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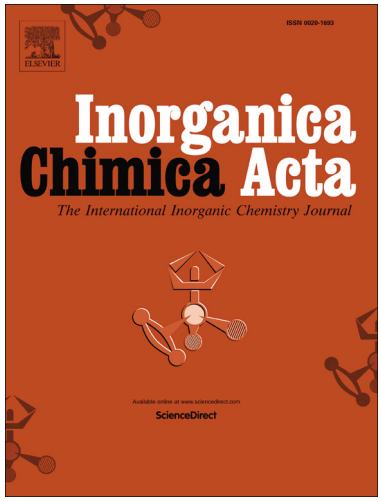

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Structure of Hypercoordinated Monoorganodihalostannanes in Solutions and in the Solid State: the Halogen Effect

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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].

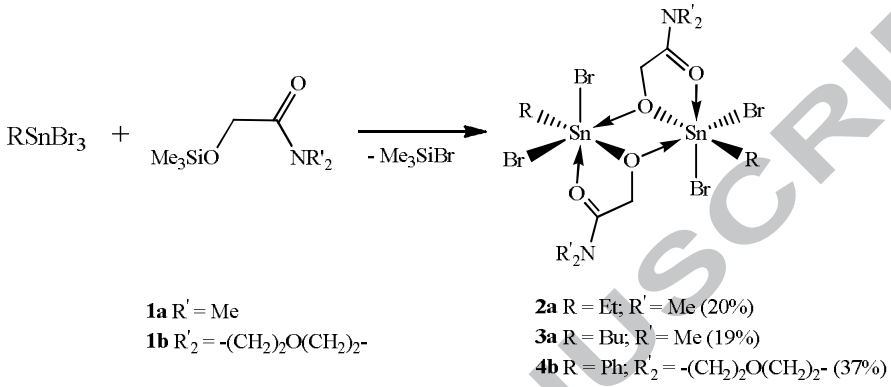
The interaction of monoorganotin trichlorides ($RSnCl_3$) with O-TMS derivatives of α-hydroxyamides resulting in the substitution of one chlorine atom with hydroxyamide residue has been studied previously in our research group [16]. In continuation of these studies we report here the detailed investigation 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 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.



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**.

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.

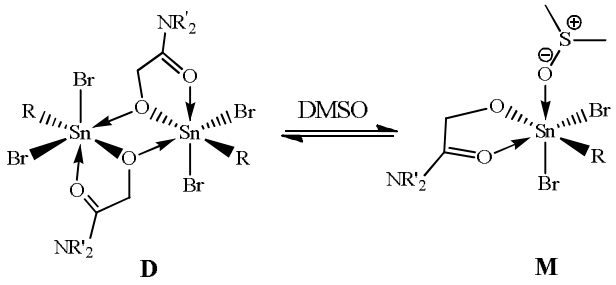
2.2. NMR spectroscopy

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 ^{1}H NMR spectra of the compounds **2a** and **3a** in the DMSO-d6 solutions recorded at 25°C the signals are broad (Figure 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 ^{1}H NMR spectrum the peaks for **3a** are resolved (Figure 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 (Figure 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

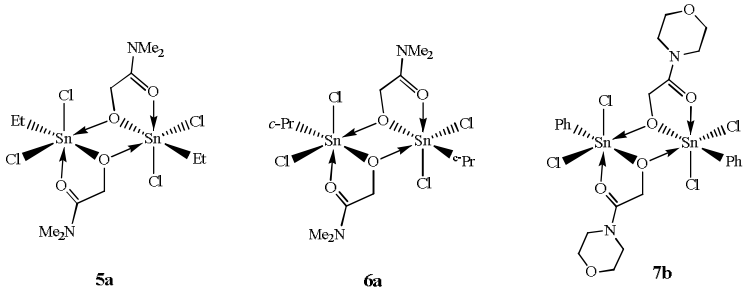
state (see below) and monomeric adduct (**M**) with coordinated DMSO (Scheme 2). In both cases tin atom is hexacoordinated [18].



