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Synthesis and spectral characterization of stannocanes of the type [O(CH$_2$CH$_2$S)$_2$SnR$_2$] (R=Me1,Bu^{n}2,Ph3)

Research Article

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Abstract: The stannocanes of the type [O(CH$_2$CH$_2$S)$_2$SnR$_2$] (R=Me**1**,Bu^n**2**,Ph**3**) have been synthesized in an improved method by the reaction of R$_2$SnCl$_2$ with 2, 2'-oxydiethanethiol O(CH$_2$CH$_2$SH)$_2$ in molar ratio of 1:1 at the presence of sodium ethoxide in anhydrous ethanol. The reactions are carried out under inert atmosphere. These compounds have been extensively characterized by FT-IR, UV-Vis spectrophotometry, multi-nuclear (^{1}H, ^{13}C, ^{119}Sn) NMR, elemental analysis and mass spectrometry. The obtained data clearly indicates that, there is a strong interaction between oxygen atom of the ligand as a donor and *Sn* atom of the organotin species as a Lewis acid acceptor. Therefore, the resulted dithiostannocanes possess a transannular secondary bonding and hypervalency at the central Sn atom which leads to an increase in the coordination number of tin from four to five-coordinated tin.

Keywords: *Stannocanes • Transannular bondings • 2-2-oxydiethanethiol ligand • Organotin compounds • Spectral characterization*

1. Introduction

Metallocanes of the type [X(CH$_2$CH$_2$S)$_2$]MRR' (X=O,S,NR"; M=Ge, Sn) have been studied for a long time in order to understand the nature of the intramolecular secondary bonding and its relation with the so-called hypervalency group 14 elements [1,2]. Among the large number of structural reports of this group, stannocanes are the most widely and systematically investigated [3]. Dräger *et al.* [4-8] and Cea-Olivares *et al.* [1,3,9,10] have dealt with this research field for a long time. The stannocanes Cl$_2$/Br$_2$/I$_2$-Sn(SCH$_2$CH$_2$)$_2$O and Cl/Br/I/Me-(Me)Sn(SCH$_2$CH$_2$)$_2$O have been prepared from (HSCH$_2$CH$_2$)$_2$O with SnHal$_4$ or MeSnHal$_3$, respectively [2,4,6,7]. In these compounds the conformation preference is the formation of an eight-membered ring and comprise of molecules in which the Sn-atom approaches a trigonal-bipyramidal penta-coordination with two sulfur-atoms and Hal$_{(eq)}$ as equatorial ligands and with oxygen-atom and Hal$_{(ax)}$ as axial ligands [7]. Therefore O....Sn....Hal$_{(ax)}$ bond are best described by means of a three-center four-electron interaction [7,8]. These rings possess a strong intramolecular interaction through the Sn as a Lewis acid acceptor and oxygen as a donor, leading to a transannular secondary bonding in stannocanes and subsequently an increase in the coordination number of tin [2,9,10]. The factors that influence the strength of transannular bonding and hypervalency at the central Sn-atom in stannocanes have been studied [2,10]. The importance of this type of bonding have also been revised in metallocanes of type [X(CH$_2$CH$_2$Y)$_2$MRR'] and [X(CH$_2$CH$_2$Y)$_2$M'R] (M=Ge(IV), Sn(IV) and Pb(IV); M'=As(III), Sb(III) and Bi(III); X=NR'',O, S; Y=O, S [3]. Once again, the transannular interaction is observed between the X (donor group) and M, a situation that leads to an increase in the coordination number of M. The spiro-bis(oxadithiastannocane) [Sn(SCH$_2$CH$_2$OCH$_2$CH$_2$S)$_2$] is also prepared from O(CH$_2$CH$_2$SNa)$_2$ and SnCl$_4$ and its molecular structure have been studied [9]. In this compound the $Sn...O$ secondary bond distance in the

