Synthesis, Infrared and Mössbauer Characterization of Some Chloridestannate (IV) Inorganic-organic Hybrid Complexes: Sn-Ph Bonds Cleavage

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To cite this article:
Dame Seye, Mouhamadou Birame Diop, Assane Toure, Tidiane Diop, Cheikh Abdoul Khadir Diop, Mamadou Sidibe, Aminata Diasse Sarr, Libasse Diop. Synthesis, Infrared and Mössbauer Characterization of Some Chloridestannate (IV) Inorganic-organic Hybrid Complexes: Sn-Ph Bonds Cleavage. *American Journal of Heterocyclic Chemistry*. Vol. 5, No.4, 2019, pp. 81-85. doi: 10.11648/j.ajhc.20190504.12

Received: February 13, 2020; Accepted: February 27, 2020; Published: March 10, 2020

Abstract: Five new compounds are isolated from reactions carried out in solution. All the compounds are characterized by, Infrared and Mössbauer spectroscopies. Spectroscopic studies have shown the presence of different characteristic bands, notably $\nu$ (PO) vibrations coming from triphenylphosphine oxide, with wide absorption due to the NH$_2$ groups coming from urea and the intense doublet which show the presence of phenyl groups. The proposed structures, in the solid state, are discrete though hydrogen bonding interactions may occur. Event in this study is the dearylation evidenced, cleaved Sn-Ph bonds occurring in the presence of triphenylphosphine oxide or urea, during some reaction processes. In the presence of triphenylphosphine oxide, the dearylation is followed by the formation of Sn-Cl new bonds while in the presence of urea, the Sn-Ph bonds cleavage undergo with a deamination of the urea giving rise to the formation of Sn-N and Sn-Cl new bonds whose presence are ascertained by the Mössbauer parameters. The oxidation of tin (II) to tin (IV) as well as the coordination behavior of the oxonium, H$_3$O$^+$ cation is also noted in this work. In the reaction of triphenylphosphine oxide with SnCl$_2$. 2H$_2$O and nitric acid, we have obtained compounds in which tin has oxidized. The reactions between urea and SnPh$_3$Cl are the site of a species exchange which can be explained by a deamination of urea and a dephenylation of SnPh$_3$Cl. Studies aimed at understanding the processes of this transformation still unknown leading to the isolation of aminochlorotin (IV) compounds and isolating their single crystals are being carried in our laboratory (LA.CHI.MI.A).

Keywords: Chloride, Infrared, Mössbauer, Sn-Ph Bonds Cleavage, Tin (IV), Urea Deamination

1. Introduction

Organotin materials display interesting properties and have multiple applications. They exhibit, for example, inhibition towards pancreatic cancer cells [1-4], anticancer activity [5-7], catalysis application [8], fungicidal activity [9]. Moreover, they are used in the preparation of some thin-film transistors matrix [10]. In the seventies, several crystalline structures of tin (IV) compounds with ligand such as Ph$_2$AsO, PyO, Ph$_3$PO were reported [11-13]. In these complexes, the OSnPh$_3$O cores are in a trans-trigonal bipyramidal arrangement whith the phenyl groups in equatorial positions. The Dakar group has been involved in the development of halo- and organotin (IV) class of compounds since more than two decades. We recently have described the spectroscopic characterization of the complex [(PhCH$_2$)$_2$PhP(NO$_2$)$_2$] [(SnPh$_3$Cl)$_3$] [14] which contains a central tridentate nitrate anion linked to tin centres. Sn-Ph bonds exhibit a reasonable labile character and can be cleaved in some conditions. Numerous works especially those reporting crystalline structures evidencing the presence of Sn-Ph bonds cleaved from partial to total dearylation [15, 16] have been published. In these studies, the dearylation generally occur when reactions happen in organic solvent solutions and, new bonds are trained because the tin atom
affords multiple possible synthons. In this work, we investigated, in organic solvent, at room temperature, the interactions between dichloridotin (II) dihydrate, SnCl₂, H₂O and, cetyltrimethyl bromide, C₁₉H₃₄Br or triphenylphosphine oxide, Ph₃PO and nitric acid, HNO₃ in the one hand, triphenyltin (IV) chloride, SnPh₃Cl and, triphenylphosphine oxide, Ph₃PO or urea, CH₂ON₂ in the other hand. These interactions afforded white powders whose infrared and Mössbauer characterization are carried out and reported herein characterization is reported herein.