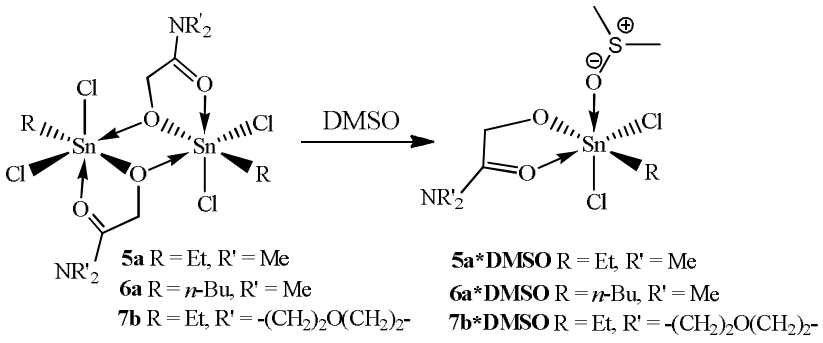
Scheme 2. Dimer (**D**) – monomer (**M**) equilibrium of tin complexes in DMSO solutions.

The chemical shifts in NMR spectra for **2a**, **3a** and **4b** in solution are typical for hexacoordinated tin atoms (δ = (-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 Experimental part). A small increase in values in compounds under investigation has been observed in comparison with the fourcoordinated tin compounds.

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 ^{1}H, ^{13}C and ^{119}Sn NMR spectra (Scheme 4).



Scheme 3. The structures of chlorides **5a**, **6a** and **7b**.



Scheme 4. Solvolysis of tin chlorides **5a**, **6a** and **7b** in DMSO solutions.

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

Table 1

^{119}Sn NMR data for **2a**, **3a**, **4b**, **5a**, **6a** and **7b** in DMSO-d6 solutions and solid state.

Compound	DMSO-d6 solutions		Solid state	
	δ ^{119}Sn ppm[a]	Monomer(**M**)/ Dimer(**D**)[b]	δ ^{119}Sn ppm[a]	Monomer(**M**)/ Dimer(**D**)[b]
2a	-427; -417	equilibrium (**M**)/(**D**)	—	—
3a	-426; -431	equilibrium (**M**)/(**D**)	—	—
4b	-489(br.); -495	equilibrium (**M**)/(**D**)	-503	(**D**)
5a	-376	(**M**)	-316	(**D**)
6a	-377	(**M**)	-311	(**D**)
7b	-437	(**M**)	-426	(**D**)

[a]The spectra were registered at 298^{0}K. [b]**M** – monomer with coordinated DMSO; **D** – dimer (see Scheme 2)

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 in coordinating solvents (such as DMSO), these dimers are solvated by the solvent, resulting in a monomer structure. Structures of several solvates were investigated by XRD (see below). The corresponding bromides in the crystal and in the amorphous phase are dimeric, too. However, unlike chlorides, for the bromides in coordinating solvents a monomer-dimer equilibrium is observed.

2.3 X-ray analysis

The molecular structures of five compounds obtained in the course of this work were investigated by X-ray analysis (Figures 1-5, Tables 2-4).

Structures **2a**, **3a** and **4b** are the first compounds containing $O_3Sn(C)Br_2$ fragment which were investigated by X-ray analysis. The compounds **2a** and **3a** are isostructural and similar to **5a** [16]; there are two independent molecules in crystal of **2a**.

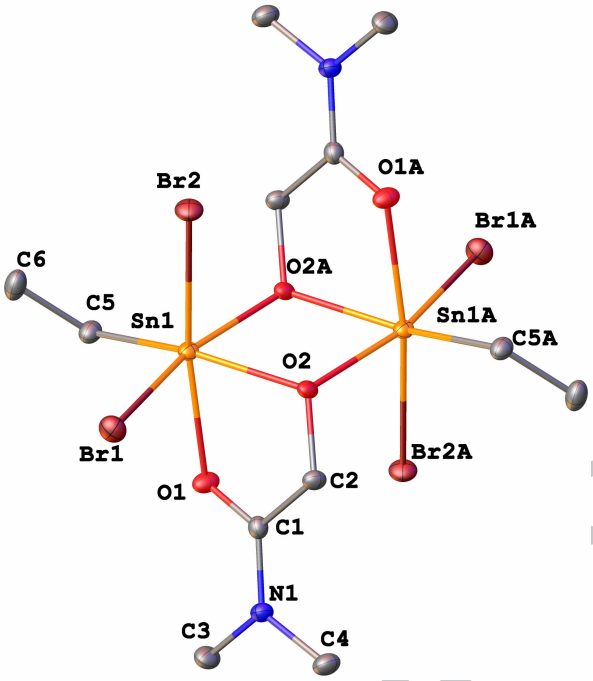


Fig. 1. The molecular structure of **2a**; only one independent molecule is presented; hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at 50 % probability level.

