result was reported for [Sn(CH$_3$)$_2$(DAP4P)] (H$_2$DAP4P, 2-hydroxyacetophenone-N(4)-phenylthiosemicarbazone) [19].

The ^{119}Sn NMR chemical shift is very sensitive to complexation and usually greatly shifted downfield or upfield on bonding to a Lewis base. The upfield chemical shift values of −80 and −79 ppm observed for compounds (**1**) and (**2**), respectively, are indicative of considerable shielding and five-coordination of the Sn(IV) nucleus [20].

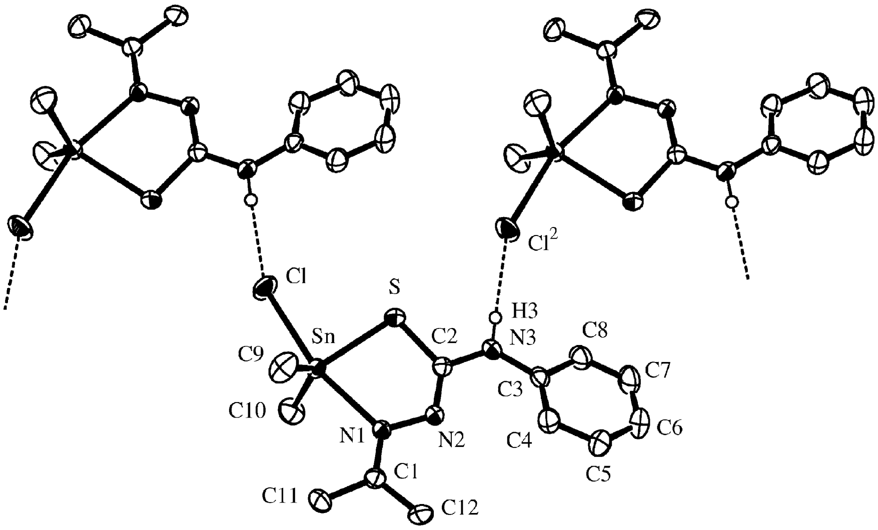

Fig. 1. ORTEP diagram of [Sn(CH$_3$)$_2$(aptsc)Cl] (**1**) showing three complex molecules linked through intermolecular hydrogen bonds, showed as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. Except H(3), the H atoms are omitted for clarity.

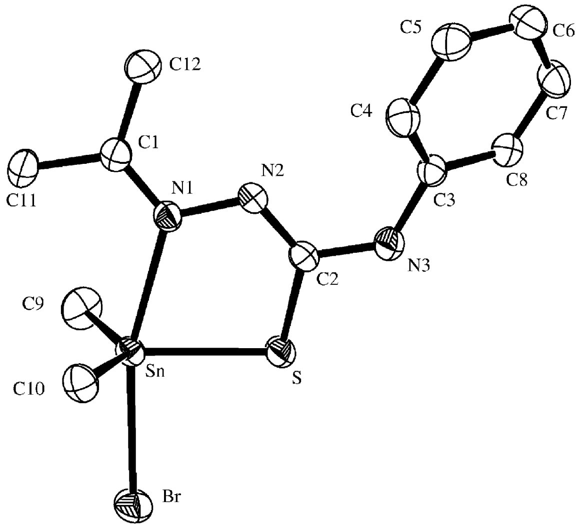

Fig. 2. ORTEP diagram of [Sn(CH_3)$_2$(aptsc)Br] (**2**). Displacement ellipsoids are drawn at the 50% probability level. The H atoms are omitted for clarity.

These chemical shift values are comparable to a −92 ppm for [Sn(CH_3)$_2$(OX)Cl], where HOX is 8-hydroxyquinoline [20] and to a −104.7 ppm for [Sn(CH_3)$_2$L], where H_2L is salicylaldehydehydethiosemicarbazone [21]. The ^{119}Sn NMR chemical shifts for $SnMe_2Cl_2$ and $SnMe_2Br_2$ has taken place at 137 and 72 ppm, suggesting that the five-coordination pattern in the solid state has remained in $CDCl_3$ solution.

