

SOME BENZYL CARBOXYLATO DERIVATIVES AND ADDUCTS: SYNTHESIS, INFRARED AND NMR STUDIES

Daouda Ndoye, Libasse Diop*

*Université Cheikh Anta Diop, Faculté des Sciences et Techniques,
Département de Chimie, Laboratoire de Chimie Minérale et Analytique
(LACHIMIA), Dakar, Sénégal*

*Corresponding author: dlibasse@gmail.com

Received: March, 15, 2014

Accepted: April, 25, 2014

Abstract: $Cy_2NH_2BzCO_2 \cdot SnPh_3Cl$, $Bz_2NH_2BzCO_2 \cdot SnPh_3Cl$, $BzCO_2SnPh_3 \cdot SnPh_3Cl \cdot 1/4Bz_2NH_2Cl$, $Bz_2NH_2BzCO_2 \cdot SnPhCl(OH)_2$, $Bz_2NH_2BzCO_2 \cdot SnBu_2Cl_2$, $[BzCO_2SnPh_3][SnPhCl_3 \cdot EtOH \cdot H_2O]$ adducts and complexes have been obtained on allowing $Cy_2NH_2BzCO_2$ or $Bz_2NH_2BzCO_2 \cdot 4H_2O$ to react respectively with $SnPh_3Cl$, $SnPh_2Cl_2$ or $SnBu_2Cl_2$ in specific ratios. The molecular structures of these compounds have been determined on the basis of infrared and NMR data. The suggested structures are discrete, dimers and tetramer, the tin atom being tetra-, penta- and hexacoordinated; the benzyl carboxylate anions are monodentate, bidentate and chelating and the cations involved in hydrogen bonds.

Keywords: *bipyramidal trigonal environment, cations, chelating $BzCO_2^-$ anion, hydrogen bonds, tin centre*

INTRODUCTION

The application of tin compounds is well known [1, 2]; organotin carboxylates have been extensively studied and summarized by Tiekink [3]. In addition, an area of current interest involves the screening of organotin compounds for potential anti-tumor and anti-bacterial activities [4, 5]. In the aim to continue the works of Spencer *et al.* [6-8] on the Lewis acidity of the organotin compounds Yoder *et al.* have synthesized triorganotin carboxylates series and have used the ^{119}Sn NMR for determining their structures in solution [9-11]. In our laboratory, Touré has synthesized and characterized by Mössbauer, infrared and NMR spectroscopies organotin benzoato compounds $[\text{R}_4\text{A}][\text{PhCO}_2\cdot n\text{SnPh}_3\text{X}]$ (R = Me, Ph; A = N, P; X = Cl, Br, SCN et $n = 1, 2$) and $[\text{Me}_4\text{N}][\text{C}_6\text{H}_5\text{CO}_2\text{SnBu}_2\text{Cl}_2]$ [12]. In this context, we have studied in this paper the interactions between $\text{Cy}_2\text{NH}_2\text{BzCO}_2$ or $\text{Bz}_2\text{NH}_2\text{BzCO}_2\cdot 4\text{H}_2\text{O}$ salts and SnPh_3Cl , SnPh_2Cl_2 or SnBu_2Cl_2 Lewis acids in specific ratios which has yielded six new adducts infrared and NMR studies of which have been carried out then structures suggested on the basis of spectroscopic data.

MATERIALS AND METHODS

$\text{Cy}_2\text{NH}_2\text{BzCO}_2$ and $\text{Bz}_2\text{NH}_2\text{BzCO}_2\cdot 4\text{H}_2\text{O}$ have been synthesized on mixing aqueous solution of BzCO_2H and Cy_2NH or Bz_2NH in 1/1 ratio. The clear solutions obtained yield white powders after submitting them to a slow solvent evaporation.