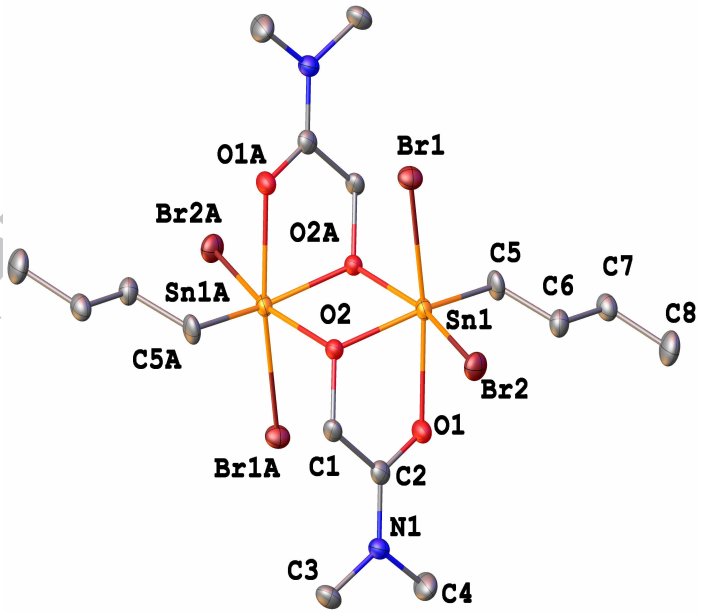


Fig. 2. The molecular structure of **3a**; hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at 50 % probability level.

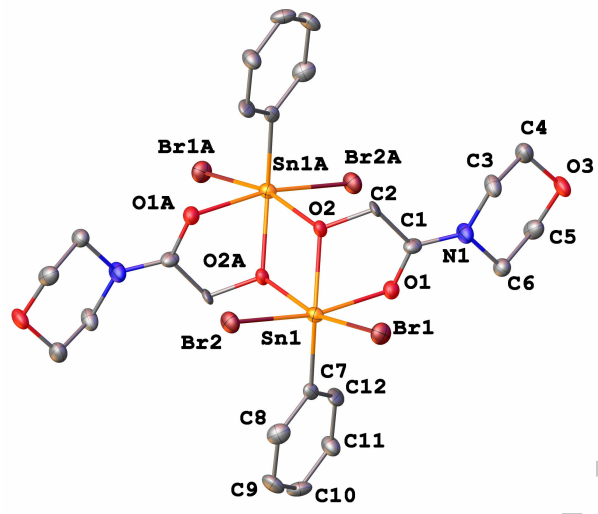


Fig. 3. The molecular structure of **4b**; hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at 50 % probability level.

Table 2

Principal bond lengths (Å) and angles (°) for compounds **2a**, **3a** and **4b**.

2a[a]		**3a**	**4b**
Sn1-Br1	Sn2-Br3	Sn1-Br1	Sn1-Br1
2.5869(4)	2.5656(4)	2.5709(7)	2.5594(9)
Sn1-Br2	Sn2-Br4	Sn1-Br2	Sn1-Br2
2.5805(4)	2.5931(4)	2.5762(7)	2.5610(9)
Sn1-O1	Sn2-O3	Sn1-O1	Sn1-O1
2.190(2)	2.207(2)	2.200(2)	2.204(5)
Sn1-O2	Sn2-O4	Sn1-O2	Sn1-O2
2.087(2)	2.089(2)	2.069(2)	2.073(5)
Sn1-O2A	Sn2-O4A	Sn1-O2A	Sn1-O2A
2.276(2)	2.269(2)	2.305(2)	2.285(5)
Sn1-C5	Sn2-C11	Sn1-C5	Sn1-C7
2.147(3)	2.138(3)	2.123(3)	2.140(7)
O2-Sn1-C5	O4-Sn2-C11	O2-Sn1-C5	O2-Sn1-C7
154.51(11)	155.65(11)	151.27(12)	154.2(2)

O2-Sn1-Br1 165.42(5)	O3-Sn2-Br3 167.18(6)	O1-Sn1-Br1 167.01(7)	O2A-Sn1-Br(1) 166.63(12)
O1-Sn1-Br2 166.42(6)	O4-Sn2-Br4 163.81(6)	O2A-Sn1-Br2 164.98(6)	O1-Sn1-Br2 166.60(13)
Sn1-O2-Sn1 108.42(9)	Sn2-O4-Sn2 108.85(9)	Sn1-O2-Sn1A 108.82(10)	Sn1-O2-Sn1A 107.53(19)
O2-Sn1-O2 71.58(9)	O4-Sn2-O4 71.15(9)	O2-Sn1-O2A 71.18(10)	O2-Sn1-O2A 72.47(12)

