

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
7 (2001)

ABOUT
3-METHOXYPROPYLTIN(IV) COMPOUNDS

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Received September 25, 2001

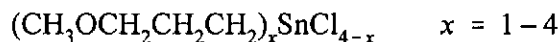
A set of novel 3-methoxypropyltin(IV) compounds of the general formula $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2)_x\text{SnCl}_{4-x}$ ($x = 1 - 4$) was synthesized and characterized. Shape of the coordination polyhedra about central tin atom and character Sn-O interaction are discussed on the basis of multinuclear NMR spectra, IR spectra and X-ray structure determination. Enhanced water solubility of these compounds was observed.

Introduction

Organotin(IV) compounds show wide spectrum of biological activity (antifungal, anticancer, antifouling, etc.). A correct evaluation of the biological merits of organotin derivatives remains often hampered by their low solubility in water medium. Recently Susperregui *et al.* have reported an interesting *in vivo* trypanocidal activity of water soluble bis[3-(2-methoxyethoxy)propyl]tin

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dichloride [1]. This finding was an inspiration for us to prepare a set of yet undocumented 3-methoxypropyltin(IV) compounds of general formula



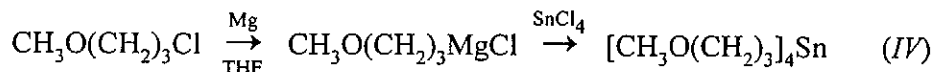
We supposed enhanced solubility in water for these compounds in comparison with butyltin(IV) analogues, which are practically insoluble.

A complete set of these compounds was successfully synthesized, analyzed and fully characterized by means of ^1H , ^{13}C , ^{17}O and ^{119}Sn NMR spectroscopy. The structure of one compound of the set, $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2)\text{SnCl}_3$, was determined by X-ray diffraction [2].

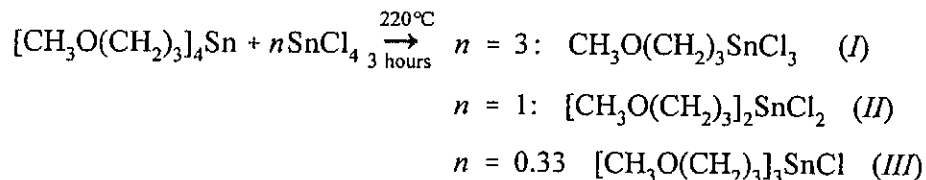
Results

Syntheses and Solubility

The studied compounds were synthesized in good yields using standard procedures. The starting tetrakis(3-methoxypropyl)stannane (*IV*) was prepared from 1-chloro-3-methoxypropane and stannic chloride by the Grignard reaction



The other 3-methoxypropylchlorostannanes were synthesized from tetrasubstituted compound *IV* and stannic chloride by the Kotchechkow synproportional reaction in yields about 90%



The raw products were purified by vacuum distillation, compounds *I* and *II* were purified also by crystallization from mixture chloroform-hexane.

Basic physical data and solubility in water (25 °C) of the studied compounds *I* – *IV* are collected in Table I.

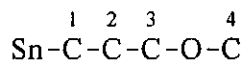
Table I Basic physical data and solubility^a in water 3-methoxypropyltin compounds *I – IV*

Compound	Formula and form	b.p., m.p., °C	Solubility at 25 °C, g l ⁻¹
<i>I</i>	C ₄ H ₉ OCl ₃ Sn, white cryst.	69 – 71	6.59
<i>II</i>	C ₈ H ₁₈ O ₂ Cl ₂ Sn, white cryst.	84 – 85	4.04
<i>III</i>	C ₁₂ H ₂₇ O ₃ ClSn, oil	113 – 115 /2 Pa	3.02
<i>IV</i>	C ₁₆ H ₃₆ O ₄ Sn, oil	118 – 120 /2 Pa	0.59

^a Calculated from Sn-content in the saturated water solution, determined by ICP-OES

