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Some new butylthiobenzoatotin(IV) compounds: spectral studies and analysis of ligand's bonding

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Dedicated to Professor V.D. Gupta on his 65th birthday.

Abstract

Five new monorganotin(IV) compounds with thiobenzoate ligand, $[BuSn(SOCPh)_2]_2O$ (**1**), $[BuSn(O)(SOCPh)]_2$ (**2**), $BuSn(Cl)(SOCPh)_2$ (**3**), $BuSn(Cl)_2(SOCPh)$ (**4**) and $[BuSn(OH)(Cl)(SOCPh)]_2$ (**5**) were synthesized and characterized by elemental analyses, IR, ^{1}H and ^{13}C NMR spectroscopy. ^{119}Sn NMR spectroscopy was used to determine the coordination geometry around Sn(IV) in the cases of **2** and **4**. **1**, **2** and **5** are dimeric while **3** and **4** are monomeric. In all these molecules the thiobenzoate ion is coordinated only through its sulfur atom. Molecular structures of the compounds have been optimized by MM2 calculations. Semi-empirical quantum mechanical calculations (PM3 method) were performed to explain the monodentate-bonding pattern of thiobenzoate ligand.

Keywords: Organotin compound; Thiocarboxylate; ^{119}Sn NMR; Molecular structure; Semi-empirical calculations

1. Introduction

Organotin(IV) compounds interact strongly with biological substrates giving rise to toxic effects [1]. Some of them are also known to exert therapeutic effects on various tumor cells [2]. Certain organotin(IV) derivatives have synthetic applications as homogeneous catalysts [3]. In past few years, a large number of organotin(IV) complexes have been synthesized and structurally characterized in solution as well as in solid state revealing incomparable multifariousness of these systems.

Despite considerable structural information, the factors influencing coordination number and geometry are not well understood in these systems [4]. Monoorganotin(IV) complexes are hexacoordinated in most of the cases [4–6] and those obtained using carboxylate ligands form clusters which exist in two distinct structural forms [7]. On the other hand, our own findings with thiocarboxylate ligands are different [8]. Discrete monomeric molecular units of $BuSn(SOCPh)_3$ and $Sn(Cl)_2(SOCPh)_2$ were found in their respective crystal lattices. More interestingly, the former molecule possesses tetracoordinated Sn(IV) center. Recently, molecular models of some partially substituted organotin(IV) complexes using N, O, S donor ligands have been reported [9,10]. Interaction modes of some of these complexes with water have also been modeled [10].

In view of the above facts, we here report syntheses and spectral characterization including MM2 molecular structures of a few monoorganotin(IV) thiobenzoate derivatives. Results of semi-empirical quantum chemical calculations performed to explain the bonding mode of the thiobenzoate anion are also reported.

2. Experimental

All experimental manipulations were carried out under anhydrous conditions. Solvents were purified and dried by standard methods. Butyltin trichloride (Aldrich) was freshly

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distilled (93 °C/10 Torr) prior to use. Butyltin hydroxide oxide (butylhydroxyoxostannane) [11], butyltin dichloride hydroxide (butyldichlorohydroxystannane) [12] and thiobenzoic acid [13] were prepared by literature procedures. Potassium salt of thiobenzoic acid was prepared by shaking an aqueous solution of KOH with an ethereal solution of thiobenzoic acid. The aqueous layer was evaporated under reduced pressure and the residue dried in a vacuum desiccator over P_4O_{10}. Sulfur and chlorine were estimated gravimetrically as $BaSO_4$ and AgCl, respectively. Micro analytical and mass spectral data were collected through RSIC (Chandigarh, India). IR spectra were recorded in the region 4000–400 cm^{-1} using a JASCO FT-IR 5300 spectrometer as KBr pellets and in the region 400–200 cm^{-1} as nujol mull over CsI disks using a Perkin-Elmer 883 instrument. ^1H and ^{13}C NMR were recorded with a JEOL FX90Q instrument and ^{119}Sn NMR with a Bruker 400 MHz spectrometer in $CDCl_3$ solutions. TMS was used as an internal reference for ^1H and ^{13}C while external reference Me_4Sn was used in a sealed capillary for ^{119}Sn NMR. MM2 computations were performed using CsChem3D Ultra program package. Semi-empirical quantum mechanical calculations by PM3 method were performed using MOPAC (Ver. 6.0).