Synthesis of $\text{Cy}_2\text{NH}_2\text{BzCO}_2\cdot\text{SnPh}_3\text{Cl}$ (A)

When ethanolic solutions of $\text{Cy}_2\text{NH}_2\text{BzCO}_2$ (0.74 mmol) and SnPh_3Cl (0.37 mmol) are mixed, clear solution is obtained and stirred during two hours. This solution yields white powder after submitting it to a slow solvent evaporation.

Synthesis of $\text{Bz}_2\text{NH}_2\text{BzCO}_2\cdot\text{SnPh}_3\text{Cl}$ (B)

When ethanolic solutions of $\text{Bz}_2\text{NH}_2\text{BzCO}_2\cdot 4\text{H}_2\text{O}$ (0.50 mmol) and SnPh_3Cl (0.25 mmol) are mixed, clear solution is obtained and stirred during two hours. This solution yields white powder after submitting it to a slow solvent evaporation.

Synthesis of $\text{BzCO}_2\text{SnPh}_3\cdot\text{SnPh}_3\text{Cl}\cdot 1/4\text{Bz}_2\text{NH}_2\text{Cl}$ (C)

When ethanolic solutions of $\text{Bz}_2\text{NH}_2\text{BzCO}_2\cdot 4\text{H}_2\text{O}$ (0.30 mmol) and SnPh_3Cl (0.60 mmol) are mixed, clear solution is obtained and stirred during two hours. This solution yields white powder after submitting it to a slow solvent evaporation.

Synthesis of $\text{Bz}_2\text{NH}_2\text{BzCO}_2\cdot\text{SnPhCl}(\text{OH})_2$ (D)

When ethanolic solutions of $\text{Bz}_2\text{NH}_2\text{BzCO}_2\cdot 4\text{H}_2\text{O}$ (0.90 mmol) and SnPh_2Cl_2 (0.45 mmol) are mixed, clear solution is obtained and stirred during two hours. This solution yields white powder after submitting it to a slow solvent evaporation.

Synthesis of $Bz_2NH_2BzCO_2 \cdot SnBu_2Cl_2$ (E)

When ethanolic solutions of $Bz_2NH_2BzCO_2 \cdot 4H_2O$ (0.37 mmol) and $SnBu_2Cl_2$ (0.37 mmol) are mixed, clear solution is obtained and stirred during two hours. This solution yields white powder after submitting it to a slow solvent evaporation.

Synthesis of $[BzCO_2SnPh_3][SnPhCl_3(EtOH)(H_2O)]$ (F)

When ethanolic solutions of $Cy_2NH_2BzCO_2$ (0.41 mmol) and $SnPh_3Cl$ (0.41 mmol) are mixed, clear solution is obtained and stirred during two hours. This solution yields white powder after submitting it to a slow solvent evaporation.

The analytical data calculated (found) have allowed to suggest the following formulae (Table 1).

Table 1. Suggested formulae of the synthesized compounds

Comp	Suggested formulae	Chemical composition (% mass)					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
A	$Cy_2NH_2BzCO_2 \cdot SnPh_3Cl$	64.93	65.20	6.60	6.31	1.99	1.99
B	$Bz_2NH_2BzCO_2 \cdot SnPh_3Cl$	66.83	66.70	5.33	5.32	1.95	1.63
C	$BzCO_2SnPh_3 \cdot SnPh_3Cl \cdot 1/4Bz_2NH_2Cl$	61.41	61.30	4.45	4.52	0.38	0.34
D	$Bz_2NH_2BzCO_2 \cdot SnPhCl(OH)_2$	57.17	56.70	5.05	4.98	2.34	2.37
E	$Bz_2NH_2BzCO_2 \cdot SnBu_2Cl_2$	56.54	56.30	6.48	6.59	2.20	2.20
F	$[BzCO_2SnPh_3][SnPhCl_3 \cdot EtOH \cdot H_2O]$	47.96	47.80	4.14	4.18	0.00	0.15

The infrared spectra were recorded by a Perkin Elmer (4400-350 cm^{-1}) spectrometer (Dakar University), the sample being as Nujol mulls while CsI windows were used. The elemental analyses have been performed at the laboratory of Microanalyses - University of Bath (UK). Infrared data are given in cm^{-1} [IR abbreviations: (br) broad, (vs) very strong, (s) strong, (m) medium, (sh) shoulder, (vw) very weak].

