SYNTHESIS AND INFRARED STUDY OF SOME PHENYLPHOSPHONATE, DIPHENYLPHOSPHINATE AND ACETATOPHOSPHONATE NEW ORGANOTIN (IV) DERIVATIVES AND ADDUCTS

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Abstract: Three organotin (IV) derivatives PhPO3HSnBu2Cl, SnBu2P2O3Cl·3/2H2O, Sn(PhPO3)Cl2·2H2O obtained on allowing PhPO3H2 or propylammonium PhPO3H to react with SnBu2Cl2, SnCl2·2H2O and two adducts [(C6H5CH2)2NH]2O2C(CH2)2PO3·3SnPh3Cl, [CyNH3(HO)POCH2N(CH2CO2H)2]·SnCl2·2H2O·NH3Cl obtained on allowing (C6H5CH2)2NH2·O2C(CH2)2PO3 or [CyNH3(HO)POCH2N(CH2 CO2H)2] and SnPh3Cl or SnCl2·2H2O to react in ethanolic media have been characterized by elemental analyses, infrared and Mossbauer techniques. The suggested structures, while considering the anionic counterpart, are discrete, dimeric, double and triple metallic components or of infinite chain types, the anion behaving as a monochelating, a bichelating or a bidentate ligand. In OH containing structures, when extra hydrogen bonds are considered, supramolecular architectures may be obtained.

Keywords: bidentate, bichelating, hydrogen bonds, monochelating, PhPO3H+, Ph3PO2-, [O2C(CH2)2PO3]-,[HOPOCH2N(CH2CO2H)2]1, infrared and Mossbauer techniques, supramolecular architectures

1. INTRODUCTION

The organotin (IV) compounds are known for several applications in the industrial field (antifouling paints, wood preservatives) and also as drugs against cancer [1, 2], that explains the focus of several research teams in the attempt to obtain new molecules of this family [3-5]. In the dynamic of our research activity, we have yet published many papers dealing with organotin chemistry [6-10]. In this paper we have initiated the study of the interactions between PhPO3H2, propylammonium PhPO3H, [(C6H5CH2)2NH]2O2C(CH2)2PO3 or [(CyNH3)(HO)POCH2N(CH2CO2H)2] and SnBu2Cl2, SnCl2·2H2O or SnPh3Cl which has yielded five new compounds. Infrared and Mossbauer studies were carried out and structures were suggested on the basis of the spectroscopic data.

2. MATERIALS AND METHODS

On allowing PhPO3H2 to react with SnBu2Cl2 or SnCl2·2H2O in 1:1 ratio, propylammonium PhPO3H with SnBu2Cl2 in 1:2 ratio, [(C6H5CH2)2NH]2O2C(CH2)2PO3 with SnPh3Cl or [CyNH3(HO)POCH2N(CH2CO2H)2] with SnCl2·2H2O respectively in ethanol 1:2 or 1:3, white powders have been obtained after a slow solvent evaporation. The analytical data calculated(found) have allowed to suggest the following formulae:

•[A]: PhPO3HSnBu2Cl; % C = 39.52 (39.74), % H = 5.69 (5.58);

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• [B]: Sn(PhPO$_3$)$_2$Cl$_2$·2H$_2$O; % C = 18.88 (18.75), % H = 2.38 (2.33);
• [C]: SnBu$_2$Ph$_2$PO$_2$Cl$_3$·3/2H$_2$O; % C = 46.86 (46.98), % H = 6.05 (5.99);
• [D]: [(C$_6$H$_5$CH$_2$)$_2$NH$_2$]$_2$O$_2$Cl$_3$SnPh$_3$Cl; % C = 62.51 (62.62), % H = 5.14 (5.18), % N = 2.21 (2.18);
• [E]: [(CyNH$_3$)(HOPOCH$_2$N(CH$_2$CO$_2$H)$_2$)]$_2$·3SnCl$_4$·2H$_2$O·NH$_4$Cl: % C = 16.95 (16.80), % H = 3.29 (3.24), % N = 4.70 (4.68).

The infrared spectra were recorded using a spectrometer Nicolet 6700 FT-IR, the sample being as Nujol mulls using CsI windows. The Mossbauer spectra were obtained as reported in [11]. Infrared data are given in cm$^{-1}$ (abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak, (vw) very weak, d (doublet)). Mossbauer parameters are given in mms$^{-1}$ (abbreviations: Q.S = quadrupole splitting, I.S = isomer shift, f = full width at half-height). All the chemicals were purchased from ALDRICH Company-Germany and used as such.