[a] Two independent molecules

The bromides **2a**, **3a**, **4b** in the solid state are centrosymmetric dimers due to the coordination bond between tin and the oxygen atom of glyoxylic fragment from another molecule. So, in these cases a ladder type fragments are formed consisting of three cycles with almost planar Sn_2O_2. Tin atom is hexacoordinated and bromine atoms (in *cis*-positions) situated *trans* to oxygens which form coordination bonds with tin atoms.

The structural parameters of the three molecules under investigation are very similar. Furthermore, there are very small bond elongations in Br derivatives in comparison with corresponding Cl compounds [16] (compare, for example, average values for **2a/5a**: Sn-O1 2.199(2)/2.193(1), Sn-O2 2.088(2)/2.086(1), Sn-O2A 2.273(2)/2.265(1), Sn-C 2.143(3)/2.135(1) Å). This gives the possibility to propose that in crystals the hypercoordinated tin atoms exhibit similar Lewis acidity both in cases of chlorides and bromides.

The molecular structures of monomeric chlorides **5a*DMSO** and **6a*DMSO** are isostructural. DMSO is coordinated via O to tin which is typical for Sn compounds [20]. In both compounds tin atom has a distorted octahedral environment in which oxygen atoms occupy *cis*-positions (*fac*-configuration). The chlorine atoms are situated in *trans*-positions to oxygen atoms which are coordinated to Sn. It should be noted that the tin compounds containing cyclopropyl group have been almost unknown to date, in fact there were only two structures of tetracoordinated Sn derivatives [21].

In general, the bond lengths in **6a*DMSO** are somewhat shorter than in **5a*DMSO** likely due to presence of the cyclopropyl group. The main feature of **5a*DMSO** are almost equal Sn-O bond lengths with coordinative O atoms from DMSO and glycolic fragment (2.2101(10) *vs.*

2.2127(10) Å). Furthermore, the similar bond lengths in **5a*DMSO** are somewhat longer than the related ones in dimer **5a** [16] (compare, for example, Sn-C 2.1364(14)/2.1351(14), Sn-Cl1 2.4550(3)/2.4190(4), Sn-O2 2.2127(10)/2.1928(10) Å) this may be explained by the fact that DMSO molecule is a better donor for Sn than oxygen atom from another complex molecule in the chlorine derivatives.

Moreover, it should be noted that the significant *trans*-effect in **5a*DMSO** and **6a*DMSO** is observed. The elongation of Sn-Cl2 bond lengths (*trans*- to DMSO) in comparison with Sn-Cl1 indicates more significant donor properties of DMSO in comparison with the coordinative $C(O)NMe_2$ group.

The Sn-O bond lengths in **5a*DMSO** and **6a*DMSO** are elongated in comparison with free DMSO (1.5456(10) and 1.5478(11) *vs.* 1.531(5) Å [22]), reflecting a significant polarized structure in coordinating DMSO molecule for these chlorides.

Due to absence of OH and NH groups the crystal packing of structures studied are constructed via weak C-H…O and C-H…Br bonds. All intermolecular distances correspond to ordinary van-der-Waals interactions.

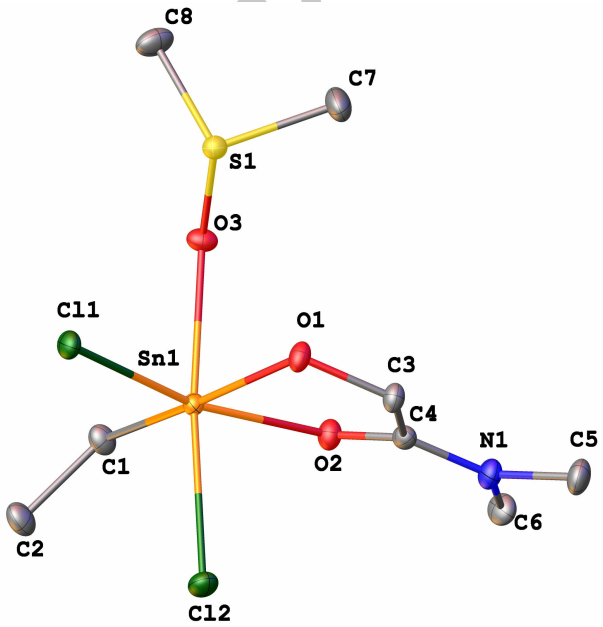


Fig.4. The molecular structure of **5a•DMSO**; hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at 50 % probability level.

