

Paulo Henrique Duarte, Silvestre Rabello Aguiar Júnior e Rosalice Mendonça Silva*

Depto. de Química - Universidade Federal de Minas Gerais - 31270-901 - Belo Horizonte - MG

Beatriz G. Guimarães e Nivaldo L. Speziali

Depto. de Física - Universidade Federal de Minas Gerais - 31270-901 - Belo Horizonte - MG

Recebido em 27/1/94; aceito em 5/4/95

The structures of two tin compounds, containing thiolate ligands, were determined by X-ray diffraction, $(\text{Ph})_3\text{Sn}(\text{SPh})$, **1**, and $(\text{Ph})_2\text{Sn}(\text{SPh})_2$, **2**. Compound **1** belongs to $P2_1/c$ space group with cell parameters $a=7.745(2)\text{Å}$, $b=16.411(3)\text{Å}$, $c=16.120(3)\text{Å}$, $\beta=93.56(3)^\circ$ and $Z=4$. Compound **2** belongs to $P\bar{1}$ space group, with cell parameters $a=9.449(2)\text{Å}$, $b=10.310(2)\text{Å}$, $c=12.430(2)\text{Å}$, $\alpha=95.390(1)^\circ$, $\beta=103.190(1)^\circ$, $\gamma=107.440(1)^\circ$ and $Z=2$. The introduction of two PhS^- ligands around the tin atom did alter the expected tetrahedral geometry for compound **2**. Some of the determined angles were $\angle\text{C21SnC31}$, $119.3(2)^\circ$; $\angle\text{S1SnC31}$, $102.4(6)^\circ$; $\angle\text{C21SnS12}$, $105.7(1)^\circ$.

Keywords: tin; thiolate ligands; X-ray diffraction.

INTRODUCTION

We have been interested in tin compounds of the type $\text{R}_x\text{Sn}(\text{SPh})_y$, where $\text{R}=\text{Ph}$, for complexation with transition metals, aimed to obtain heterobimetallic complexes with M-Sn bond, where M = early transition metal.

The chemistry of the thiolate complexes has been attracting much attention due to its importance in biological¹, catalytic² and industrial² processes. As examples, in the active site of the enzyme nitrogenase the thiolate ligands around the metal plays a central role^{1,3} and the H_2 activation in hydrodesulfurization reactions, complexes with S containing ligands are involved². Also, the thiolate ligands are particularly interesting because they can bind to more than one metal center through the S lone pairs, making the formation of heterobimetallic complexes⁴ easier, besides the fact that S is a good σ and π donor (and acceptor), in this way stabilizing metals in both high and low oxidation states.

In this paper the X-ray crystal structure elucidation of compounds (benzenethiolato)triphenyltin(IV), $(\text{Ph})_3\text{Sn}(\text{SPh})$, **1**, and bis(benzenethiolato)diphenyltin(IV), $(\text{Ph})_2\text{Sn}(\text{SPh})_2$, **2**, are described. The structure of compound **1** was first proposed by Timofeeva et al⁵. However they did not publish all the complete data obtained from the X-ray diffraction studies, being much more interested to use the data to determine the conformation and the barriers to internal rotation in alkyl aryl sulfides, thiophenols and their organotin derivatives.

This study was done in order to compare properties such as bond strength and geometry in the two compounds that possess a different number of thiolate ligands around the tin atom.

EXPERIMENTAL SECTION

Methods and Materials

All the solvents were distilled before use. Compounds **1** and **2** were prepared according to modifications of the procedures described in the literature⁶. Proton NMR spectra were recorded on a Bruker AC 80 spectrometer and I.R. spectra on a Perkin Elmer 283B.

(Ph)₃Sn(SPh) - 5.0g (12.99 mmol) of $(\text{Ph})_3\text{SnCl}$ was put to react with 1.715g (12.99 mmol) of NaSPh, in ether, under reflux for 1 hour. After this the solvent was removed under vacuum. The residue was extracted with petroleum ether and filtered. The solution was left under room temperature and white crystals were obtained.