2. Materials and Methods

2.1. General

Chemicals were purchased from Sigma-Aldrich (Germany) and were used without any further purification. Elemental analyses were performed at the Institut de Chimie Moléculaire, Université de Bourgogne Franche-Comté, Dijon, France. The infrared spectra were recorded on a Bruker Vector 22 spectrometer equipped with a Specac Golden Gate™ ATR device. The ¹¹⁹Sn Mössbauer spectra were obtained from the Centro de Desenvolvimento da Tecnologia Nuclear (CDTN), Servicio de Nanotecnologia (SENA), Laboratorio de Fisica Aplicada, Brazil. The ¹¹⁹Sn Mössbauer spectra were obtained from a constant-acceleration spectrometer moving a CsSnO₃ source at room temperature. The samples were analyzed at liquid N₂ temperature, and the isomer shift values are given with respect to that source. All the Mössbauer spectra were computer-fitted assuming Lorentzian lineshapes. Mössbauer parameters are given in mm/s [abbreviations: Q, S=quadrupole splitting, I. S=isomer shift, Γ=full width at half-height, A=area (%)].

2.2. Synthesis

Cetyltrimethyl bromide, C₁₉H₃₄Br (m=511 mg; 1.4 mmol), was preliminary dissolved in 15 mL of slightly hydrated methanol. A 10 mL methanol solution equimolar amount of dichloridotin (II) dihydrate, SnCl₂·2H₂O (m=316 mg; 1.4 mmol) was then added. A white powder was obtained after some days of a slow solvent evaporation at room temperature and was characterized as 1. Compound 2 was isolated as a white powder by mixing 15 mL methanol solutions of dichloridotin (II) dihydrate, SnCl₂·2H₂O (m=519 mg; 2.3 mmol) and triphenylphosphine oxide, Ph₃PO (m=641 mg; 2.3 mmol) and, an amount of nitric acid, HNO₃ (4.6 mmol). Compound 3 was isolated as a white powder on allowing 15 mL acetonitrile solutions of triphenylltin (IV) chloride, SnPh₃Cl (m=386 mg; 1 mmol) and triphenylphosphine oxide, Ph₃PO (m=279 mg; 1 mmol) to react. Compounds 4 and 5 were obtained as white powders from reaction between 20 mL methanol solution of triphenylltin (IV) chloride, SnPh₃Cl and 10 mL methanol solution of urea, CH₂ON₂: SnPh₃Cl (m=386 mg; 1 mmol) and CH₂ON₂ (m=121 mg; 2 mmol), SnPh₃Cl (m=771 mg; 2 mmol) and CH₂ON₂ (m=61 mg; 1 mmol), respectively.

All mixtures were stirred around 2h at room temperature under a not controlled atmosphere.

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

### Table 1. Results of the elemental analyses of compounds 1-5.

| Compound | Chemical formula | Elemental analysis [%] |  |  |  |
|----------|------------------|------------------------|---|---|---|
|          |                  | C                      | H | N |
|          |                  | Calc. | Found | Calc. | Found | Calc. | Found |  |
| 1        | (C₁₉H₃₄Br)[SnCl₂]·7H₂O | 32.00 | 31.63 | 6.59 | 6.71 | 1.96 | 2.01 |
| 2        | 4(SnCl₂OPPh₃)·NO₂·H₂O | 38.93 | 39.86 | 2.88 | 3.45 | 0.67 | 0.63 |
| 3        | [SnCl₂(OPPh₃)₂]·C₆H₆·0.27CH₃CN | 56.35 | 57.35 | 4.05 | 3.45 | 0.66 | 0.59 |
| 4        | [SnCl₂(NH₂)₂(Ph)₃CO·CH₂OH]·C₆H₆ | 48.57 | 49.55 | 3.58 | 4.56 | 8.50 | 8.46 |
| 5        | [SnCl₂(NH₂)₂(Ph)₃CO·CH₂OH]·3C₆H₆ | 54.31 | 54.88 | 5.13 | 4.08 | 1.98 | 1.31 |

### Table 2. Compound and chemical formula.

| Compound | Chemical formula |
|----------|------------------|
| 1        | (C₁₉H₃₄N)[SnCl₂]·7H₂O |
| 2        | 4(SnCl₂OPPh₃)·NO₂·H₂O |
| 3        | [SnCl₂(OPPh₃)₂]·C₆H₆·0.27CH₃CN |
| 4        | [SnCl₂(NH₂)₂(Ph)₃CO·CH₂OH]·C₆H₆ |
| 5        | [SnCl₂(NH₂)₂(Ph)₃CO·CH₂OH]·3C₆H₆ |