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observed eight – membered ring is larger than distances found in the related monocyclic diorgano stannocances [2,4]. Since the tin compounds which most often used for the synthesis of the above stannocanes were either tin tetrachloride or monoorganotin halides, we decided to employ diorganotin dichloride instead to see the possible effect of the replacement of chlorine atoms in $SnCl_4$ by two alkyl groups. Moreover, to the best of our knowledge it seems that the dibutyl derivative of the thiastannocanes **(2)** which is reported here is a new compound. In addition, in the case of the stannocanes **(1)** and **(3),** the employed base in our experiments is sodium ethoxide in anhydrous ethanol which is also different from the most reported procedures [2,3]. Therefore, to continue our study of ligands containing S-reactive sites and their reactions towards organotin halides [11-17] and considering additional importance due to already established biological effects of organotin complexes [18-21], the interaction between 2,2-oxydiethanethiol $(HSCH_2CH_2)_2O$, and R_2SnCl_2(R=Me, Bu^n, Ph) (in the presence of sodium ethoxide) is investigated here. Dialkyl-1-oxa-4,6-dithiastannocanes such as $[O(CH_2CH_2S)_2SnMe_2]$ **(1)**, $[O(CH_2CH_2S)_2SnBu^n{}_2]$ **(2)** and $[O(CH_2CH_2S)_2SnPh_2]$ **(3)** are synthesized and reported. These compounds have been fully characterized by using elemental analysis, IR, UV-Vis, multinuclear (^1H, ^{13}C, ^{119}Sn) NMR spectroscopy, as well as mass spectrometry. The formation of eight-membered rings and transannular secondary bonding at the central tin atom will also be discussed on the basis of the obtained spectroscopic data.

2. Experimental procedure

2.1. Materials and instrumentation

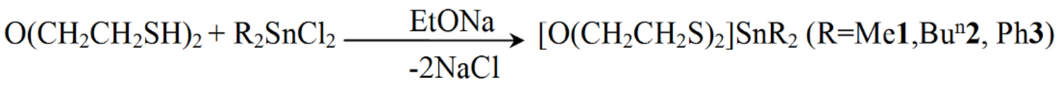
All experiments requiring inert atmosphere were carried out in N_2-flushed glove bags or standard Schlenk apparatus. All solvents, sodium ethoxide, dimethyltin dichloride, dibutyltin dichloride and $O(CH_2CH_2SH)_2$ were purchased from Merck, and diphenyltin dichloride was purchased from Acros company. The FT-IR spectra were recorded using KBr- pellets in the range of 4000-400cm^{-1} on Bomen FT-IR spectrophotometer. NMR spectra were obtained on a Bruker Avance 400MHz at ambient temperature. ^1H NMR (400.13 MHz) and ^{13}C NMR (100.61MHz) were recorded using $CDCl_3$ as solvent with TMS as an external reference. ^{119}Sn NMR spectra were recorded at 149.21 MHz in $CDCl_3$ with $SnMe_4$ as an external reference. Elemental analysis (C and H) were performed by the microanalytical service of the N.I.O.C. Research Institute of Petroleum Industry. The UV-Vis spectra were recorded on double beam GBC model Cintra 101 spectrophotometer in $CHCl_3$ as a solvent. The mass spectra determinations of these compounds were performed on a Shimadzu spectrometer model GCMS-QP 1000 EX.