Solution NMR spectra were recorded from a saturated $CDCl_3$ solution, at 250.53 and 89.27 MHz for 1H and ^{119}Sn , respectively. 1H and ^{119}Sn chemical shifts are given in ppm and are referred, respectively, to $SiMe_4$ and $SnMe_4$, all set to 0.00 ppm. These NMR data were recorded by means of a Bruker 300 MHz at University of Bath (UK) and University of Montpellier II (France).

All the chemicals are from Aldrich Company (Germany) and were used without any further purification.

RESULTS AND DISCUSSION

Let us consider the infrared (cm^{-1}) and NMR (ppm) data of benzyl carboxylato derivatives and adducts:

(A):

IR: $\nu_{as}(CO_2) = 1620$ s; $\delta(NH_2) = 1581$ vs, 1546 vs; $\nu_s(CO_2) = 1429$ s; $\nu(Ph) = 730$ vs, 697 vs; $\nu(NH_2) = 2900$ br;

1H NMR ($CDCl_3$, δ ppm): 1.20-2.10 (br m, 22H, C_6H_{11}), 2.90 (s, 2H, NH_2), 3.70 (s, 2H, CH_2), 7.20-7.60 (br m, 20H, C_6H_5);

^{119}Sn NMR (CDCl_3 , δ ppm): -110 ppm.

(B):

IR: $\nu_{\text{as}}(\text{CO}_2) = 1600$ s; $\delta(\text{NH}_2) = 1501$ s; $\nu_{\text{s}}(\text{CO}_2) = 1411$ s; $\nu(\text{Ph}) = 728$ s, 695 s; $\nu(\text{NH}_2) = 2900$ br.

(C):

IR: $\nu_{\text{as}}(\text{CO}_2) = 1620$ s; $\delta(\text{NH}_2) = 1541$ vs; $\nu_{\text{s}}(\text{CO}_2) = 1396$ m; $\nu(\text{Ph}) = 730$ m, 698 m;

^1H NMR (CDCl_3 , δ ppm): 3.70 (s, 2H, CH_2), 7.27-7.75 (br m, 35H, C_6H_5);

^{119}Sn NMR (CDCl_3 , δ ppm): -45.2, -106.9 ppm.

(D):

IR: $\nu_{\text{as}}(\text{CO}_2) = 1620$ s; $\delta(\text{NH}_2) = 1567$ vs; $\nu_{\text{s}}(\text{CO}_2) = 1410$ s; $\nu(\text{Ph}) = 728$ m, 697 m; $\nu(\text{NH}_2) = 2900$ br;

^1H NMR (CDCl_3 , δ ppm): 3.47 (s, 2H, NH_2), 3.53 and 3.77 (s, 6H, CH_2), 7.10-7.40 (br m, 15H, C_6H_5);

^{119}Sn NMR (CDCl_3 , δ ppm): -540.3 ppm.

(E):

IR: $\nu_{\text{as}}(\text{CO}_2) = 1620$ s; $\delta(\text{NH}_2) = 1545$ vs; $\nu_{\text{s}}(\text{CO}_2) = 1380$ s; $\nu(\text{Ph}) = 729$ vs, 696 vs; $\nu_{\text{s}}(\text{SnBu}_2) = 605$ vw; $\nu(\text{NH}_2) = 2900$ br.

(F):

IR: $\nu_{\text{as}}(\text{CO}_2) = 1620$ s; $\delta(\text{NH}_2) = 1541$ vs; $\nu_{\text{s}}(\text{CO}_2) = 1395$ s; $\nu(\text{Ph}) = 730$ s, 698 s;

^1H NMR (CDCl_3 , δ ppm): 3.50 (s, 2H, CH_2), 4.60 (s, 2H, H_2O), 7.10-7.80 (br m, 25H, C_6H_5);

^{119}Sn NMR (CDCl_3 , δ ppm): -109, -541 ppm.