Compounds 1-5 were investigated by FT-IR spectroscopy in ATR mode. In the past, several works with FT-IR tetraalkylammonium cations, triphenylphosphine oxide, carboxylates and multiples other vibration bands investigation have been reported [17]. The spectrum of 1 shows absorption bands that can be assigned to cetyltrimethylammonium cation (N–C, and C–H bonds) and water molecules. In fact, vibration band located at 3400 cm⁻¹ assigned to O–H water stretching vibrations corroborate its presence in 1. Vibration bands located at 2922 cm⁻¹ and 2849 cm⁻¹ and 1468 cm⁻¹ are attributed to C–H stretching and bending vibrations, whereas those at 1200 cm⁻¹ and 1100 cm⁻¹ correspond to C–N stretching and deformation vibrations of the cetyltrimethylammonium. The rocking CH₃ and CH₂ vibrations are present about 1000-1100 cm⁻¹ while their elongation vibrations are observed at 719 cm⁻¹. The

3. Structure Description

It seems worthy to outline the oxidation of tin (II) into tin (IV) in achievement processes of complexes 1 and 2, the Sn-Ph bonds cleavage within the formation of compound 3, the Sn-Ph bonds cleavage and urea deamination occurring during the formation processes of compounds 4 and 5.

**FT-IR spectroscopy**
spectrum of 2 notices a band at 1150 cm\(^{-1}\) assigned to PO vibrations likewise a band at 1436 cm\(^{-1}\) which corresponds to nitrate stretching vibrations. The shift of the v (PO) band is an important observation which can be explained by the coordination of PPh\(_3\)O molecule to Sn atom through the oxygen atom. Additional vibration bands, characteristic of phenyl ligands, are also observed at 725 cm\(^{-1}\) and 695 cm\(^{-1}\) corresponding to phenyl groups C−H and C=C elongations, respectively. The spectrum of 3 evidences vibration bands at 1149 cm\(^{-1}\), 722 cm\(^{-1}\) and 690 cm\(^{-1}\) attributed to PO vibrations and, C−H and C=C elongations of phenyl groups, respectively. The v (PO) shift band is also observed enabled by the coordination of PPh\(_3\)O molecule to tin atom. In the spectrum of 4 are ascertained O−H vibrations at 3350 cm\(^{-1}\) and, N−H stretching and bending vibrations at 2985 cm\(^{-1}\) and 2956 cm\(^{-1}\), and 1503 cm\(^{-1}\), respectively. Vibrations bands observed at 1628 cm\(^{-1}\) and 1262 cm\(^{-1}\), 721 and 692 cm\(^{-1}\) well corroborate the presence of carbonyl and phenyl groups, respectively. For 5, the infrared spectrum enables to diagnose N−H stretching and bending vibrations at 3014 cm\(^{-1}\), 2978 cm\(^{-1}\) and 1517 cm\(^{-1}\); CO antisymmetric and symmetric vibrations at 1597 cm\(^{-1}\) and 1248 cm\(^{-1}\), phenyl groups C−H and C=C elongations at 720 cm\(^{-1}\) and 688 cm\(^{-1}\) likewise.

Infrared characteristic absorption vibration bands evidence presence of moieties that are present in the proposed formulae. Thus, the infrared investigations are in accordance with suggested formulæ.

**Mössbauer spectroscopy and molecular structures**

Compounds 1-5 were also investigated by tin mössbauer spectroscopy (Table 2).

| Compound | Phases | IS (mm/s) (± 0.05) | QS (mm/s) (± 0.05) | Γ (mm/s) (± 0.04) | Area (%) (± 1) |
|----------|--------|-------------------|-------------------|-----------------|--------------|
| 1        | 1      | 0.17              | 0.56              | 0.99            | 100          |
| 2        | 1      | 0.11              | 0.53              | 0.96            | 100          |
| 3        | 1      | 0.20              | 0.49              | 0.90            | 100          |
| 4        | 1      | 0.12              | 0.60              | 0.97            | 100          |
| 5        | 1      | 0.21              | 0.56              | 0.91            | 100          |

For 1, the mössbauer parameters evidence one arrangement fashion at tin atom. The isomer shift and the quadrupole splitting values found for [SnCl\(_4\)]\(^2-\) are 0.59 mm. s\(^{-1}\) and 0.77 mm. s\(^{-1}\), respectively [18]. The isomer shift and the quadrupole splitting values of 0.17 mm. s\(^{-1}\) and 0.56 mm. s\(^{-1}\) are in accordance with an hexacoordinated metallic chloride component and thus corroborate the suggested formula [18]. Various [SnCl\(_4\)]\(^2-\) containing crystalline structures are known, to date [19, 20]. We suggest in the solid state, on the basis of spectroscopic data, a discrete structure with a SnCl\(_4\)– complex-anion coordinated to a water molecule to give the [SnCl\(_3\)(H\(_2\)O)] complex which electrostatically interacts with the cetyltrimethylammonium cation (Figure 1); the remaining water molecules are considered as lattice.