3. RESULTS AND DISCUSSION

Let us consider the main infrared data of the studied derivatives and adducts:
• [A]: v (PO$_3$) 1129 (s), 1066 (s), 1015 (w), 996 (w), v as (SnBu$_2$) 691 (s);
• [B]: v (PO$_3$) 1140 (m), 1034 (s), 1009 (s), 991 (s);
• [C]: v (PO$_3$) 1132 (m), 1097 (s), 1073 (m), v as (SnBu$_2$) 692 (s), v (SnBu$_2$) 617 (w);
• [D]: v (NH$_3$) 3043 (broad), 2991 (broad), 2931 (broad), v as COO$^-$ 1644 (m), 1573 (m), v COO$^-$ 1430 (vs), v (PO$_3$) 1079 (broad), v (SnPh$_3$) 1000 (t), 700 (d);
• [E]: v (NH$_3$) 2937 (broad), 2860 (broad), v COO$^-$ 1654 (broad), 1500 (m), 1447 (m), v COO$^-$ 1354 (s), 1280 (w), v (PO$_3$) 1068, 1015 (broad).

![Fig. 1. Proposed structure for compound A.](image)

![Fig. 2. Proposed structure for compound B.](image)
The value of the quadrupole splitting of compound A indicates the presence of a *trans* octahedrally coordinated SnBu₂ group according to Parish and Platt [12]: the suggested structure is discrete with a monochelating anion (Figure 1).

In compound B the value of the quadrupole splitting is consistent with both *cis* or *trans* octahedrally coordinated SnCl₂ framework.

The suggested structures are reported in Figures 2a, 2b (discrete ones) with the anion behaving as a monochelating ligand or on Figures 2c and 2d (infinite chain structures) with a bidentate anion. The environment around the tin center in all cases is octahedral.

For SnBu₂Ph₂PO₂Cl·3/2H₂O while considering a dimerization followed by a rearrangement C can be written as: [SnBu₂Cl₂]SnBu₂(Ph₂PO₂)₂·3H₂O.

The values of the quadrupole splitting allow to suppose the presence of both a *trans* octahedrally coordinated SnBu₂ residue and a second SnBu₂ residue in a trigonal bipyramidal environment according to Parish and Platt [12]. A two metallic components structure may be suggested:

- a first metallic component is SnBu₂(Ph₂PO₂)₂ which contains bridging anions and a *trans* octahedral environment around the tin centre leading to an infinite chain (4.46mm⁻¹);
- a second metallic component H₂O-SnBu₂Cl₂ contains a Sn centre in a bipyramidal trigonal environment (3.16mm⁻¹).

These two metallic components may connect via hydrogen bonds to give the structure (Figure 3) (the 2 extra water molecules are considered as lattice).

The discrete suggested structure of compound [D] is reported on Figure 4.

![Diagram of proposed structure for compound C.](image)
Fig. 4. Proposed structure for compound D.

Considering the adduct \([(C_6H_5CH_2)NH_2)_2O_2C(CH_2)PO_3H\cdot3SnPh_3Cl\] \([D]\), we know that many SnPh_3Cl adducts with oxygens atoms containing ligands are O monocoordinated [13]. In the complex anion \([O_2C(CH_2)PO_3H\cdot3SnPh_3Cl]^-\), three of its five oxygen atoms monocoordinate a SnPh_3Cl molecule.
Fig. 5. Proposed structure for the compound E.

The anion is tridentate, the environment around the tin center being \textit{trans} trigonal bipyramidal. The cations ensure the dimerization.

The compound (CyNH$_3$)(HOPOCH$_2$-N(CH$_2$CO$_2$H)$_2$)$_2$·3SnCl$_4$·2H$_2$O NH$_4$Cl [E] contains three SnCl$_4$ molecules which are generally present in a SnCl$_4$O$_2$ octahedral arrangement. This allows for the compound compound [E] to suggest the four structures reported on Figures 5 (a, b, c, d) - NH$_4$Cl is lattice in the three first structures while being coordinated through the chloride to SnCl$_4$ in the structure 5d.

Three first structures of compound [E] are discrete (Figure 5a-c) while the last one (Figure 5d) is a three metallic component one. The anion behaves as:
- a monochelating and monodentate ligand in the first structure and last structure;
- a monochelating and hydrogen bond involved ligand in the second structure;
- a bridging bidentate ligand in the third structure.

In these structures when the cations are involved in hydrogen bonds a supramolecular architecture may be obtained.

4. CONCLUSION

The five adducts studied have discrete, dimeric, two or three metallic components or infinite chain type structures, the anion behaving as a monodentate, bidentate, tridentate, mono- or bichelating ligand. The environments of the tin (IV) centres are trigonal bipyramidal or octahedral. In free OH or NH containing structures, when extra hydrogen bonds are considered, supramolecular architectures may be obtained.

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