Characterization of $\text{Cy}_2\text{NH}_2\text{BzCO}_2\cdot\text{SnPh}_3\text{Cl}$ (A) and $\text{Bz}_2\text{NH}_2\text{BzCO}_2\cdot\text{SnPh}_3\text{Cl}$ (B)

For the **A** and **B** compounds, the broad band centred at 2900 cm^{-1} on the infrared spectrum indicates the presence of hydrogen bonds.

On the ^{119}Sn (Cl_3CD) spectrum of **A** compound, the signal at -110 ppm shows a single tin type consistent with a SnPh_3Cl molecule coordinated because the signal of the free SnPh_3Cl molecule is -44.7 ppm [13, 14].

The suggested structure for the two **A** and **B** compounds is a dinuclear dimer. Every one of the two BzCO_2^- anions monocoordinates a SnPh_3Cl molecule providing to the tin atom a trigonal bipyramidal environment. The two anionic $[\text{BzCO}_2\text{SnPh}_3\text{Cl}]^-$ components are linked each other by hydrogen bonds involving the non-coordinated oxygen atoms from the BzCO_2^- anions and the labile hydrogen atoms from the R_2NH_2^+ cations (Figure 1).

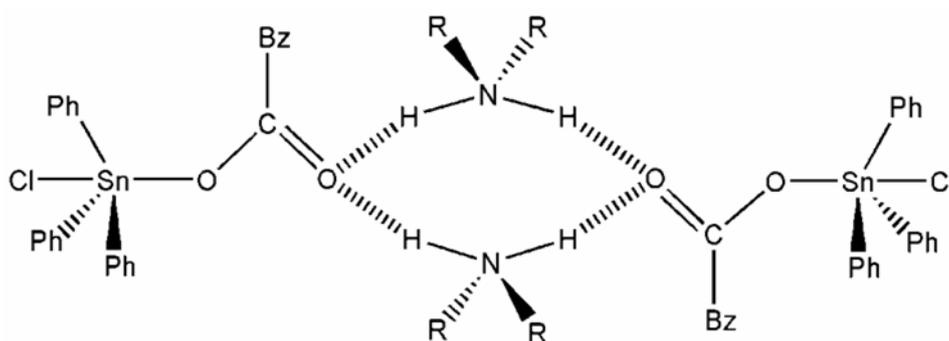


Figure 1. Suggested structures for compounds A and B

Characterization of $\text{BzCO}_2\text{SnPh}_3 \cdot \text{SnPh}_3\text{Cl} \cdot 1/4\text{Bz}_2\text{NH}_2\text{Cl}$ (C)

The ^{119}Sn NMR spectrum shows two values (-45.2 ppm and -106.9 ppm) consistent with tetrahedral environments of the tin atoms [13, 14]. The value of the chemical shift -45.2 ppm is very close to that (-44.7 ppm) attributed by Holeček to free SnPh_3Cl molecule [13, 14]. Thus, there is a non-coordinated SnPh_3Cl molecule in solution. The other chemical shift -106.9 ppm attributed to tin atom in $\text{BzCO}_2\text{SnPh}_3$ complex is consistent with those (between -110 ppm and -120 ppm) attributed by Alvarez-Boo to Ph_3SnO in triphenyltin (IV) sulfanyl carboxylates in which the tin atom has a tetrahedral environment [4].

The suggested discrete structure in solution has two components $\text{BzCO}_2\text{SnPh}_3$ and SnPh_3Cl in which the two metallic centres have a tetrahedral environment (Figure 2), considering a coordinated SnPh_3Cl in the solid state and the cleavage of this coordination in solution leading to a free SnPh_3Cl seems relevant.