I.R. (KBr, cm^{-1}): $\nu_{\text{Sn-S}}=323$; $^1\text{H NMR}$ (CDCl_3 , 80 MHz, ppm): 7.7- 7.2 (m, $3\text{C}_6\text{H}_5$); 7.0- 6.8 (m, SC_6H_5); m.p. = 104°C ;

(Ph)₂Sn(SPh)₂ - In a Schlenk flask were added 1.0g (2.90 mmol) of $(\text{Ph})_2\text{SnCl}_2$ and 0.383g (2.90 mmol) of NaSPh in 20 ml of ethanol, under nitrogen. After being refluxed for 4h the solution was filtered and the volume of ethanol reduced under vacuum. Upon addition of n-hexane the solution was left in the refrigerator overnight and a white microcrystalline solid precipitated.

I.R. (KBr, cm^{-1}): $\nu_{\text{Sn-S}}=340$; $^1\text{H NMR}$ (CDCl_3 , 80 MHz, ppm): 7.8-7.25 (m, $2\text{C}_6\text{H}_5$); 7.2-7.0 (m, $2\text{SC}_6\text{H}_5$); m.p. = 61°C .

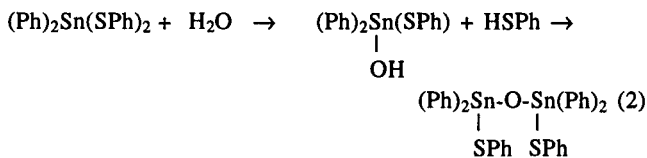
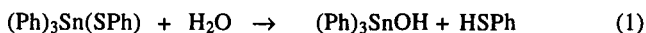
X-Ray Crystal Structure Determination

Data collection for both compounds were performed on a Siemens P4 diffractometer using graphite-monochromated $\text{MoK}\alpha(\lambda=0.71073\text{Å})$ radiation. The reflections were collected at room temperature in 2θ - θ scan mode with a variable scan rate (1 to $60^\circ/\text{min}$). Three reference reflections were measured for every 247 reflections and no significant change in their intensity was verified. No absorption correction was necessary since $\mu=1.35\text{mm}^{-1}$ for both compounds. The structures were solved by a direct method employing a SHELXTL-PCTM program package⁷. The structures were refined to convergence by full-matrix least-squares methods, the quantity minimized being $\sum w[F_o - F_c]^2$. Details of crystallographic data collection, structure refinement and crystal data are given in Table 1.

Compound **1** crystallizes in $P2_1/c$ space group. Cell constants were obtained from the refinement of 52 reflections. A total of 4508 reflections were collected of which 2195 were independent and 2080 were flagged as observed ($F > 4.0\sigma(F)$). Tin, sulfur and all carbon atoms were refined anisotropically, while all hydrogens were placed at idealized positions with individual isotropic thermal motion factor at 0.08Å^2 . The largest peak in the final difference Fourier map was $0.85\text{e}\text{Å}^{-3}$ in the neighbourhood of the Sn atom. This value is not very significant once it is of the same order as the peaks found at the hydrogens positions. Compound **2** crystallizes in $P\bar{1}$ space group. Cell constants were obtained from the refinement of 33 reflections. A total of 2542 reflections were collected of which 2117 were independent and 1852 were flagged as observed ($F > 4.0\sigma(F)$). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions with individual isotropic thermal factor fixed at 0.08Å^2 .

RESULTS AND DISCUSSION

Although Omae⁸ reports that the thiolate compounds of Sn are harder to hydrolyse than the corresponding chlorides, giving the corresponding thiol and the hydroxy compounds, eq. 1 and 2,



precautions should be taken to keep the thiolates under anhydrous conditions, better under N₂, otherwise after some days their appearance is that of an oily solid. This process is faster for compound 2. In the ¹HNMR spectra of the oily solids, clean peaks can be detected due to the thiols, that is, peaks due to the S-H proton resonance, as well as modifications in the region of the Ph protons. In the solid state I.R. modifications are easily found in the fingerprint region. The same happens if the solvents used in the preparations are not rigorously dried.