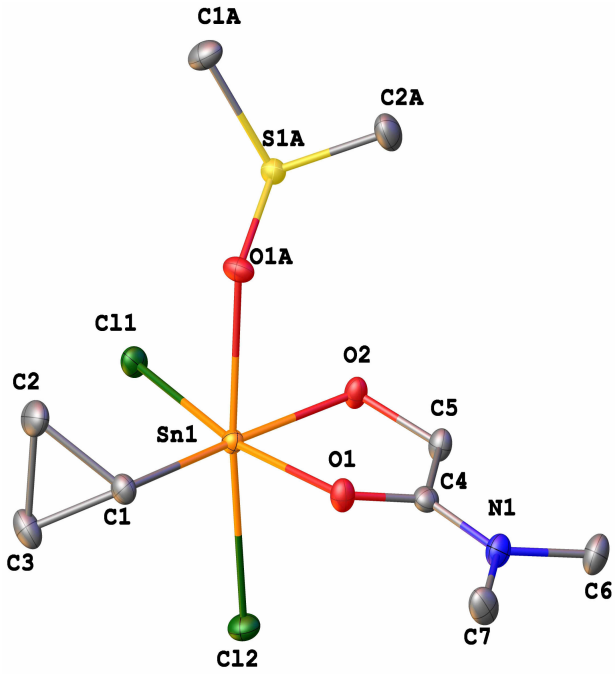


Fig.5. The molecular structure of **6a•DMSO**; hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at 50 % probability level.

Table 3

Principal bond lengths (Å) and angles (°) for compounds **5a*DMSO** and **6a*DMSO**.

5a*DMSO	**6a*DMSO**
Sn1-Cl1 2.4550(3)	Sn1-Cl1 2.4467(4)
Sn1-Cl2 2.4730(4)	Sn1-Cl2 2.4719(4)
Sn1-O1 2.0064(10)	Sn1-O2 2.0081(11)
Sn1-O2 2.2127(10)	Sn1-O1 2.1974(11)
Sn1-O3 2.2101(10)	Sn1-O1A 2.2073(11)
Sn1-C1 2.1364(14)	Sn1-C1 2.1062(15)
S1-O3 1.5456(10)	S1A-O1A 1.5478(11)
O1-Sn1-C1 166.92(5)	O2-Sn1-C1 166.00(5)
O2-Sn1-Cl1 166.30(3)	O1-Sn1-Cl1 169.48(3)
O3-Sn1-Cl2 173.33(3)	O1A-Sn1-Cl2 172.72(3)

3. Experimental

3.1. General

All solvents were purified using standard procedures (hexane and C_6D_6 were refluxed over Na; diethyl ether was stored over KOH, refluxed over Na/benzophenone; MeCN was refluxed over CaH_2; DMSO-d6 was refluxed over CaH_2 and after distillation in vacuum is stored over molecular sieves) and redistilled prior to use. Syntheses of the compounds **2a**, **3a** and **4b** were carried out in the argon atmosphere using standard Schlenk technique.

The IR spectra were recorded by using a 200 Thermo Nicolet apparatus. ^{1}H, ^{13}C and ^{119}Sn NMR spectra for solutions were recorded by using a Bruker Avance 400 NMR spectrometer (400.1, 100.6 and 106.2 MHz, respectively). The chemical shifts were measured using tetramethylsilane (^{1}H, ^{13}C) or tetramethyltin (^{119}Sn) as the internal references. The ^{119}Sn CP/MAS NMR spectra were recorded on a JEOL EX 400 NMR (149.1 MHz) using a DOTY solid state probe and 5mm rotors, at room temperature (25°C); contact time 5 ms; relaxation delay 5 s; number of scans 12800. The chemical shifts were externally referenced to tetramethyltin.

O-TMS derivatives of *N*,*N*-dimethylamide (**1a**) [16] and morpholinyl (**1b**) [23] of glycolic acid, $EtSnBr_3$ [24] and *n*-$BuSnBr_3$ [25], complexes **5a**, **6a** and **7b** [10] were synthesized according to the described procedures.