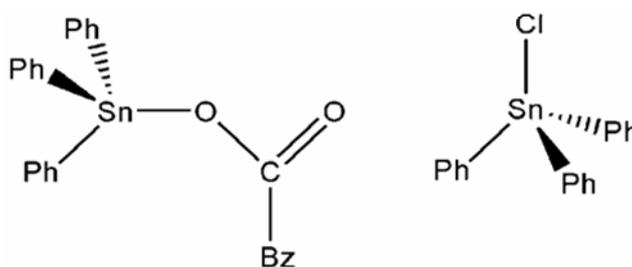


Figure 2. Suggested structure for compound C

Characterization of $\text{Bz}_2\text{NH}_2\text{BzCO}_2 \cdot \text{SnPhCl}(\text{OH})_2$ (D)

On the infrared spectrum, the broad band centred at 2900 cm^{-1} shows the presence of hydrogen bonds.

On the ^{119}Sn NMR spectrum, the single signal at -540.3 ppm indicates the presence of a hepta-coordinated tin centre as reported in the literature [15].

The suggested dimer structure consists of two tin centres each hepta-coordinated to a phenyl group, two hydroxyl groups, two bridged chlorine atoms and one chelating

BzCO₂⁻ anion (Figure 3). When Cy₂NH₂⁺ cations are involved through hydrogen bonds a supramolecular architecture is obtained with hydroxyl groups.

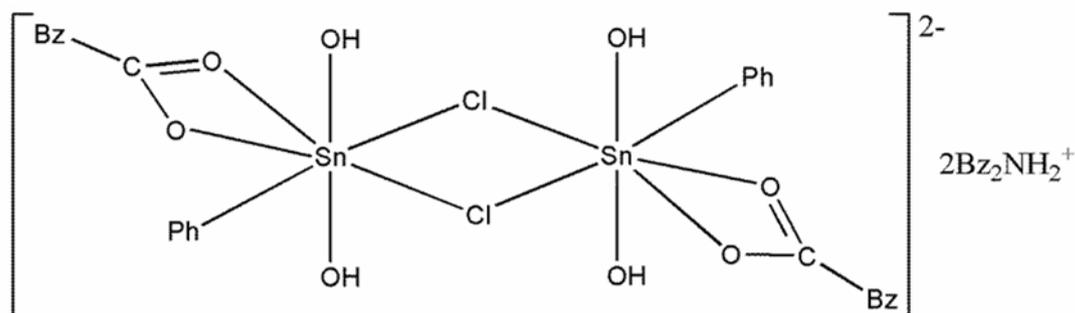


Figure 3. Suggested structure for compound **D**

Characterization of Bz₂NH₂BzCO₂·SnBu₂Cl₂ (**E**)

On the infrared spectrum, the presence of hydrogen bonds in the structure is certified by the broad band centred at 2900 cm⁻¹. The presence of a very weak band at 605 cm⁻¹ due to $\nu_s(\text{SnBu}_2)$ indicates the presence of a linear SnBu₂ residue.

The suggested structure is a dinuclear dimer. Each metallic centre is hexa-coordinated to two butyl groups, two chlorine atoms and one monochelating BzCO₂⁻ anion. The two anionic [BzCO₂SnBu₂Cl₂]⁻ components are linked by NH...Cl hydrogen bonds type involving the chlorine atoms and the Cy₂NH₂⁺ cations.