X-Ray Crystal Structures - The crystals for X-ray structure elucidation were obtained from an ether solution, upon slow evaporation, under room temperature. Crystallographic data for

Table 1. Summary of crystallographic data for (Ph)₃Sn(SPh), 1, and (Ph)₂Sn(SPh)₂, 2.

	1	2
molecular formula	C ₂₄ H ₂₀ SSn	C ₂₄ H ₂₀ S ₂ Sn
formula weight	459.1	491.2
space group	P2 ₁ /c	P $\bar{1}$
a, Å	7.745(2)	9.449(2)
b, Å	16.411(3)	10.310(2)
c, Å	16.120(3)	12.430(2)
α, deg	90.00	95.390(1)
β, deg	93.56(3)	103.190(1)
γ, deg	90.00	107.440(1)
V, Å ⁻³	2044.9(10)	1107.5(5)
temp, °C	22	22
Z	4	2
D(calcd), Mg.m ⁻³	1.491	1.473
radiation	MoKα	MoKα
	(λ= 0.71073 Å)	(λ= 0.71073 Å)
μ, mm ⁻¹	1.356	1.348
Crystal size, mm	0.20x0.18x0.30	0.20x0.22x0.28
index ranges	-13 ≤ h ≤ 7	-1 ≤ h ≤ 7
	-13 ≤ k ≤ 16	-7 ≤ k ≤ 7
	-16 ≤ l ≤ 16	-9 ≤ l ≤ 9
R _{int}	0.061	0.024
data to parameter ratio	8.9:1	7.6:1
largest and mean Δ/σ	0.005; 0.001	0.000; 0.000
largest difference peak, e Å ⁻³	0.85	0.28
largest difference hole, e Å ⁻³	-0.67	-0.36
R	0.0310	0.0301
wR*	0.0504	0.0431
goodness of fit, S*	0.94	0.82
g	0.0025	0.0020

* wR=[Σw(F_o-F_c)²/Σ(F_o)²]^{1/2}; w=[σ²(F)+gF²]⁻¹; S=[Σw(F_o-F_c)²/N_{data}-N_{par}]^{1/2}.

compounds 1 and 2 are summarized in Table 1. Atom positions and selected bond length and bond angle parameters are presented for compound 1 in Tables 2 and 3 respectively and for compound 2 in Tables 4 and 5. Dihedral angles between carbon rings are found in Table 6. The molecular structures and labelling schemes for compounds 1 and 2 are shown in Figures 1 and 2 respectively.

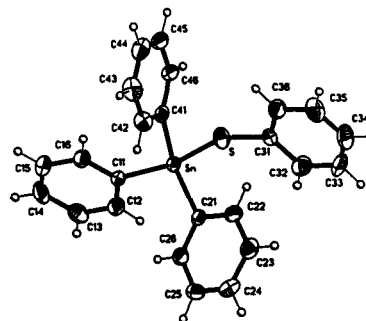


Figure 1. Thermal ellipsoid plot (30% probability) of (Ph)₃Sn(SPh), 1, with complete numbering scheme.

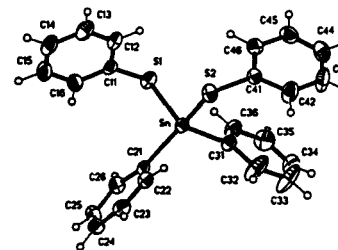


Figure 2a. Thermal ellipsoid plot (30% probability) of (Ph)₂Sn(SPh)₂, 2, with complete numbering scheme.