3.2. Synthesis

3.2.1. Phenytin tribromide ($PhSnBr_3$)

The mixture of Ph_4Sn (1.68 g, 3.90 mmol) and $SnBr_4$ (5.12 g, 12.00 mmol) were stirred under argon at 190°C for 16 hours. Fractionation in vacuum gave 5.16 g (75 %) of $PhSnBr_3$ as a colourless liquid, b.p. 101°C at 0.5 mm Hg, lit. [26] b.p. 182-183°C at 29 mm Hg. ^{1}H NMR (400.1 MHz, C_6D_6, 25°C): δ = 7.08-7.05 (m, 2H, aromatic hydrogens), 6.93-6.96 (m, 3H, aromatic hydrogens) ppm. ^{13}C NMR (100.6 MHz, C_6D_6, 25°C): δ = 137.86, 133.30, 132.40 and 129.88 (aromatic carbons) ppm. ^{119}Sn NMR (106.2 MHz, C_6D_6, 25°C): δ = -225.3 ppm.

*3.2.2. Synthesis of compound **2a***

To a stirred solution of $EtSnBr_3$ (0.97 g, 2.50 mmol) in hexane (7 mL) the solution of compound **1a** (0.44 g, 2.50 mmol) in hexane (7 mL) was added drop wise at ambient temperature, the mixture was stirred for 30 min at the same temperature and refluxed for 1 hour. After cooling the precipitate formed was filtered off, washed with hexane and dried in vacuum. Yield was 0.91 g of product containing some impurities according to ^{1}H NMR. Recrystallization from acetonitrile gave 0.21 g (20%) of pure product as a white crystalline solid, m. p. 203-204°C. IR (KBr): ν = 1640, 1468, 1383, 1060 cm^{-1}. ^{1}H NMR (400.1 MHz, DMSO-d6, 25°C): δ = 4.56-4.40 (br s, 2H, OCH_2), 3.06 (s, 3H, NCH_3), 3.02 (s, 3H, NCH_3), 1.68-1.55 (m, 2H, $SnCH_2$), 1.18 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, CH_3) ppm. ^{119}Sn NMR (106.2 MHz, DMSO-d6, 25°C): δ = -427.4 and -417.5 ppm. Found: C 17.49, H 3.10, N 3.45. $C_6H_{13}NO_2SnBr_2$. Calcd. C 17.56, H 3.17, N 3.41.

*3.2.3. Synthesis of compound **3a***

The mixture of *n*-$BuSnBr_3$ (1.00 g, 2.40 mmol) and **1a** (0.42 g, 2.40 mmol) in acetonitrile (15 mL) was refluxed for 8 hours. After cooling to room temperature diethyl ether (20 mL) was added and the resulting mixture was kept at 4ºC overnight. The precipitate was filtered off, washed with diethyl ether and dried in vacuum to yield 0.20 g (19%) of **3a** as white crystals, m. p. 170-171 °C. IR (KBr): ν = 1637, 1491, 1410, 1051 cm^{-1}. ^{1}H NMR (400.1 MHz, DMSO-d6, 25°C): δ = 4.53 (br s) and 4.44 (br s) (2H, OCH_2), 3.06 (s, 3H, NCH_3), 3.02 (s, 3H, NCH_3), 1.76-1.29 (m, 6H, $SnCH_2CH_2CH_2$), 0.86 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_3) ppm. ^{1}H NMR (400.1 MHz, DMSO-d6, 65°C): δ = 4.47 (s, $^3J_{119Sn,\ H}$ = 87.2 Hz, 2H, OCH_2), 3.07 (s, 3H, NCH_3), 3.03 (s, 3H, NCH_3), 1.72-1.62 (m, $^2J_{119Sn,\ H}$ = 131.6 Hz, 4H, $SnCH_2CH_2$), 1.41-1.32 (m, 2H, CH_2), 0.86 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_3) ppm. ^{1}H NMR (400.1 MHz, CD_3CN, 25°C): δ = 4.57 (br s, 2H, OCH_2), 3.05 (s, 3H, NCH_3), 3.00 (s, 3H, NCH_3), 2.03-2.19 (m, 2H, OCH_2), 1.70-1.79 (m, 2H, CH_2), 1.41-1.51 (m, 2H, CH_2), 0.94 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_3) ppm. ^{13}C NMR (100.6 MHz, CD_3CN, 25°C): δ = 178.10 (C=O), 62.16 (OCH_2), 38.00 (NCH_3), 36.74, 29.19, 26.15, 14.35 (Bu) ppm. ^{13}C NMR (100.6 MHz, DMSO-d6, 65°C): δ = 177.67 (C=O), 59.98 (OCH_2), 36.32 (NCH_3), 34.77, 27.02, 24.09, 13.02 (Bu) ppm. ^{119}Sn NMR (106.2 MHz, CD_3CN, 25°C): δ = -344.3 (br s) ppm. ^{119}Sn NMR (106.2 MHz, DMSO-d6, 25°C): δ = -425.7 and - 431.4 ppm. ^{119}Sn NMR (106.2 MHz, DMSO-d6/C_6D_6 (2:1), 25°C): δ = -424.2 and - 430.5 ppm. ^{119}Sn NMR (106.2 MHz, DMSO-d6/ C_6D_6 (1:1), 25°C): δ = -423.0 ppm. ^{119}Sn NMR (106.2 MHz, DMSO-d6, 65°C): δ = -427.9 ppm. Found C 21.88, H 3.74, N 3.28. $C_8H_{17}NO_2SnBr_2$. Calcd. C 21.92, H 3.88, N 3.20.