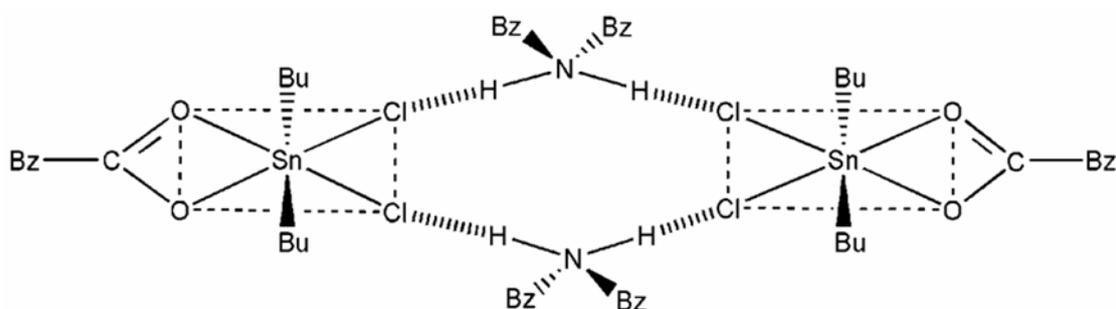


Figure 4. Suggested structure for compound **E**

Characterization of [BzCO₂SnPh₃][SnPhCl₃·EtOH·H₂O] (**F**)

The two signals at -109 ppm and -541 ppm on the ¹¹⁹Sn NMR spectrum indicate the presence of two different metallic centres in the structure. These values are characteristic to respectively penta-coordinated and hepta-coordinated tin centres [13, 16].

The suggested structure is a tetranuclear dimer. There are two different metallic centres respectively tetra-coordinated to three phenyl groups and one BzCO₂⁻ carboxylate anion and hepta-coordinated to one phenyl group, one water molecule, four chlorine atoms of which two bridged chlorine atoms and one BzCO₂⁻ carboxylate anion.

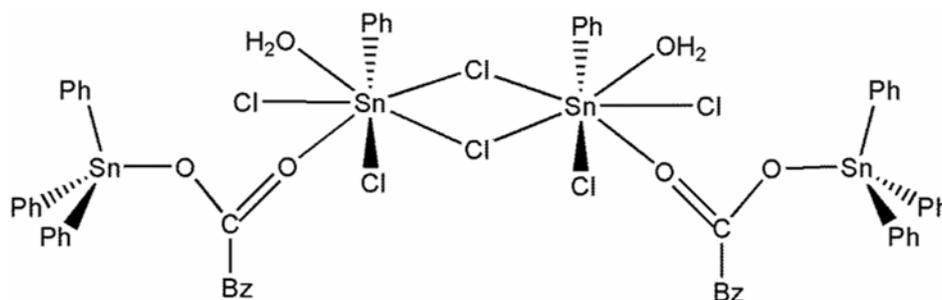


Figure 5. Suggested structure for compound F

CONCLUSION

The structures of the studied adducts are discrete or dimeric, the tin centre being tetra-, penta-, hexa- and hepta-coordinated, the benzyl carboxylate behaving as a mono- and bidentate ligand. The crucial role of $R_2NH_2^+$ cations ($R = Cy$ and Bz) *via* hydrogen bonds in the dimerization process and in the establishment of the supramolecular architecture through hydrogen bonds is noteworthy.

ACKNOWLEDGEMENTS

We thank Professor A. Tidjani – Dakar University (Senegal) for performing the IR spectra and Professor K.C. Molloy – University of Bath (UK) for performing the elemental analyses.

