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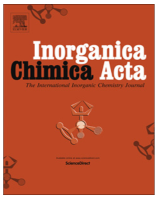

Structure of hypercoordinated monoorganodihalostannanes in solutions and in the solid state: the halogen effect

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ABSTRACT

A series of hypercoordinated monoorganotin dibromides formed by glycolic acid amides, $[RSnBr_2(OCH_2C(O)NR'_2)]_2$ (**2a**, R = Et, $NR'_2 = NMe_2$; **3a**, R = *n*-Bu, $NR'_2 = NMe_2$; **4b**, R = Ph, NR'_2 = morpholin-4-yl), were obtained and investigated by X-ray analysis, multinuclear NMR spectroscopy in solutions (^{1}H, ^{13}C, ^{119}Sn) and solid state (CP/MAS). It has been established that **2a**, **3a** and **4b** in solid state are dimeric. For the solutions in coordinating solvents the slow monomer–dimer equilibrium has been observed. The structures of related solvated monomeric chlorides, $RSnCl(DMSO)(OCH_2C(O)NR'_2)$, **5a·DMSO** and **6a·DMSO**, were also investigated by X-ray analysis.

1. Introduction

Organic compounds of tin attract nowadays significant attention. There are several main subjects in organotin chemistry: the investigation of compounds with multiple bonds of Sn with elements [1], hypercoordinated derivatives and synthesis of low valent Sn(II) compounds [2]. Organotin compounds have applications in fine organic synthesis (e.g. reagents for Stille cross-coupling [3]) and in industry (catalysts for ROP [4]). They are being studied as potential pharmaceuticals (particularly due to the toxicities of polyorganotin compounds) [5], as the precursors for new materials [6] and as PVC stabilizers [7]. Substantial understanding of the chemistry of organotins comes from the studies of the complexes with an extended coordination sphere [8]. Interest in these derivatives includes also investigation of new structural features and dynamic behavior [9] or possible application of hypercoordinated Sn compounds as precursors for new unusual chemical reactions [10]. Whereas tri- and diorganotin(IV) complexes remain the most investigated among the series of hypercoordinated tin, monoorganotin(IV) complexes are very rare and have been studied mostly with monodentate electrondonating ligands [11]. Notable exceptions include "estertin" (β-carboalkoxyethyltins) compounds [12], stannatranes [13], stannocanes [14] and related compounds [15].

The interaction of monoorganotin trichlorides ($RSnCl_3$) with O-TMS 2derivatives of α-hydroxyamides resulting in the substitution of one chlorine atom with hydroxyamide residue has been studied previously in our research group [16]. In continuation of these studies we report here the detailed investigation concerning hypercoordinated monoorganotin bromides. It should be noted that the bromine containing organotin compounds (with only one organic substituent) are very rare [17] and studies of these compounds in comparison with related chlorides are rather difficult. A number of corresponding hypercoordinated compounds, **2a**, **3a**, **4b** were obtained by interactions of monoorganotin tribromides ($RSnBr_3$) with O-TMS derivatives of amides of glycolic acid (**1a**–**b**). The structures of these compounds in solutions and in solid state have been studied. The structures of the related chloride adducts with DMSO, **5a*****DMSO**, **6a*****DMSO** and **7b*****DMSO** were also studied in solid state and in solutions.

2. Results and discussion

2.1. Synthesis

To synthesize the desired compounds well proven earlier reaction for obtaining analogous chlorides was employed. The

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advantage of this methodology is simplicity of procedure and ease of isolation of target compounds. As a result of interaction of monoorganotin tribromides ($RSnBr_3$; R = Et, *n*-Bu, Ph) with O-TMS derivatives of *N*,*N*-disubstituted amides of glycolic acid (**1a**–**b**) the products of substitution of one halogen atom with the glycolic amide residue were isolated in moderate yields (Scheme 1). Compounds **2a**, **3a** and **4b** are new. It should be noted that reaction of **1a** with $PhSnBr_3$ and **1b** with $EtSnBr_3$ or *n*-$BuSnBr_3$ resulted in complex mixtures of tin compounds from which it was impossible to isolate the pure substances. Attempts to obtain analogous compounds interacting monoorganotin tribromides ($RSnBr_3$; R = Et, *n*-Bu) with O-TMS derivatives of amides of lactic and mandelic acids were unsuccessful; in these cases complicated mixtures of unidentified compounds were formed, too.

Compounds **2a**, **3a** and **4b** were isolated as white powders soluble in polar organic solvents (MeCN, DMSO). These substances are sensitive to the air moisture and should be stored in the inert atmosphere.

The structures of compounds **2a**, **3a**, and **4b** have been studied in solid state using X-ray analysis and ^{119}Sn CP/MAS spectroscopy and in solutions by multinuclear NMR spectroscopy.

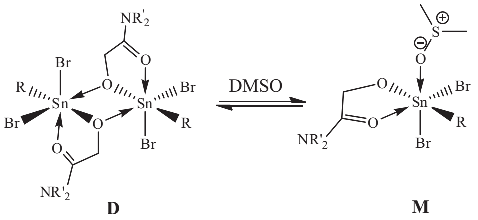
2.2. NMR spectroscopy

Whereas the structures of the compounds in solid state were established unambiguously with X-ray analysis, it was rather difficult to identify the nature of the species present in solutions.