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement coefficients (Å² x 10³) for (Ph)₂Sn(SPh)₂.

	x	y	z	U _{eq} ^a
Sn	3896(1)	6831(1)	4597(1)	45(1)
S	7003(2)	6956(1)	4819(1)	60(3)
C(11)	3340(4)	6238(2)	3427(2)	46(1)
C(12)	3954(5)	5471(2)	3246(3)	53(1)
C(13)	3571(5)	5141(3)	2470(3)	67(2)
C(14)	2631(5)	5549(3)	1874(3)	68(2)
C(15)	1983(6)	6302(3)	2041(3)	68(2)
C(16)	2341(6)	6640(3)	2808(3)	60(1)
C(21)	2877(5)	6173(2)	5604(2)	46(1)
C(22)	2969(5)	6489(3)	6397(2)	54(1)
C(23)	2304(6)	6068(3)	7040(3)	66(2)
C(24)	1526(6)	5311(3)	6894(3)	64(2)
C(25)	1434(5)	5007(2)	6109(3)	60(1)
C(26)	2114(5)	5422(2)	5473(3)	56(1)
C(31)	7210(4)	7265(2)	5884(2)	46(1)
C(32)	7923(8)	6734(3)	6453(3)	69(2)
C(33)	813(10)	6975(3)	7283(4)	93(2)
C(34)	7644(6)	7735(4)	7516(3)	84(2)
C(35)	6907(8)	8255(3)	6951(4)	82(2)
C(36)	6736(7)	8035(3)	6133(3)	62(2)
C(41)	2909(5)	8043(2)	4495(3)	47(1)
C(42)	1150(7)	8184(2)	4545(3)	65(2)
C(43)	469(6)	8449(3)	4427(3)	79(2)
C(44)	1506(7)	9593(3)	4253(3)	72(2)
C(45)	3257(7)	9472(3)	4217(3)	67(2)
C(46)	3953(5)	8704(2)	4318(3)	54(1)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths(Å) and angles (deg) for (Ph)₃Sn(SPh).

Bond Lengths			
Sn-S	2.421(1)	Sn-C(31)	1.787(4)
Sn-C(11)	2.142(3)	S-C(41)	2.134(4)
Sn-C(21)	2.139(3)		
Bond Angles			
S-Sn-C(11)	108.2(1)	Sn-C(21)-C(22)	121.0(3)
S-Sn-C(21)	109.9(1)	S-Sn-C(41)	106.4(1)
C(21)-Sn-C(41)	112.4(1)	Sn-S-C(31)	101.2(1)
C(21)-Sn-C(11)	112.1(1)	S-C(31)-C(36)	122.2(3)
C(11)-Sn-C(41)	107.7(1)	Sn-C(41)-C(46)	121.9(3)

Table 4. Atomic coordinates (x10⁴) and equivalent isotropic displacement coefficients (Å²x10³) for (Ph)₂Sn(SPh)₂.

	x	y	z	U _{eq} ^a
Sn	2886(1)	1064(1)	2257(1)	56(1)
S(1)	788(2)	1959(2)	1840(1)	73(1)
S(2)	4491(2)	2024(2)	4140(1)	72(1)
C(11)	-328(6)	1212(5)	2734(5)	59(3)
C(12)	105(7)	1766(7)	3864(6)	77(3)
C(13)	-815(9)	1219(9)	4529(6)	97(4)
C(14)	-2141(9)	140(9)	4110(9)	98(5)
C(15)	-2579(8)	-408(8)	2999(9)	101(4)
C(16)	-1687(7)	109(6)	2322(6)	82(3)
C(21)	2035(5)	-1108(5)	2202(4)	54(2)
C(22)	2752(7)	-1734(7)	3002(5)	69(3)
C(23)	2228(8)	-3118(8)	2937(6)	82(4)
C(24)	1009(9)	-3939(7)	2072(7)	92(4)
C(25)	295(8)	-3343(8)	1270(7)	93(3)
C(26)	806(7)	1933(7)	1343(5)	73(3)
C(31)	4155(6)	1848(6)	1116(4)	62(3)
C(32)	548(1)	163(1)	1104(8)	134(6)
C(33)	636(1)	219(1)	421(9)	161(8)
C(34)	588(1)	2929(9)	-294(7)	107(5)
C(35)	454(1)	3148(8)	-325(6)	103(5)
C(36)	3691(8)	2643(7)	385(5)	82(3)
C(41)	5657(7)	3572(6)	3836(4)	61(3)
C(42)	7163(9)	3786(8)	3885(7)	106(4)
C(43)	8059(9)	496(1)	3642(8)	125(5)
C(44)	747(1)	5960(9)	3361(6)	104(4)
C(45)	599(1)	5805(7)	3340(6)	94(4)
C(46)	5108(8)	4629(7)	3594(5)	80(3)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Selected bond lengths(Å) and angles (deg) for (Ph)₂Sn(SPh)₂.