For 2, the mössbauer parameters confirm the presence of only coordinated trans-coordinated SnCl\(_4\) molecules [21-24]. The Dakar group has yet reported complexes [NO\(_3\)(SnPh\(_3\)NO\(_3\))(SnPh\(_3\)Cl\(_2\))][Et\(_3\)N] and [(PhCH\(_2\)) P\(_2\)Cl \_][([SnPh\(_3\)Cl\(_3\]) whose described structures are comprised of a central tricoordinating nitrate anion linked to tin centres [14, 25]. In comparison to this nitrate behaviour, we therefore suggest, in the solid state, a two components structure. The first component contains a central tridentate nitrate anion coordinated to tin centres of SnCl\(_4\) molecules which are, each one, yet coordinated by a PPh\(_3\)O molecule. The second component is a SnCl\(_4\) molecule coordinated to an oxonium (H\(_2\)O\(^+\)) cation and to a PPh\(_3\)O molecule. In both components, the tin atom is about a centre of an octahedron (Figure 2).
iso-structural discrete structure comprised of a SnCl₄ molecule cis-coordinated in an octahedral fashion to two PPh₃O molecules, the benzene molecule is considered lattice (Figure 3).

For 4 and 5, the Mössbauer quadrupole splitting low values of 0.60 mm. s⁻¹ and 0.56 mm. s⁻¹ (< 1 mm. s⁻¹) evidence clearly absence of SnPh₃ residues, thus Sn-Ph bonds cleavage. In fact, the Sn-Ph containing compounds isomer shift and the quadrupole splitting values are generally higher than 1 mm. s⁻¹ [14, 18, 21, 27]. These Mössbauer parameters are in accordance with the proposed formulae presumably obtained after an in situ urea degradation and Sn–Ph bonds cleavage followed by a rearrangement. The presumable exchange is uncommon. In the past, several compounds occurring a Sn–Ph bond cleavage during their isolation processes have been reported [15, 16]. On the basis of spectroscopic data we suggest, in the solid state, a discrete structure which is comprised of a central tin atom coordinated to:

i. For 4, a chlorine atom and three amino groups giving a SnCl(NH₂)₃ molecule whose octahedral coordination sphere is completed by Ph₂CO and methanol molecules through Sn–O bonds, the benzene molecules being lattice (Figure 4).

ii. For 5, three chlorine atoms and one amino group giving a SnCl₃(NH₂) molecule whose octahedral coordination sphere is completed by Ph₂CO and methanol molecules through Sn–O bonds, the benzene molecules being lattice (Figure 5).

In the proposed structures except of 2, O–H group of methanol molecule, N–H amino group or O–H water molecules may interact through hydrogen bonds leading to supramolecular architectures.

4. Conclusion

In this study, the reaction between dichloridotin (II) dihydrate, SnCl₂.2H₂O exhibits a tin oxidation from 2⁺ to 4⁺. This oxidation led to the isolation of three complexes which have discrete structures. Interactions between urea and triphenyltin chloride, SnPh₃Cl diagnosed an event in tin chemistry, an uncommon process exchange between species giving rise to aminochlorotin (IV) based compounds, when reactions are carried out in polar organic solvents, methanol for example, and in a not controlled atmosphere. This exchange follows a 1: 3 (default material: excess material) ratio and can be explained by deamination of urea and dearylation, Sn–Ph bonds cleavage of SnPh₃Cl. Further studies in attempts to well understand the yet unknown transformation processes leading to the isolation of the aminochlorotin (IV) compounds and, isolate their single crystals are in progress in our Laboratory (LA.CHI.MI.A).

Acknowledgements

The authors acknowledge the Cheikh Anta Diop University of Dakar (Sénégal), the University of Bourgogne Franche-Comté, Dijon (France) and the Centro de Desenvolvimento da Tecnologia Nuclear (CDTN), Servicio de Nanotecnologia (SENA), Laboratorio de Fisica Aplicada, Pampulha, Belo Horizonte (Brazil) for facilities.

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