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Journal of Organometallic Chemistry 691 (2006) 1622–1630

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Preparation and structural characterization of $[Ph_3Sn(IV)]^+$ complexes with pyridine-carboxylic acids or hydroxypyridine, -pyrimidine and -quinoline

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Received 2 December 2005; accepted 2 December 2005
Available online 19 January 2006

Abstract

A number of $[Ph_3Sn(IV)]^+$ complexes formed with ligands containing –OH (–C=O), or –COOH group(s) and aromatic {N} donor atom have been prepared. The binding sites of the ligands were identified by FT-IR spectroscopic measurements. In the complexes containing hydroxy and carboxylate functions, the carboxylato group is coordinated to the organotin(IV) centres in monodentate or bridging bidentate manner. It was also found that in the hydroxypyridine and -pyrimidine complexes the $[Ph_3Sn(IV)]^+$ moiety in most cases reacts with the phenolic form of the ligands. The rationalisation of the experimental ^{119}Sn Mössbauer nuclear quadrupole splittings, $|\Delta_{exp}|$ – according to the point charge model formalism – together with the FT-IR data support the formation of trigonal bipyramidal (Tbp) or octahedral (O_h) molecular structures. Furthermore, X-ray diffraction analysis has been performed on the triphenyltin(IV)-3-phenolato-2(1*H*)-pyridinone-*O*,*O*′ single crystals. The penta-coordinated tin center exhibits a Tbp geometry. In case of 2-picolinic acid, a *trans*-phenylation was observed during the complexation, resulting $[Ph_2Sn(IV)]^{2+}$ complex and $Ph_4Sn(IV)$.

Keywords: Triphenyltin(IV); Hydroxypyridine, -pyrimidine and pyridinecarboxylato complexes; Mössbauer; FT-IR; X-ray diffraction

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1. Introduction

It is well known that organotin(IV) compounds exhibit high biological (for example fungicide and antitumor) activity [1,2]. Organotin(IV) complexes with ligands containing phenolic –OH or –COOH group(s), as well as, aromatic {N} donor atom represent an interesting class of such complexes, however, up to now only a few works have dealt with the molecular structures of them.

It has recently been demonstrated that the reaction of pyridine mono- and dicarboxylato anions with $[Bu_2Sn(IV)]^{2+}$ [3] and $[^tBu_2Sn(IV)]^{2+}$-cations [4] results in the formation of polynuclear complexes. In these di-*n*-butyltin(IV) and di-*t*-butyltin(IV) 2-picolinato and pyridine-2,6-dicarboxylato complexes the central tin(IV)-ion is hepta- and penta-coordinated in pentagonal-bipyramidal (Pbp) [3] and in square-pyramidal (Sp) [4] environment. Later, a systematically designed series of complexes containing $[Bu_2Sn(IV)]^{2+}$ and $[^tBu_2Sn(IV)]^{2+}$ ions and hydroxypyridine, hydroxypyrimidine and hydroxyquinoline ligands have also been prepared. The structural data obtained reveal the influence of the nature and steric position of donor atoms on the

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doi:10.1016/j.jorganchem.2005.12.019

coordination sphere of the tin center. Accordingly, the molecular structures of the complexes were established by FT-IR and Mössbauer-spectroscopy. Single-crystals of complexes of 8-hydroxyquinolinate with $[Bu_2Sn(IV)]^{2+}$ and $[^tBu_2Sn(IV)]^{2+}$ were prepared. The X-ray diffraction studies revealed that the central {Sn} atoms are in *cis*-O_h environment [5].

Therefore, as organic continuation of former works the goal of present paper to demonstrate the influence on the structure of the bulky $[Ph_3Sn(IV)]^+$ moiety within the complexes formed.