In ^1H NMR spectra of the compounds **2a** and **3a** in the DMSO-d6 solutions recorded at 25 °C the signals are broad (Fig. S1, Supporting Information) and ^{13}C NMR spectra were not observed at this temperature. ^{119}Sn NMR spectra showed two signals at −417.5, −427.4 ppm and −425.7, −431.4 ppm for **2a** and **3a**, respectively. At 65 °C in ^1H NMR spectrum the peaks for **3a** are resolved (Fig. S1, Supporting Information), ^{13}C NMR spectrum was recorded and there is only one signal at −427.9 ppm for ^{119}Sn NMR spectrum, albeit broad (Fig. S2, Supporting Information).

We believe, that the data obtained indicate the dynamic processes in solution for these bromides. One can assume the equilibrium between dimer (**D**), which also exists in the solid state (see below) and monomeric adduct (**M**) with coordinated DMSO (Scheme 2). In both cases tin atom is hexacoordinated [18].

The chemical shifts in NMR spectra for **2a**, **3a** and **4b** in solution are typical for hexacoordinated tin atoms ($\delta = (-417)$–(-496) ppm) [18,19]. The tin – proton spin–spin coupling constants ($^3J_{119Sn-H}$ 87–93 Hz in $Sn-OCH_2$ fragment and $^3J_{119Sn-H}$ 130–132 Hz in Sn–Alk(Ar) fragment) are typical for hypercoordinated tin halide compounds [10,11,16]. The tin – carbon coupling constants are observed only in the case of **4b** (see Section 3). A small increase in values in compounds under investigation has been observed in comparison with the fourcoordinated tin compounds.



Scheme 2. Dimer (**D**) – monomer (**M**) equilibrium of tin complexes in DMSO solutions.

Unfortunately, we failed to obtain for the compounds **2a**, **3a** and **4b** from DMSO solutions crystals, suitable for X-ray analysis. Nevertheless, the described earlier DMSO adducts of the related chlorides **5a** and **6a** (Scheme 3) were studied by X-ray analysis (see below). It is noteworthy that the monomer–dimer equilibrium in solution is shifted toward monomer (**M**) in case of chlorides **5a**, **6a**, **7b** [10]; this has been confirmed by ^1H, ^{13}C and ^{119}Sn NMR spectra (Scheme 4).

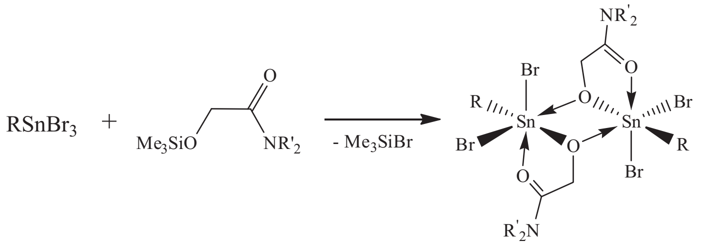
In ^{119}Sn CP/MAS NMR [19] spectrum of **4b** there is only one isotropic signal at $\delta = -503$ ppm, whereas in DMSO solution there are two peaks at $\delta = -489.7$ (broad) and −494.7 ppm. Chlorides **5a** and **6a** (Scheme 3) in the solid state gave ^{119}Sn chemical shifts at $\delta = -316$ and −311 ppm, respectively. For the phenyltin compound **7b** the signal in ^{119}Sn CP/MAS NMR spectrum was observed at $\delta = -426$ ppm.

Of particular interest is comparison of ^{119}Sn NMR data for bromides (**2–3a**, **4b**) and chlorides (**5–6a**, **7b**) in solutions and solid state (Table 1).

From Table 1 it is evident that for alkyltin derivatives **2a**, **3a**, **4b**, **5a** and **6a** the signals in ^{119}Sn NMR spectra are shifted to high field in bromine derivatives in comparison with the corresponding chlorides. On dissolving in coordinating solvents the ligand exchange is observed for chlorides resulting in coordination of tin with the more polarized DMSO.

We performed additional experiments for compound **3a**. Firstly, the solvent was changed from DMSO-d6 to CD_3CN. The target signal has transformed into very broad signal. Secondly, the spectra were registered in mixtures (2:1, 1:1) of polar and strongly coordinating DMSO-d6 and nonpolar and noncoordinating C_6D_6. It was established that addition of C_6D_6 results in decreasing (and full disappearance) of one of the signals (Figs. S3, S4, Supporting Information), which may be attributed to the monomer. So, the data obtained indicate the dependence of the behavior of the tin compounds in solutions on the solvent's nature and confirm the dissociation–association equilibrium between hypercoordinated tin bromides in solutions.

Thus, in the case of chlorides the dimeric structures obtained for the crystals are also retained in the amorphous phase. In solutions



1a R' = Me
1b R'$_2$ = -$(CH_2)_2O(CH_2)_2$-

2a R = Et; R' = Me (20%)
3a R = Bu; R' = Me (19%)
4b R = Ph; R'$_2$ = -$(CH_2)_2O(CH_2)_2$- (37%)

Scheme 1. Synthesis of bromide tin complexes **2a**, **3a** and **4b**.