NMR Spectroscopy

The ¹H, ¹³C and ¹¹⁹Sn NMR spectra were measured in the solution of non-coordinating CDCl₃. In order to evaluate the existence and strength of Sn-O coordination, ¹⁷O NMR spectra were measured in the same solvent. All important NMR parameters are in Table II. Numbering of carbon atoms in 3-methoxypropyl chain is shown in scheme

Table II Important NMR parameters of 3-methoxypropyltin compounds *I – IV* in CDCl₃

Compound	$\delta(^{119}\text{Sn})$, ppm	$\delta(^{13}\text{C})$, ppm / ($^n\text{J}(^{119}\text{Sn}, ^{13}\text{C})$, Hz)				$\delta(^{17}\text{O})$, ppm
		C1	C2	C3	C4	
<i>I</i>	-138.5	26.0(845.3)	23.8(67.0)	70.2(79.3)	58.5(-)	-3.0
<i>II</i>	-108.6	26.6(731.6)	24.5(42.7)	72.4(34.0)	58.6(-)	-13.0
<i>III</i>	49.0	14.7(434.6)	25.6(26.5)	74.7(55.7)	58.5(-)	-15.0
<i>IV</i>	-4.3	4.9(324.5)	26.7(18.6)	76.0(59.3)	58.4(-)	-17.0

IR Spectroscopy

IR spectra studied compounds *I – IV* were measured as a thin film on KBr or polyethylene window, respectively, in the region 4000 – 200 cm⁻¹. Values of the structurally significant absorption bands of the vibrations associated to C-O-C and Sn-Cl bonds are collected in Table III.

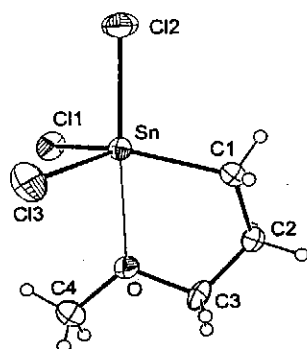
Table III Values of the structurally important absorptions in the IR spectra of 3-methoxypropyltin compounds *I–IV*

Compound	$\nu(\text{COC})$, cm^{-1}	$\nu(\text{SnCl})$, cm^{-1}	$\Delta\nu(\text{COC})^a$
<i>I</i>	1087	354, 320	33
<i>II</i>	1089	299, 287	31
<i>III</i>	1115, 1098	291	5, 22
<i>IV</i>	1120	-	0

^a The difference between the value $\nu(\text{COC})$ of 3-methoxypropylchloride ($\nu = 1120 \text{ cm}^{-1}$) and that of the given compound

X-Ray Diffraction

As already said, we managed to determine the structure of compound *I* by means of X-ray diffraction [2]. From schematic picture of its structure (see Fig. 1) and selected structural data it follows that the substance has trigonal bipyramidal arrangement of the central tin atom with strong intramolecular coordination of the O-atom 3-methoxypropyl group.



Selected bond length [pm] and angles [°] for *I*

Sn-Cl(1)	233.17	Cl(2)-Sn-Cl(1)	95.10
Sn-Cl(2)	239.04	Cl(2)-Sn-Cl(3)	98.17
Sn-Cl(3)	232.74	C(1)-Sn-Cl(1)	129.3
Sn-C(1)	209.00	C(1)-Sn-Cl(2)	102.9
Sn-O	239.40	C(1)-Sn-Cl(3)	120.5

Fig. 1 Molecular structure of compound *I*

Discussion

Chemical shifts $\delta(^{119}\text{Sn})$ of 3-methoxypropylstannanes *I–IV* in solution of non-coordinating CDCl_3 are shifted upfield with respect to analogous 1-butyltin(IV) compounds ($\Delta\delta(^{119}\text{Sn})$ are 132.4, 239.4, 103.8 and 1.3 ppm, respectively). The values of $\delta(^{17}\text{O})$ are shifted downfield (oxygen atom in 3-methoxypropyl group

is a pure σ -donor [3]) as the Lewis acidity of the central tin atom increases in the order $IV < III < II < I$. In the same order are shifted the $\nu(\text{COC})$ values to lower frequency in the infrared spectra (values of $\Delta\nu(\text{COC})$ increases) [4]. These experimental data distinctly show, that in the order $IV < III < II < I$ the donor-acceptor interaction between central tin atom and oxygen donor in 3-methoxypropyl substituent is increased.