2.2. Synthesis of $[O(CH_2CH_2S)_2SnMe_2]$ (1)

To a stirring solution of 2.2-oxydiethanethiol (0.138 g, 1 mmol) in 40 mL of dry benzene under $N_{2(g)}$ atmosphere. 0.136 g (2 mmol) of sodium ethoxide solution in ethanol was slowly added. Then dimethyltin dichloride (0.219 g, 1 mmol) dissolved in 10 mL of dry benzene was added dropwise to the above mixture at room temperature and was stirred for another 10 h at refluxing temperature (70-75°C) under nitrogen atmosphere. After cooling and filtering the colorless solid (NaCl), the solvent was removed on a rotary evaporator in vacuo and the resulting white solid was washed with n-hexane and dried under vacuum. Yield 85%, m.p. 192ºC, Anal. Calc. for $C_6H_{14}OS_2Sn$(%): C, 25.26; H, 4.95. Found:C, 25.18; H, 4.91. IR(KBr, Cm^{-1}): v (C-H)2917, 2875, δ CH_2-S 662, $v_{as,s}$C-O-C1050-985, v Sn-$C_{(eq)}$ 536, v Sn-$C_{(ax)}$ 516, v Sn-$S_{(eq)}$ <400. ^1H NMR (δ, ppm, $CDCl_3$): 3.54 (t, 4H, CH_2-O), 2.84 (t, 4H, CH_2-S), 0.54 (s, 3H, $CH_{3(ax)}$), 0.71(s, 3H, $CH_{3(eq)}$). $^{13}C\{^1H\}$ NMR (δ, ppm, $CDCl_3$): 27.9 (CH_2-S), 72.1(CH_2-O) [$^2J(^{117/119}Sn-^{13}C)$ 20.2 and $^3J(^{117/119}Sn-^{13}C)$ 14.1 Hz], 0.9 ($CH_{3(ax)}$), 1.1 $CH_{3(eq)}$). ^{119}Sn NMR (δ, ppm, $CDCl_3$): -91.2. Ms: m/z, 275, 273, 271, 269, 267, 266, 265, 263, 213, 211, 209, 197, 195, 193, 167, 165, 163, 150, 149, 148, 137, 135, 133, 120, 118, 116, 61, 60, 59, 58, 57, 47, 46, 45, 43, 28, 27, 26,15. UV-Vis (λ_{max} nm): 231.

2.3. Synthesis of $[O(CH_2CH_2S)_2SnBu_2^n]$ (2)

The synthesis procedure was almost the same as **(1)** in section 2.2 and the resulting product was obtained in a similar way. A solution of di-n-butyltin dichloride (0.303g, 1 mmol) in benzene (45 mL) was slowly added to a solution of 2.2-oxydiethanethiol (0.138 g, 1 mmol) in 20 mL dry benzene which contained sodium ethoxide in ethanol (0.136 g, 2 mmol) to afford a white solid product. Yield 82%, m.p.215 °C Anal. Calc. for $C_{12}H_{26}OS_2Sn$(%):C, 39.02: H, 7.10. Found: C, 39.11; H, 7.04. IR(KBr, Cm^{-1}): v (C-H) 2955, 2921, 2854, v CH_2-S 400, $v_{as,s}$C-O-C1060-980, v Sn-$C_{(eq)}$ 593, v Sn-$C_{(ax)}$ 665, v Sn-$S_{(eq)}$ <400. ^1H NMR (δ, ppm, $CDCl_3$): 3.56 (t, 4H, CH_2-O), 2.87 (t, 4H, CH_2-S), [1.2(H_α), 1.5(H_β), 1.3(H_γ), 0.8(H_δ)] Bu^n_{ax}, or Bu^n_{eq}, $^{13}C\{^1H\}$ NMR (δ, ppm, $CDCl_3$): 27.8 (CH_2-S), 71.1(CH_2-O) [$^2J(^{117/119}Sn-^{13}C)$ 21.5 and $^3J(^{117/119}Sn-^{13}C)$ 16.8 Hz], [12(C_α), 17(C_β), 24(C_γ), 27(C_δ)] Bu^n_{ax} [14(C_α), 19(C_β), 26(C_γ), 28(C_δ)] Bu^n_{eq}. ^{119}Sn NMR (δ, ppm, $CDCl_3$): -95.5. Ms: m/z, 317, 315, 313, 311, 309, 257, 256, 255, 253, 251, 201, 199, 197, 195, 193, 152, 151, 149, 60, 47, 46, 45, 44, 41, 29. UV-Vis (λ_{max} nm): 209.



$$O(CH_2CH_2SH)_2 + R_2SnCl_2 \xrightarrow[\text{-2NaCl}]{\text{EtONa}} [O(CH_2CH_2S)_2]SnR_2\ (R{=}Me\mathbf{1}, Bu^n\mathbf{2}, Ph\mathbf{3})$$

Scheme 1. The reaction procedure for the production of the stannocanes (1), (2) and (3).

