NEW SELENATO TRIPHENYLTIN (IV) AND TRIMETHYLTIN (IV) DERIVATIVES: SYNTHESIS, INFRARED AND NMR STUDIES

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Abstract: Five derivatives of general formulae [cation] [SeO4SnR3] (R = Ph, Me) have been studied by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. The suggested structures are infinite chains or oligomers, the environment around the tin centre being trans trigonal bipyramidal, the phenyl and methyl substituants occupying equatorial positions, the selenate anion behaving as a bridging bidentate ligand and occupying the apical positions. When cations are involved, supramolecular architectures may be obtained.

Keywords: bridging anion, derivatives, supramolecular architectures, trans trigonal bipyramidal environment, triorganotin (IV) residues

1. INTRODUCTION

The applications of many molecules belonging to organotin family explain the focus of several research groups in this field until nowadays [1 - 3]. Dealing with selenato complexes according to the Cambridge Database 2016, some X ray structures of selenato complexes have been reported so far:

- ethylenediamine $(SeO_4)_2Cd\ 2H_2O$ with a layered structure, the anion behaving as a bridging bidentate ligand [4];
- piperaziniumZn$(SeO_4)_2\ 4H_2O$ with a discrete structure, the environment around Zn being octahedral [5].

Some selenato tin (IV) complexes structures have been reported by our group [6 - 7]. Compared to the data of oxalato complexes, the selenato ones are very scarce. This has prompt us to study the interactions between $(R_2NH_2)_2SeO_4.xH_2O$, (R = Bu, Me), and $(CyNH_3)_2SeO_4.yH_2O$ with: $SnPh_3Cl$, $SnPh_3OH$ and $SnMe_3Cl$. This has yielded five new derivatives which infrared study has been carried out, then structures suggested on the basis of infrared data.

2. MATERIALS AND METHODS

A, B and **C** have been obtained as a white precipitate **A** or a white powder **B-C** on mixing:

- $SeO_4(CyNH_3)_2.2,5H_2O$ with $SnPh_3OH$ in 1:1 ratio in methanol for **A**;
- Bu_2NH with SeO_4H_2 and $SnPh_3Cl$ in 1:2:2 ratio in ethanol for **B**;
- Me_2NH with SeO_4H_2 and $SnPh_3OH$ in 1:2:2 ratio in methanol for **C**.

D and **E** are obtained on mixing $(Me_2NH_2)_2SeO_4$ (obtained as a powder on neutralizing SeO_4H_2 with Me_2NH in water-) with $SnMe_3Cl$ in 1:1 ratio in methanol (**D**) or Bu_2NH, SeO_4H_2 and $SnMe_3Cl$ in 1:1:1 ratio in methanol (**E**).

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The analytical data have allowed suggesting the following formula (Table 1).

Table 1. Results of the elemental analyses of compounds A-E.

Compound	Chemical formula	Elemental analysis [%]					
		C		H		N	
		calc.	found	calc.	found	calc.	found
A	$CyNH_3SeO_4SnPh_3$	48.60	48.54	4.93	4.52	2.36	2.33
B	$Bu_2NH_2SeO_4SnPh_3$	50.10	50.39	5.66	5.57	2.25	2.21
C	$Me_2NH_2SeO_4SnPh_3$	44.56	44.03	4.30	4.42	2.60	2.37
D	$Me_2NH_2SeO_4SnMe_3$	16.97	16.45	5.13	4.88	3.96	4.28
E	$Bu_2NH_2SeO_4SnMe_3$	30.23	30.46	6.69	6.54	3.21	3.19

Infrared spectra were recorded on a Bruker Vector 22 spectrometer equipped with a Specac Golden Gate^{TM} ATR device. $^{119}Sn\{^1H\}$ NMR spectrum was recorded on a Bruker Avance 400 MHz spectrometer with a wide band sensor BBFO. $^{119}Sn\{^1H\}$ NMR spectra are reported downfield from Me_4Sn, as the internal standard. Infrared data are given in cm^{-1} and chemical shifts (δ in ppm. [IR abbreviations are: (br) broad, (vs) very strong, (s) strong, (m) medium, (sh) shoulder, (w) weak, (vw) very weak]. Elemental analyses were performed at the “Institut de Chimie Moléculaire”, University of Bourgundy, Dijon-France. H_2SeO_4 was purchased from Merck Chemicals, Hohenbrunn bei München, Germany while Cy_3NH, *n*-Me_2NH, *n*-Bu_2NH, and $SnPh_3OH$, SnR_3Cl (R=Ph, Me) were acquired from Sigma-Aldrich Chemie GmbH, Steinheim, Germany and used without any further purification.

3. RESULTS AND DISCUSSION

Let us consider the spectroscopic data of the studied compounds.