REFERENCES

1. Ayrey, G., Poller, R.C.: *Developments in Polymers Stabilization*, 2nd edition (Editor: Scott, G.) Applied Science Publishers, London, **1980**;
2. Evans, C.J., Karpel, S.: Agricultural Chemicals and Medical Uses (Chapters 6 and 7) in: *Organotin Compounds in Modern Technology (Journal of organometallic chemistry library, 16)*, Elsevier Science Ltd., Amsterdam, **1985**, 178-215;
3. Tiekink, E.R.T.: The rich diversity in tin carboxylate structures, *Trends in Organometallic Chemistry*, **1994**, 1, 71-116;
4. Gielen, M., El Khloufi, A., Biesemans, M., Kayser, F., Willem R.: Diorganotin 2-fluorocinnamates and 4-fluorophenylacetates: synthesis, characterization and *in vitro* antitumor activity, *Applied Organometallic Chemistry*, **1993**, 7 (3), 201-206;
5. Alvarez-Boo, P., Casas, J.S., Couce, M.D., Farto, R., Fernández-Moreira, V., Freijanes, E., Sordo, J., Vázquez-López, E.: Synthesis, characterization and antibacterial activity of some new triphenyltin(IV) sulfanylcarboxylates: Crystal structure of $[(SnPh_3)_2(p\text{-mpspa})]$, $[(SnPh_3)_2(cpa)]$ and $[(SnPh_3)_2(tspa)(DMSO)]$, *Journal of Organometallic Chemistry*, **2006**, 691 (1-2), 45-52;
6. Spencer, J.N., Barton, S.W., Cader, B.M., Corsico, C.D., Harrison, L.E., Mankuta, M.E., Yoder, C.H.: Lewis acidities of trimethylchlorosilane, -germane, and -stannane, *Organometallics*, **1985**, 4 (2), 394-396;
7. Spencer, J.N., Belser, R.B., Moyer, S.R., Haines, R.E., DiStravalo, M.A., Yoder, C.H.: Lewis acidities of trialkylhalostannanes, *Organometallics*, **1986**, 5 (1), 118-120;

8. Spencer, J.N., Enders, B.G., Grushow, A., Kneizys, S.P., Nachlis, W.L., Mokrynka, D., Coley, S.M., Otter, J.C., Yoder, C.H.: The stoichiometry of organotin trihalides in solution, *Journal of Organometallic Chemistry*, **1989**, 362 (1-2), 53-58;
9. Yoder, C.H., Mokrynka, D., Coley, S.M., Otter, J.C., Haines, R.E., Grushow, A., Ansel, L.J., Hovick, J.W., Mikus, J., Shermak, M.A., Spencer, J.N.: Stoichiometry of diorganotin dihalide adducts in solution, *Organometallics*, **1987**, 6 (8), 1679-1684;
10. Yoder, C.H., Otter, J.C., Grushow, A., Ganunis, T.F., Enders, B.G., Zafar, A.I., Spencer J.N.: The Lewis acidities of organotin halides toward tributylphosphine and tributylphosphine oxide: the effect of the donor site, *Journal of Organometallic Chemistry*, **1990**, 385 (1), 33-37;
11. Yoder, C.H., Morreall, R.A., Butoi, C.I., Kowalski, W.J., Spencer J.N.: The structure and Lewis acidity of some triorganotin carboxylates, *Journal of Organometallic Chemistry*, **1993**, 448 (1-2), 59-61;
12. Touré, A., Diop, C.A.K., Diop, L., Mahieu, B.: Synthèse et étude par spectroscopie Mossbauer, infrarouge et RMN de nouveaux complexes carboxylato organostanniques, *Comptes Rendus Chimie*, **2007**, 10 (6), 493-497;
13. Holeček, J., Nádvorník, M., Handlíř, K., Lyčka, A.: ^{13}C and ^{119}Sn NMR study of some four- and five-coordinate triphenyltin (IV) compounds, *Journal of Organometallic Chemistry*, **1983**, 241 (2), 177-184;
14. Holeček, J., Nádvorník, M., Handlíř, K., Lyčka, A.: ^{13}C and ^{119}Sn NMR spectra of di-n-butyltin (IV) compounds, *Journal of Organometallic Chemistry*, **1986**, 315 (3), 299-308;
15. Dakternieks, D., Duthie, A., Smyth, D.R., Stapleton, C.P.D., Tiekink, E.R.T.: Steric control over molecular structure and supramolecular association exerted by tin- and ligand-bound groups in diorganotin carboxylates, *Organometallics*, **2003**, 22 (22), 4599-4603;
16. Kayser, F., Biesemans, M., Boualam, M., Tiekink, E.R.T., El Khouloufi, A., Meunier-Piret, J., Bouhdid, A., Jurkschat, K., Gielen, M., Willem, R.: A novel 2:3 condensation complex of salicyladoxime and di-n-butyltin (IV) oxide, *Organometallics*, **1994**, 13 (4), 1098-1113.