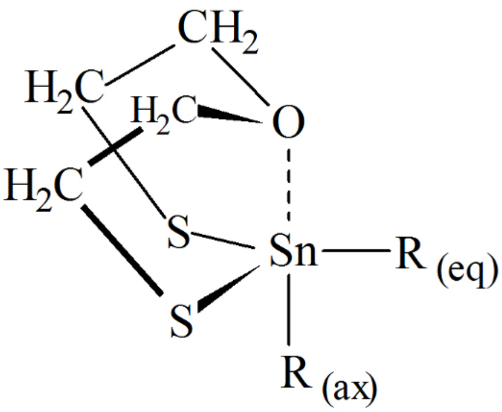


Figure 1. The structure of stannocanes of the type O(CH$_2$CH$_2$S)$_2$SnR$_2$ (R=Me1, Bu^{n}2, Ph3).

2.4. Synthesis of [O(CH$_2$CH$_2$S)$_2$SnPh$_2$] (3)

The same method as **(1)** and **(2)** was also used to obtain **(3)**. A solution of diphenyltin dichloride (0.343 g, 1 mmol) in dry benzene (45 mL) was gradually added to a solution of 2.2-oxydiethanethiol (0.138 g, 1 mmol) in 10 mL of dry benzene containing sodium ethoxide in anhydrous ethanol (0.136 g, 2 mmol) to obtain a white solid product. Yield 87%, m.p. 126°C , Anal. Calc. for $C_{16}H_{18}OS_2Sn$(%): C,46.95; H, 4.43. Found: C, 46.87; H, 4.35. IR(KBr, Cm^{-1}): v (C-H) 3060, 2865, v CH$_2$-S 658, v$_{as,s}$C-O-C1055-990, v Sn-C$_{(eq)}$, v Sn-C$_{(ax)}$, v Sn-S$_{(eq)}$ <400. ^{1}H NMR (δ, ppm, CDCl$_3$): 3.61 (t, 4H, CH$_2$-O), 2.92 (t, 4H, CH$_2$-S), [3.6(H$_1$), 7.5(H$_{2,6}$), 7.3(H$_{3,5}$), 7.2(H$_4$)] Ph$_{ax}$, [3.8(H$_1$), 7.9(H$_{2,6}$), 7.5(H$_{3,5}$), 7.3(H$_4$)] Ph$_{eq}$, ^{13}C{^{1}H} NMR (δ, ppm, CDCl$_3$): 28.1 (CH$_2$-S), 71.5(CH$_2$-O) [^{2}J($^{117/119}$Sn-^{13}C) 18.4.2 and ^{3}J($^{117/119}$Sn-^{13}C) 14.7 Hz], 129-135 {[(C$_1$), (C$_{2,6}$), (C$_{3,5}$), (C$_4$)] Ph$_{ax}$ and [(C$_1$), (C$_{2,6}$), (C$_{3,5}$), (C$_4$)] Ph$_{eq}$}. ^{119}Sn NMR (δ, ppm, CDCl$_3$): -108.7. Ms: m/z, 337, 335, 333, 332, 331, 330, 274, 272, 271, 270, 232, 230, 229, 227, 225, 224, 222, 197, 195, 193, 154, 153, 152, 151, 137, 136, 135, 78, 77, 76, 62, 61, 60, 59, 58, 57. UV-Vis (λ$_{max}$ nm): 252.