2.1. Synthesis of $[BuSn(SOCPh)_2]_2O$ and $[BuSn(O)(S(O)CPh)]_2$

A solution of thiobenzoic acid in benzene (~10 ml) was added to a stirred suspension of butyltin hydroxide oxide in benzene (~20 ml) 2:1 or 1:1 molar ratio at room temperature (28 °C). Stirring was continued for 2 h during which the reaction mixture became homogeneous. The solvent was then evaporated under reduced pressure and the product was dried in vacuo for 1 h at 0.05 Torr/28 °C. **1** was recrystallized from a 1:1 mixture of diethyl ether/*n*-hexane and **2** from slow cooling of a hot acetone solution.

2.2. Synthesis of $BuSn(Cl)(SOCPh)_2$ and $BuSn(Cl)_2(SOCPh)$

A solution of butyltin trichloride in dichloromethane (~10 ml) was added to a stirred suspension of potassium thiobenzoate in the same solvent (~20 ml) at room temperature. After stirring for 1 h, the KCl precipitate was filtered off and the solvent evaporated under reduced pressure. The resulting residue was dried in vacuo for 1 h at 0.05 Torr/28 °C. **3** was recrystallized from a diethyl ether/*n*-hexane 1:1 mixture.

2.3. Synthesis of $[BuSn(OH)(Cl)(SOCPh)]_2$

An acetone solution of potassium thiobenzoate was added to a stirring suspension of $[BuSn(OH)Cl_2H_2O]_2$ in acetone (~10 ml) at room temperature. After stirring for 1 h, the precipitated KCl was filtered off and the solvent was evaporated under reduced pressure. The residue thus obtained was dried under vacuo for 6 h at 0.01 Torr/39 °C. The pasty product solidified on refrigeration overnight.

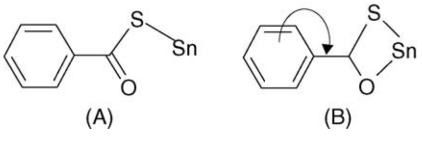
3. Results and discussion

3.1. Synthesis of the compounds

Two butyloxotin(IV) thiobenzoates, $[BuSn(SOCPh)_2]_2O$ (**1**) and $[BuSn(O)(SOCPh)]_2$ (**2**), two butylchlorotin(IV) thiobenzoates, $BuSn(Cl)(SOCPh)_2$ (**3**) and $BuSn(Cl)_2(SOCPh)$ (**4**) and another hydroxochloro derivative, $[BuSn(OH)(Cl)(SOCPh)]_2$ (**5**) were prepared (Table 1). **1** and **2** are readily formed in high yields when butyltin hydroxide oxide was reacted with thiobenzoic acid in 1:2 and 1:1 molar ratios, respectively. Compounds **3** and **4** were obtained from the reactions of butyltin trichloride with potassium thiobenzoate in appropriate molar ratios (1:2 and 1:1). The hydroxochloro compound **5** was obtained from a reaction of $[BuSn(OH)Cl_2{\cdot}H_2O]_2$ and KO(S)CPh in equimolar ratio. Attempt to replace the second chlorine from this complex using 2 moles of thiobenzoate salt led to the formation of the previously reported tris-thiobenzoate compound [8]. All the compounds are quite stable in open atmosphere in solid state as well as in solution and are solids except **4**, which is a viscous liquid.

3.2. IR spectra

The infrared spectrum of thiobenzoic acid displays three characteristic bands at 1685, 1213 and 950 cm^{-1}, respectively, due to C=O, Ph–C and C–S bond stretching vibrations. Shift in the positions of these bands can be used as a diagnostic tool to detect the coordination mode of the thiobenzoate anion [14]. In the spectra of the compounds (Table 2), the CO stretching band is observed in a narrow range between 1595 and 1610 cm^{-1} providing a strong evidence for existence of a double bond between the two atoms. It implies that the carbonyl oxygen atoms are not involved in coordination with Sn(IV) atoms. This is further substantiated by the appearance of the ν(C–S) band between 922 and 939 cm^{-1} indicating presence of single bond between carbon and sulphur atoms. We have reported earlier that on chelation with Sn(IV) atoms, the ν(C–S) band shifts to a higher wave number [8]. Furthermore, the ν(Ph–C) absorption in the region 1211–1219 cm^{-1} is also indicative of monodentate attachment of the ligand, since on chelation the π–electron drift as shown in Scheme 1 would shift this band to a higher frequency as has been observed in $Cl_2Sn(SOCPh)_2$. In the far IR



Scheme 1.