*3.2.4. Synthesis of compound **4b***

The mixture of $PhSnBr_3$ (3.15 g, 7.20 mmol) and **1b** (1.57 g, 7.20 mmol) in acetonitrile (15 mL) was stirred at ambient temperature for 15 hours. The precipitate was filtered off, washed with diethyl ether and dried in vacuum. Yield 1.34 g (37 %), white crystalline powder, m.p.

>250°C. IR (KBr): ν = 1616, 1479, 1436, 1273, 1114, 1064, 1031 cm^{-1}. ^1H NMR (400.1 MHz, DMSO-d6, 25°C): δ = 7.73-7.67 (m, $^3J_{119Sn,\ H}$ = 131.8 Hz, 2H, Ph), 7.44-7.27 (m, 3H, Ph), 4.71 (s, $^3J_{119Sn,\ H}$ = 92.3 Hz) and 4.56 (s, $^3J_{119Sn,\ H}$ = 92.3 Hz) (2H, OCH_2), 3.73-3.50 (m, 8H, NCH_2CH_2O) ppm. ^{13}C NMR (100.6 MHz, DMSO-d6, 25°C): δ = 176.77 and 176.56 (C=O), 152.42 (*ipso*-C_6H_5); 133.99 and 133.28 ($^2J_{119Sn,\ 13C}$ = 76.3 Hz, *o*-C_6H_5), 128.69 and 128.49 ($^3J_{119Sn,\ 13C}$ = 212.0 Hz, *m*-C_6H_5), 127.74 ($^4J_{119Sn,\ 13C}$ = 134.2 Hz, *p*-C_6H_5), 65.82 (NCH_2CH_2O), 60.49 (br) and 60.14 ($SnOCH_2$), 44.61, 44.27 and 44.04 (NCH_2CH_2O) ppm. ^{119}Sn NMR (106.2 MHz, DMSO-d6, 25°C): δ = -489.7 (br) and -494.7 ppm. ^{119}Sn CP/MAS NMR: δ = -503 ppm. Found C 28.33, H 3.15, N 2.78. $C_{12}H_{15}NO_3SnBr_2$. Calcd. C 28.84, H 3.03, N 2.80.

3.3. Single crystal X-ray studies

All measurements were carried out with Bruker APEX II and APEX DUO diffractometers. The structures were solved by direct methods and refined in anisotropic approximation against F^2. Hydrogen atoms were calculated from geometrical point of view and refined with restraints applied on the C-H bond length and thermal parameters. The calculations were carried out with SHELX software [27]. Molecular graphics were drawn using OLEX2 program [28]. Atomic coordinates and thermal parameters and the information about experimental conditions were submitted to Cambridge Crystallographic Data Centre (CCDC numbers are 1029878-1029882) and can be obtained free of charge via Web Service http://www.ccdc.cam.ac.uk/Community/Requestastructure/pages/Requestastructure.aspx.

Table 4
Crystallographic data for compounds **2a**, **3a**, **4b**, **5a•DMSO** and **6a•DMSO**.