3. Results and discussion

The reactions of diorganotin dichloride R$_2$SnCl$_2$ (R; Me**1**, Bu^n**2**, Ph**3**) with 2,2-oxydiethanethiol were conducted in dry benzene in a 1:1 stochiometric ratio in the presence of sodium ethoxide in anhydrous ethanol and an inert atmosphere for all the compounds **(1)** to **(3)**. The synthesis procedure was shown in Scheme 1.

This method is a convenient approach to the synthesis of diorgano-derivaties of thiastannocanes; O(CH$_2$CH$_2$S)$_2$SnMe$_2$ **(1)**, O(CH$_2$CH$_2$S)$_2$SnBu$^n_2$ **(2)** and O(CH$_2$CH$_2$S)$_2$SnPh$_2$ **(3)**. It should be mentioned that this method is a modified procedure with a higher yield than previously reported [3-10]. The proposed structures of **(1)** to **(3)** are illustrated in Fig. 1, and are in a good agreement with those reported earlier. As it is mentioned in the introduction section, this kind of eight-membered rings containing transannular $Sn.....O$ secondary interaction structures are well known for the thiastannocanes and are suggested by a considerable number of authors working in this field [3-10]. The compounds **(1-3)** were fully characterized by UV-Vis, FT-IR, mass spectrometry and multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR spectroscopy, as well as elemental analysis. Spectroscopic data are discussed and interpreted below and the most significant FT-IR bands; (^{1}H, ^{13}C, and ^{119}Sn) NMR signals are summarized in Table 1.

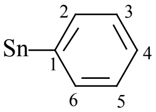
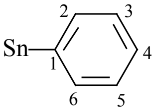
3.1. IR spectra

The IR spectra of **(1)** and **(2)** show the (C-H)$_{aliphatic}$ stretching absorptions at 2917, 2875 and 2955, 2921, 2854, respectively. The absorption bands which are seen in the region 1060-985 cm^{-1} are characteristic of symmetrical and asymmetrical stretching vibrations for, C-O-C group in stannocanes. In these compounds the absorption band of the S-H group is eliminated indicating that the O(CH$_2$CH$_2$SH)$_2$ is coordinated to Sn as an anionic ligand. The bands at 662, 665, and 658 cm^{-1} are corresponding to CH_2-S groups in **(1)**, **(2)** and **(3)** respectively. The IR spectra of compound **(1)** clearly exhibits absorption bands for Sn-C$_{(ax)}$ and Sn-C$_{(eq)}$ at 516 and 536, respectively and Sn-C$_{(ax)}$ and Sn-C$_{(eq)}$ for **(2)** are seen at 593 and 665 cm^{-1} respectively. In these compounds due to the nucleophilic attack of oxygen donor atom at the tin central atom, the bond length of the axial groups increase while the bond length of the equatorial groups slightly decrease. This leads to an elongation of the axial bonds and consequently result in a shift of the corresponding stretching vibrations v(Sn-R$_{ax}$) to lower energy compared to v(Sn-R$_{aq}$). The absorption bands at 3060 and 2865 cm^{-1} in **(3)** are belong to (C-H)$_{aromatic}$ and (C-H)$_{aliphatic}$, respectively (Table 1).

3.2. ^{1}H NMR spectra

The ^{1}H NMR spectra of **(1)**, **(2)** and **(3)** clearly exhibit signals for the protons of CH_2-O groups at δ 3.54, 3.56

Table 1. Selected spectroscopic results for the stannocanes (1) to (3).