IR(cm^{-1}):

A: υNH_3 3065-2946(br), δNH_3 1789 (m), 1694(m), 1556(m), $\upsilon_3 SeO_4$ 857(s), 807(s);

B: υNH_2 3043-2933(br), δNH_2 1603(m), $\upsilon_3 SeO_4$ 862(vs);

C: υNH_2 2934(vs), 2857(vs), δNH_2 1609(s), 1507(s), $\upsilon_3 SeO_4$ 821(vs), $\upsilon_1 SeO_4$ 764(s);

D: υNH_2 3649-2922(br), δNH_2 1642(m), 1558(m), $\upsilon_3 SeO_4$ 860(vs), $\upsilon_{as} SnMe_3$ 553(s), $\upsilon_s SnMe_3$ 515 (vw);

E: υNH_2 3118-2868(br), δNH_2 1564 (s), 1454 (s), $\upsilon_3 SeO_4$ 872 (vs), $\upsilon_1 SeO_4$ 768 (vs), $\upsilon_{as} SnMe_3$548 (vs), $\upsilon_s SnMe_3$ 518(w).

^{119}Sn NMR (ppm):

A: $\delta(C_6D_6) = -126$; **B:** $\delta(C_6D_6) = -194$; **D:** $\delta(CD_3OD) = +43$; **E:** $\delta(CD_3OD) = +50$.

The presence of strong bands due to the selenate anion υ_3 indicates its involvement in the structures. In all the IR spectra, the broad band around 2900 cm^{-1} and the strong bands around 1600 cm^{-1} are indicative of the presence of N-H---O hydrogen bonds. The values of the ^{119}Sn chemical shift at -126 ppm and -194 ppm for $SnPh_3$ residue containing derivatives are consistent with the presence of a *trans* coordinated residue according to Holecek et al. [8]. Dealing with the two $SnMe_3$ residue containing derivatives the values of the ^{119}Sn chemical shift at ≈ +43 ppm and ≈ +51 ppm indicate also *trans* coordinated $SnMe_3$ residue (in the compound $(CyNH_3)[4\text{-}NO_2C_6H_4PO_4(SnMe_3)]$ the ^{119}Sn NMR shift value in C_6D_6 is also +43 ppm (br) [9]; pentacoordinated trimethyltin formate HCO_2SnMe_3 has a chemical shift of +2.5 ppm and +152 ppm for the tetrahedral monomer) [10].

From these data, we can suggest in the solid state, while considering $[SnR_3SeO_4]^-$ (R=Ph, Me) complex-anion, two structures:

- an infinite chain one with a bridging selenate, the substituents occupying the equatorial positions as in [11] (Figure 1);
- an oligomeric one with a *trans* trigonal bipyramidal SnR_3O_2 framework (Figure 2), (We have arbitrary chosen the tetramer while any oligomer works) [12].

While considering the involvement of the cation, a supramolecular architecture as in $Cy_2NH_2C_2O_4SnMe_3$ or $Bu_2NH_2C_2O_4SnMe_3$ [13] may be obtained.

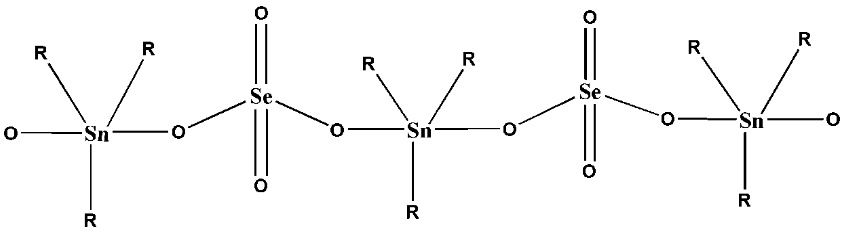

Fig. 1. Proposed structure $CyNH_3SeO_4SnPh_3$ or $R_2NH_2SeO_4SnR'_3$ (R=Me, Bu; R'=Me, Ph): as infinite chain structure.

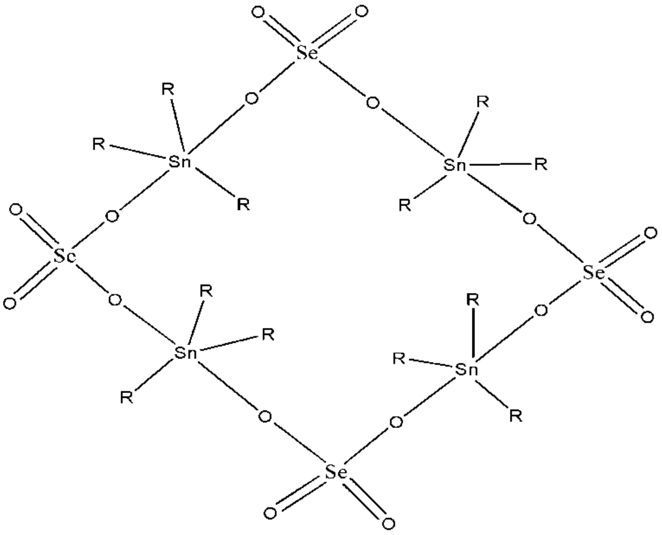

Fig. 2. Proposed structure $CyNH_3SeO_4SnPh_3$ or $R_2NH_2SeO_4SnR'_3$ (R=Me, Bu; R'=Me, Ph): as oligomer structure.

4. CONCLUSION

The studied derivatives containing triphenyl and trimethyl residues have an infinite chain or an oligomeric structure in the solid state, the environment around the tin centre being *trans* trigonal bipyramidal, the selenate acting as a bridging ligand. When the cations involved in hydrogen bonding are considered, supramolecular architectures may be obtained.

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