In the case of tetraorganotin compound *IV* the value of $\Delta\delta(^{119}\text{Sn})$ is negligible. The same is true of $\Delta\nu(\text{COC})$. Thus, the interaction Sn-O (if any) must be very weak. The average value of interatomic angle C-Sn-C calculated from value $^1J(^{119}\text{Sn}, ^{13}\text{C})$ [5] is 107° , and the coordination polyhedron of tin atom is then an only slightly deformed tetrahedron.

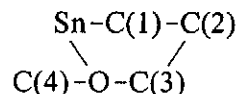
For mono- and triorganotin(IV) compounds *I* and *III* an increase of $\Delta\delta(^{119}\text{Sn})$ (132.4 and 103.8 ppm, respectively) denotes pentacoordinated tin atom. The shape of coordination polyhedron of *I* is evident from X-ray diffraction (see Fig. 1). From selected structural data it is evident that there is a certain deformation of the trigonal bipyramidal arrangement and weaker bond of the axial chlorine atom in comparison with two chlorine atoms in equatorial plane. The presence of two strong absorptions $\nu(\text{Sn-Cl})$ in the IR-spectrum is in accordance with this observation.

The average angle C-Sn-C in *III* (118°), calculated from the $^1J(^{119}\text{Sn}, ^{13}\text{C})$ value, indicates that the coordination polyhedron of tin atom has the shape of trans-trigonal bipyramid too. Three Sn-C bonds lie in equatorial plane, and the chlorine atom is bonded axially. It seems to be highly probable, that one oxygen atom of the methoxypropyl group is bonded to tin atom, while the other two are nonbonded (with presumption of rapid exchange in NMR time scale). This idea is also in agreement with IR spectrum of *III*. The doublet of strong absorption bands $\nu(\text{COC})$ was detected in the spectrum. One absorption band is shifted to lower frequencies only slightly, the second one is shifted markedly ($\Delta\nu(\text{COC})$ are 5 cm^{-1} and 22 cm^{-1} , respectively).

The value of $\Delta\delta(^{119}\text{Sn})$ 234.9 ppm observed for diorgano- compound *II* corresponds to the six-coordinated tin with both oxygen donor atoms coordinating tin atom. In accordance with this idea, only one $\nu(\text{COC})$ absorption was detected in IR spectrum. The value of interatomic angle C-Sn-C calculated from $^1J(^{119}\text{Sn}, ^{13}\text{C})$ is 148° . The neighbourhood of tin atom has an apparently distorted octahedral geometry with carbon atoms in nearly *trans*- position. This distortion is frequent for organotin(IV) compounds with octahedral geometry [5]. The X-ray diffraction study of compound *II* is in progress.

In the case of compounds *I-III* the values of $^2J(^{119}\text{Sn}, ^{13}\text{C})$ are higher and, on the other hand, the values of $^3J(^{119}\text{Sn}, ^{13}\text{C})$ are lower than the values of the same parameters in analogous 1-butyltin(IV) compounds. For compound *II* the order $^2J > ^3J$ was observed. It is just reversed compared to the usual trend ($^3J > ^2J$), which is probably due to the sum of contributions of both pathways to the

value of interaction constant in the oxa-stannacycle



It has been find out that the solubility of compounds *I* – *IV* in water is unusually high. This seems to be an interesting stimulation for a study of their aqueous solutions as well as for synthesis of other water-soluble organotin compounds.

Acknowledgements

The research was supported by Ministry of Education, Youth and Sport of Czech Republic (project VZ 3310/CZ310006/2010).

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