Assignment	**$O(CH_2CH_2S)_2SnR_2$**		
	R= Me(1)	**R= Bu^n(2)**	**R= Ph(3)**
	(a) IR Data (ν, cm^{-1})		
(CH_2-O)	1050-985	1060-980	1055-990
(CH2-S)	662	665	658
(C-H)	2917, 2875	2955, 2921, 2854	3060(Ar), 2865
(Sn-C_{ax})	516	593	-
(Sn-C_{eq})	536	665	-
	(b) ^{1}H NMR Data (δ, ppm)		
CH_2-O	3.45	3.56	3.61
CH_2-S	2.84	2.87	2.92
Sn-CH_3	0.54, 0.71	-	-
Sn-$^\alpha CH_2$-$^\beta CH_2$-$^\gamma CH_2$-$^\delta CH_3$	-	1.2(α),1.5(β),1.3(γ),0.8(δ)	-
		-	3.6(H_1),7.5($H_{2,6}$)7.3($H_{3,5}$),7.2(H_2)
	(c) ^{13}C NMR Data (δ, ppm)		
CH_2-O	72.1	71.1	71.5
CH_2-S	27.9	27.8	28.1
Sn-CH_3	0.9, 1.1	-	-
Sn-$^\alpha CH_2$-$^\beta CH_2$-$^\gamma CH_2$-$^\delta CH_3$	-	14, 19, 26, 28 12, 17, 24, 27	-
	-	-	129-135
	(d) ^{119}Sn NMR Data (δ, ppm)		
119Sn	-91.2	-95.5	-108.7

Note: NMR data for the starting ligand $O(CH_2CH_2SH)_2$: **δ(^{1}H)**; *(CH_2-O)=3.51(t), (CH_2-S)=2.62(doublet of triplet); (SH)=2.10(t).* **δ(^{13}C)**; *(CH_2-S)=24.1, (CH_2-O)=72.2 ppm.*

and 3.61 ppm respectively (Table 1). These chemical shifts are almost identical to those measured for CH_2-O moieties in $O(CH_2CH_2SH)_2$ at 3.51 ppm. The ^{1}H NMR signals at δ 2.84, 2.87 and 2.92 are related to the CH_2-S groups in **(1)**, **(2)** and **(3)** respectively. These signals are shifted down field in comparison to the protons of CH_2-S groups in the free ligand, which appears at δ 2.62 ppm due to coordination and subsequently formation of an eight–membered ring. In ^{1}H NMR spectrum of **(1),** two singlets are seen for the methyl groups at δ 0.54 and 0.71 ppm. This should be related to the axial and equatorial position of methyl groups and are assigned to the $Me_{(ax)}$ and $Me_{(eq)}$, respectively. A similar situation is also seen for butyl- and phenyl-groups in compounds **(2)** and **(3)**; however, in these compounds exact values of chemical shifts for different protons in two groups cannot be easily extracted due to the complexity of multiplets. It seems that the alkyl or the aryl groups in the axial position are much more shielded than the equatorial ones in the approach of the oxygen donor atom to the central tin atom (see Table 1).

3.3. ^{13}C NMR spectra

As expected, the ^{13}C NMR spectra exhibit two signals for the eight –membered ring which belong to CH_2-O and CH_2-S groups in each compound. These signals are at δ 72.1 and 27.9 for **(1)**; 71.1 and 27.8 for **(2)**; 71.5 and 28.1 ppm for **(3)**; in CH_2-O and CH_2-S groups, respectively. The ^{13}C chemical shift value for CH_2-O groups are almost the same as the chemical shift for CH_2-O group in the ligand (72.2ppm), while the carbon signals belongs to CH_2-S in these compounds are shifted towards down field in comparison to the free ligand which appears at 24.1 ppm. These observations indicate that the coordination is taken place between sulfur and tin atom. In ^{13}C NMR spectrum of **(1),** two ^{13}C signals appeared for methyl groups at 0.9 and 1.1 ppm, indicating that the two methyl groups are non-equivalent. This should be related to the axial ($Me_{(ax)}$ 0.9ppm) and the equatorial ($Me_{(eq)}$ 1.1ppm) position of methyl groups. There is a link between the chemical shifts and electron densities on the carbon atoms. It seems that the carbon atoms in the axial positions are much more shielded that the equatorial carbon atoms.