Bond Lengths			
Sn-S(2)	2.409(1)	Sn-C(31)	2.125(6)
Sn-S(1)	2.410(2)	S(1)-C(11)	1.769(6)
Sn-C(21)	2.129(5)	S(2)-C(41)	1.775(6)
Bond Angles			
S(2)-Sn-S(1)	110.8(1)	S(2)-Sn-C(21)	105.7(1)
S(1)-Sn-C(21)	110.4(2)	Sn-S(1)-C(11)	101.8(2)
C(21)-Sn-C(31)	119.3(2)	Sn-S(2)-C(41)	97.3(2)
S(2)-Sn-C(31)	108.4(1)	S(2)-C(41)-C(42)	121.0(6)
S(1)-Sn-C(31)	102.4(2)	S(1)-C(11)-C(16)	120.4(4)

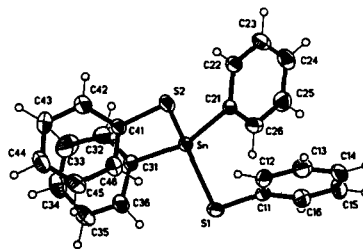
Table 6. Dihedral angles between carbon rings in compounds 1 and 2. Ring i corresponds to the carbons C_{ij}.

a - (Ph) ₃ Sn(SPh)	
R ₁ -R ₂	60.71 ^o
R ₁ -R ₃	11.07 ^o
R ₁ -R ₄	80.28 ^o
R ₂ -R ₃	52.09 ^o
R ₂ -R ₄	79.62 ^o
R ₃ -R ₄	89.33 ^o
b - (Ph) ₂ Sn(SPh) ₂	
R ₁ -R ₂	61.97 ^o
R ₁ -R ₃	74.53 ^o
R ₁ -R ₄	88.96 ^o
R ₂ -R ₃	74.00 ^o
R ₂ -R ₄	55.15
R ₃ -R ₄	32.43 ^o

The coordination geometry about the Sn atom in compound 1 is tetrahedral, with angles varying about 109.0 ± 3.0, as expected for tin compounds with C.N. = 4, in general. The determined Sn-C and Sn-S bond distances were 2.138(mean value) and 2.421Å, respectively. However, the introduction of another thiolate ligand around tin in compound 2 did markedly alter some of the angles, e. g., < C21SnC31, < S1SnC31, < C21SnS12. As a result, the coordination geometry around tin in compound 2 is that of a distorted tetrahedron, as can better be seen in Figure 2b. The angle related to one of the CSnC bonds increases up to 119.3^o. This corresponds to a strengthening of the Sn-C bond. The determined bond distance was 2.127 Å (mean value), Table 5, smaller than in compound 1, Table 3. There is also an unexpected variation of the angles related to the SSnC bonds. There are two such bonds related to each sulfur atom. In both cases, S1 and S2, one of the angles remains around the tetrahedral value, S2SnC31=108.4 and S1SnC21=110.4, but the other two decrease, S2SnC21=105.7 and S1SnC31=102.4. The determined Sn-S bond distance is also smaller in compound 2, 2.409Å, Table 5. In both compounds the C-C bond distances related to the phenyl rings as well as the angles are within the expected range⁹.