3.3. Crystal structures

The geometry around the Sn(IV) center in both complexes is best described as a distorted trigonal bipyramid (TBP), with the sulfur atom and the two methyl carbons, C(9) and C(10), positioned at the equatorial plane, while the azomethyne nitrogen N(1) and halogen [Cl in (**1**) and Br in (**2**)] atoms are occupying the axial positions.

Table 3
Main vibration bands (cm^{-1}) of Haptsc and its complexes

Compound	ν(N–H)	ν(C=C) + ν(C=N)	ν(C–S) + ν(C–N)	ν(C=S)
Haptsc	3249s 3170m	1593m, 1537s 1495m, 1443m	1382w, 1342m	1193s
[Sn(CH_3)$_3$ (aptsc)Cl] (**1**)	3307s	1557s, 1516s 1497m, 1438s	1364m	1187w
[Sn(CH_3)$_3$ (aptsc)Br] (**2**)	3374s	1548s, 1501s 1435s	1360w	1188m

The considerable values for the Sn–S and Sn–C bond distances found in both complexes, 2.433 and 2.119 Å, are in agreement with those previously reported for organotin(IV) thiolates containing bidentate ligands [14,15].

The distances Sn–N(1) [2.328(2) Å in (**1**) and 2.359(2) Å in (**2**)] are remarkable close to the value of 2.359(4) Å found in [Sn(CH_3)$_2$(FPT)Cl]·0.5H_2O, where HFTP is 2-formylpyridinethiosemicarbazone. The sulfur and nitrogen atoms are bonded to the Sn(IV) core in the latter forming a five-membered chelate ring [16]. On the other hand, the distances Sn–Cl = 2.5242(8) Å and Sn–Br = 2.6559(4) Å are shorter than the values of 2.6722(9) and 2.9075(6) Å, found in Sn(IV) hexacoordinate complexes, namely [Sn(CH_3)$_2$(AP4P)Cl] and [Sn(CH_3)$_2$(AP4P)Br], where HAP4P is 2-acetylpyridine N(4)-phenylthiosemicarbazone [10].

The average equatorial angles S–Sn–C(9) (112.9°), S–Sn–C(10) (114.3°) and C(9)–Sn–C(10) (132.4°) as well as the axial angles N(1)–Sn–X (164.8°) are quite different from the equivalent angles found in [Sn(CH_3)$_2$(FPT)Cl]·0.5H_2O [108.3(2), 107.2(2), 143.0(3) and 155.39(9)°, as a result of the Sn···N(py) intermolecular interaction present in the latter [16].

The chelate ring atoms Sn, N(1), N(2), C(2), S, and N(3) inclusive, are coplanar with a mean deviation from the plane of 0.0226 Å in (**1**) and of 0.0017 Å in (**2**). The angle between this plane and the phenyl ring formed by the atoms C(3), C(4), C(5), C(6), C(7) and C(8) has 25.1(1)° in (**1**) and 33.5(1)° in (**2**).

The crystal structures of (**1**) and (**2**), differ from each other mainly by their packing mode, what can be clearly distinguished in the crystallization systems. The structure of (**1**) has presented intermolecular N(3)–H(3)···Cl hydrogen bonds, forming a one-dimensional chain, as shown in Fig. 1. The latter is directed along the crystallographic *c* axis, with N(3)···Cl = 3.292(2) Å, H(3)···Cl = 2.43(4) Å and N(3)–H(3)–Cl = 178(3)°. Such an interaction does not occur in (**2**).

4. Supplementary data

Crystallographic data for the structural analysis of complexes (**1**) and (**2**) have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1 EZ, UK, and are available free of charge from the Director on request quoting the deposition numbers CCDC 203905 and 203906, respectively (Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

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