In ^{13}C NMR spectrum of **(2)** two sets of ^{13}C signals are also seen for butyl groups and each set compose of four signals, indicating that the two butyl groups are not equivalent. It seems that the signals at 12(C_α), 17(C_β), 24(C_γ) and 27(C_δ) are corresponding to the butyl group at the axial position and the signals at 14(C_α), 19(C_β), 26(C_γ) and 28(C_δ) belong to the butyl at the equatorial position. In ^{13}C NMR spectrum of **(3)**, ^{13}C signals for phenyl groups are appear in the range of δ 129-135 ppm. These signals can be assigned for either axial or equatorial position and the exact chemical shift can not be extracted due to complexity of signals (Table 1).

3.4. ^{119}Sn NMR spectra

The ^{119}Sn NMR spectra of the stannocanes **(1)**, **(2)** and **(3)** in $CDCl_3$ exhibit signals as singlets at -91.2, -95.5 and -108.7 ppm respectively. These resonances appear significantly at higher magnetic field than those of the organotin halides precursors [$MeSnCl_2$, δ+137, $Bu^n_2SnCl_2$ δ+123 and Ph_2SnCl_2, δ-27] [22,23], partly due to the elimination of the halogen withdrawing groups and mainly because of increasing coordination number. It should also be noted that the ^{119}Sn chemical shift is strongly dependent on the coordination number of tin and an increase in the coordination number produces large upfield shifts. These chemical shifts which are observed in the ^{119}Sn NMR spectra of **(1)**, **(2)** and **(3)** in comparison with those values reported for similar organotin compounds are consisted with a five coordinated tin atom. It seems that the transannular $Sn \leftarrow O$ interaction in **(1)**, **(2)** and **(3)** is responsible for increasing the coordination number in these stannocanes and thus, confirming the presence of the secondary intramolecular bonding.

3.5 UV-Vis spectra

The n → σ* absorption band of O(CH_2CH_2SH)$_2$ appeared at λ_{max} 198nm. This absorption is shifted and broadened and is seen at λ_{max}/nm (log e): 231 (3.62), 209 (3.48), 252 (3.21) for the compounds **(1)**, **(2)** and **(3)** respectively.

3.6 Mass spectra

The mass spectrum of **(1)** shows expected peaks at m/z 275, 273, 271, 269, 267, 266, 265, 263 which are attributable to ($M^{\cdot+}$-Me 100%) or [O(CH_2CH_2S)$_2$SnMe]$^{\cdot+}$ with ^{124}Sn, ^{122}Sn, ^{120}Sn, ^{119}Sn, ^{118}Sn, ^{117}Sn, ^{116}Sn and ^{112}Sn isotopes, respectively. It should be noted that the tin atom has ten naturally occurring isotopes which eight of them have the relative abundance more than 0.95%. The natural relative abundance of ^{115}Sn and ^{114}Sn are 0.34% and 0.65%, respectively [22,23]. This quasi ion is consistent with the structure proposed for **(1)** on the basis of other spectroscopic data [24]. The mass spectrum of **(1)** also exhibits peaks at m/z 213 ($Me_2{}^{120}SnS_2$)$^+$ 45%, 211($Me_2{}^{118}SnS_2$)$^+$ 85%, and 209 ($Me_2{}^{116}SnS_2$)$^+$ 70% which indicates the formation of S-Sn-S bonds. The spectrum of **(1)** clearly shows a number of important fragments at m/z 197,195,193 for ($MeSnS_2$)$^+$ 30%, 167, 165, 163 for (MeSnS)$^+$ 42%, 150, 149, 143 for (SnS)$^+$ 38%, , 137, 135, 133 for (MeSn)$^+$ 70% and 120, 118, 116 for Sn$^+$. The mass spectrum of **(1)** exhibits peaks at m/z 61, 60, 59, 58, 57 which belong to (S-CH_2- CH_2)$^+$ 65% and peaks at m/z 47, 46, 45, 43 which is attributable to fragments such as (CH_2- O-CH_2)$^+$.