2. Experimental

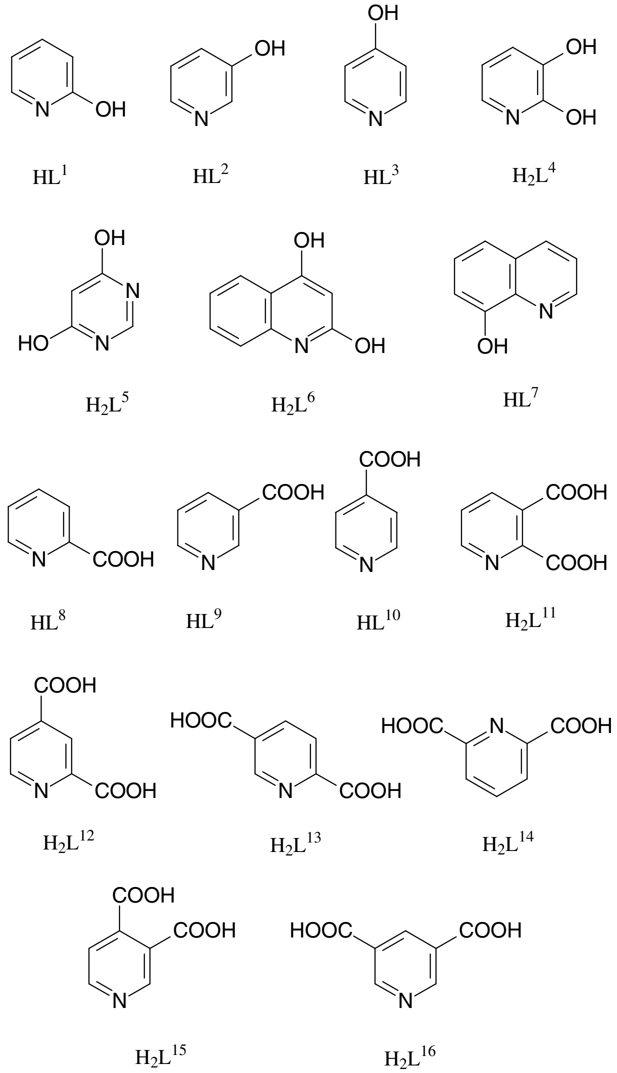
2.1. Starting materials

The triphenyltin-hydroxide (Ph_3SnOH) and ligands 2-hydroxypyridine {HL^1}, 3-hydroxypyridine {HL^2}, 4-hydroxypyridine {HL^3}, 2,3-dihydroxypyridine {H_2L^4}, 4,6-dihydroxypyrimidine {H_2L^5}, 2,4-quinolinediol {H_2L^6} and 8-hydroxyquinoline {HL^7} were purchased from Sigma–Aldrich. Ligands containing –COOH group(s) as 2-picolinic (HL^8), nicotinic (HL^9), *iso*-nicotinic (HL^{10}), pyridine-2,3-(H_2L^{11}) pyridine-2,4-(H_2L^{12}), pyridine-2,5-(H_2L^{13}), pyridine-2,6-(H_2L^{14}), pyridine-3,4-(H_2L^{15}) and pyridine-3,5-dicarboxylic (H_2L^{16}) acids were purchased from Fluka. All the starting reagents are of A.R. grade and were used as purchased. The structures of the ligands are shown in Scheme 1.

2.2. Syntheses

The complexes were prepared as described in [3], according to the reaction described in Scheme 2. First, the appropriate quantity of Ph_3SnOH (2 mmol) was dissolved and refluxed in dry methanol (50 cm^3) for 1 h. Then methanolic solution (50 cm^3) containing 2 mmol of the monobasic ($HL^{1-3,7-10}$) or 1 mmol of the dibasic ($H_2L^{4-6,11-16}$) ligand was added to the solution of the Ph_3SnOH and refluxed for another 2 h. In the case of dibasic ligands ($H_2L^{4-6,11-16}$) we have been used two different, 1:1 and 2:1 starting metal to ligand molar ratios for the preparation of the compounds. The analytical and spectroscopic studies reveal formation of complexes with 1:1 M:L for ligands $H_2L^{4-6,14}$ and 2:1 for the rest dibasic ligands.

Compounds **1**, **4**–**8**, and **13**–**16** were obtained via slow evaporation of the solvent at room temperature and were separated by filtration and washed with dry methanol. The other compounds precipitated immediately from the reaction mixture. The complexes were recrystallized from methanol. The obtained compounds were white solids, except **2**, **7**, **13** and **15**, which were yellow, **4** and **6**, which were light-brown. All of them were insoluble in water and benzene. Compounds **1**, **4**, and **7**–**10** were obtained as single crystals, while the others are amorphous solids. The synthesis and X-ray diffraction analysis of **8**–**10** were already reported [6–8]. The X-ray diffraction analysis of **9** and **10** showed that the Sn(IV) is penta-coordinated in distorted Tbp environment, in which the bulky phenyl groups are in equatorial positions. The complexes have a chain-like polymeric structure, where the monodentately co-ordinated $–COO^-$ group and the pyridine {N} atom act as bridges between the neighbouring {Sn} atoms.



Scheme 1. Structure of the ligands studied.

$$nPh_3SnOH + H_nL \rightarrow (Ph_3Sn)_nL + nH_2O$$

Scheme 2. Preparation of the complexes.

The analytical data are presented in Table 1 together with other characteristic physical constants. Microanalyses were performed at the Department of Organic Chemistry, University of Szeged. The Sn contents were measured by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP) and found to correspond to the theoretically calculated values.