Both electronic and steric factors can be argued to explain the observed data in compound 2. As sulfur is a better σ donor than the phenyl group, the introduction of two PhS⁻ groups around the tin atom, strengthens the Sn-S bond, and more electron density is available on Sn to be shared with carbon. As a consequence the Sn-C bond is stronger, which accounts for the CSnC angle change to 119.3^o. For the SSnC bonds all the angles should be close to the tetrahedral value, as the SSnS angle, Table 5. However, due to steric reasons (that is, the space occupied by two PhS⁻ groups around tin), just two of these angles are near the expected value and the other two decrease, as can better be seen in Fig. 2b.

Poller and Ruddick⁶ have measured the Mössbauer spectra of compounds 1 and 2 and according to their results in both compounds the tin atom is tetrahedrally bonded, that is, the distortions around tin in compound 2 could not be determined.

**Figure 2b.** Another view of (Ph)₂Sn(SPh)₂, 2.

CONCLUSIONS

The parameters obtained from the X-ray crystal structure elucidation of compounds **1** and **2** permitted to conclude that as two PhS⁻ groups are introduced around tin both Sn-C and Sn-S bonds are strengthened and there is a distortion in the geometry. Electronic and steric factors are responsible for these facts.

ACKNOWLEDGMENT

The financial support for this research have been provided by CNPq, PADCT, FINEP and Fapemig. Fapemig provided funds to purchase the Siemens P4 X-ray diffractometer and the crystallographic computing system.

Supplementary Material

Tables of bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and packing diagrams are available upon request.

REFERENCES

1. a. Bögge, H.; Müller, A.; Dieman, E.; Jostes, R.; *Angew. Chem. Int. Ed. Engl.* (1981), **20**, 934; b. Dubois, M. R.; Bernatis, P.; Haltiwanger, R. C.; *Organomet.* (1992), **11**, 2424.
2. a. Gates, B. C.; Kwart, H.; Schuit, G. C. A.; *Journal of Catalysis* (1980), **61**, 128; b. Angelici, R. J.; Hockett, S. C.; Saue, N. N.; *Organomet.* (1987), **6**, 591; c. Dubois, M. R.; *Chem. Reviews* (1989), **89**, 1; d. Dubois, M. R.; Caewit, C. J.; *J. Am. Chem. Soc.* (1986), **108**, 5482.
3. Sellman, D.; Käppler, O.; *Angew. Chem. Int. Ed. Engl.* (1988), **27**, 689.
4. a. Stephan, D. W.; Nadashi, T. T.; Huang, Y.; *Inorg. Chem.* (1993), **32**, 347; b. Rätthlein, K. H.; Köpf, H.; *Angew. Chem. Int. Ed. Engl.* (1969), **8**, 980; c. Stephan, D. W.; Wark, T. A.; *Organomet.* (1989), **8**, 2836.
5. Timofeeva, T. V.; Kravtsov, D. N.; Bokll, N. G.; Struchkov, Yu.T.; *Zh. Strukt. Khim.* (1977), **18**, 882.
6. a. Poller, R. C.; Ruddick, J. N. R.; *J. Organomet. Chem.* (1973), **60**, 87; b. Schmidt, M.; Dersin, Hans-Jüngen and Schumann, H.; *Chem. Ber.* (1962), **95**, 1428.
7. Sheldrick, G. M.; *Shelxtl/PC Users Manual* (1990).
8. Omae, I.; "Organotin Chemistry", *Journal of Organometallic Chemistry Library*, Elsevier, Tokyo, pp. 81-106, (1989).
9. Clarke, P. L.; Cradwick, M. E.; Wardell, J. L.; *J. Organomet. Chem.* (1973), **63**, 279.