The mass spectrum of **(2)** exhibits expected quasi-ion peaks at m/z 317, 315, 313, 311 and 309 which is attributable to ($M^{\cdot+}$-Bu^n 100%) or [O(CH_2CH_2S)$_2$SnBu]$^{\cdot+}$ with ^{124}Sn, ^{122}Sn, ^{120}Sn, ^{118}Sn, and ^{116}Sn isotopes, respectively. The peaks at m/z 257, 256, 255, 253 and 251 are related to the [OSn(CH_2CH_2S)$_2$]$^+$ 42% with the isotopes of ^{124}Sn, ^{122}Sn, ^{120}Sn, ^{118}Sn, and ^{116}Sn. The peaks at m/z 201, 199, 197, 195 and 193 belong to [SnS_2-CH_2]$^+$ 22% with ^{124}Sn, ^{122}Sn, ^{120}Sn, ^{119}Sn, and ^{116}Sn, respectively. These fragments clearly indicate the coordination of tin and the formation of S-Sn-S bonds. The peaks at m/z 152, 151, 149 and 148 are attributable to S^{120}Sn, S^{119}Sn, S^{117}Sn and S^{116}Sn, respectively. In the spectrum of **(2)**, [S-CH_2CH_2]$^+$ fragment is seen at m/z 60, and a (CH_2-O-CH_2)$^+$ fragment at m/z 46, 45 and 44. Finally, the butyl group and its fragmentations are also seen at m/z 57 ($C_4H_9{}^+$), 41($C_3H_5{}^+$), 29 ($C_2H_5{}^+$) and 15 ($CH_3{}^+$).

The mass spectrum of **(3)** shows Sn-containing fragments (^{124}Sn-^{115}Sn) at m/z 337, 335, 333, 332, 331, 330, attributable to $[O(CH_2CH_2S)SnPh]^+$ 98% which is the molecular ion after eliminating one phenyl group. This spectrum also exhibits peaks at m/z 274, 272, 271 and 270 which belong to $[Ph_2Sn]^+$ 35% with ^{120}Sn, ^{118}Sn, ^{117}Sn, ^{116}Sn isotopes. The peaks at m/z 232, 230, 229, 227, 225, 224 and 224 are due to $[SnS(CH_2CH_2)_2O]^+$ 32% with ^{122}Sn-^{116}Sn 54%. The peaks at m/z 197, 195, 193 are corresponding to Ph^{120}Sn 42%, Ph^{118}Sn 55% and Ph^{116}Sn 35%, respectively. The spectrum of **(3)** also shows Sn-containing fragments at m/z 154, 153, 152, 151 for $(SnS)^+$ 26%. The peaks at m/z 137, 136, 135 belong to $O(CH_2CH_2S)^+$ 45%.

4. Conclusion

The stannocanes **(1)**, **(2)** and **(3)** have been prepared in an improved method and fully characterized by the various spectroscopic techniques. All the experimental results and the spectroscopic data are in an excellent agreement with the assumed transannular secondary bonding at Sn atom and the formation of an eight-membered ring such as proposed structure shown in the Fig. 1. It should be noted that the nature of the substituents at Sn atom and their positions play an important role in the formation of O….Sn…R$_{(axial)}$ bond, because, their influence depends on, whether if they are equatorial or axial substituents. It is worth to note that the O-Sn-R bond is preserved in solution because the ^{119}Sn NMR clearly shows the increase in the coordination number of tin and ^{1}H and ^{13}C NMR spectra exhibit two groups instead of one in the form of two singlets. Finally the mass and IR spectra data supports the presence of the transannular secondary bonding also in the solid state.

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