	2a	**3a**	**4b**	**5a•DMSO**	**6a•DMSO**
empirical formula	$C_{12}H_{26}Br_4N_2O_4Sn_2$	$C_8H_{17}Br_2NO_2Sn$	$C_{24}H_{30}Br_4N_2O_6Sn_2$	$C_8H_{19}C_{12}NO_3SSn$	$C_9H_{19}C_{12}NO_3SSn$
M_w	819.37	451.76	999.52	398.89	410.40
temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
size (mm)	0.16 x 0.12 x 0.10	0.25 x 0.16 x 0.12	0.15 x 0.12 x 0.10	0.36 x 0.35 x 0.29	0.21 x 0.17 x 0.13
space group	$P2_1/c$	$P2_1/c$	*P*bca	$P2_1/c$	$P2_1/c$
a (Å)	14.1935(8)	7.7675(18)	9.9829(13)	11.1337(4)	11.0622(8)
b (Å)	14.5891(8)	14.882(4)	15.273(2)	9.4847(4)	9.5005(7)
c (Å)	11.3952(6)	11.791(3)	19.742(3)	14.9293(6)	15.3362(11)
β (deg)	104.0050(10)	102.577(4)	90	111.3220(10)	111.0160(10)
V ($Å^3$)	2289.5(2)	1330.3(5)	3010.1(7)	1468.62(10)	1504.56(19)
Z	4	4	4	4	4
ρ_{cald} ($g*cm^{-3}$)	2.377	2.256	2.206	1.804	1.812
abs coeff. (mm^{-1})	9.180	7.911	7.010	2.239	2.188
F(000)	1536	864	1904	792	814
θ range (deg)	2.31 – 30.53	2.24 – 27.59	2.44 – 28.60	2.60 – 31.24	2.573 – 34.554
no. of collected/unique	21526 / 5469	18164 / 3244	37134 / 2779	19192 / 4415	25004 / 4024

rflns.					
R_{int}	0.0428	0.0722	0.1606	0.0212	0.0320
data/restraints/params.	7024 / 0 / 223	4473/ 0 / 130	4601 / 0 / 172	4692 / 0 / 150	4412 / 0/ 158
goodness of fit on F^2	0.996	0.955	1.059	1.028	1.043
R_1 ($I > 2\sigma(I)$)	0.0304	0.0343	0.0573	0.0173	0.0178
wR_2 (all data)	0.0569	0.0702	0.1271	0.0391	0.0405
largest diff. peak/hole (e/Å^3)	1.072 / -0.957	0.890 / -1.343	2.127 / -1.505	0.522 / -0.589	0.538 / -0.379

4. Conclusions

In conclusion, the bromides **2a**, **3a**, **4b** were synthesized via 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**). It was established in the solid state that **2a**, **3a**, **4b** (X-ray analysis) are dimeric and found to be similar to the analogous chlorides. In solution the behavior of these bromides differs significantly from the related chlorides. The dynamic equilibrium between dimer and monomer adducts with DMSO molecules is observed. In the case of related chlorides **5a**, **6a**, **7b** the equilibrium is shifted towards monomers, for **5a** and **6a** the crystalline monomer adducts with DMSO were isolated and studied by X-ray analysis.

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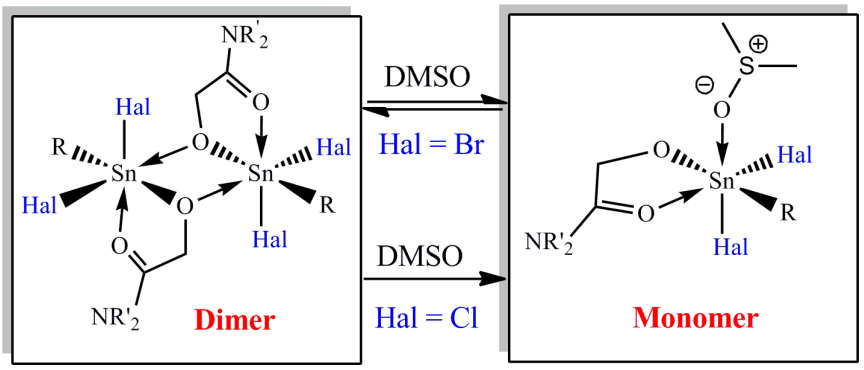
The hypercoordinated monoorganodibromides were synthesized by interaction of tribromides $RSnBr_3$ with O-TMS derivatives of *N*,*N*-disubstituted amides. In solution behavior of bromides differs from the analogous chlorides, including equilibrium dimer/monomer adducts with DMSO. In the case of chlorides the equilibrium is shifted towards monomers. In solid state tin compounds are dimeric.



- A series of hypercoordinated monoorganotin dibromides was obtained
- The bromides studied are dimeric in solid state
- In solution for bromides the equilibrium dimer/solavated monomer is observed
- In solution for chlorides the equilibrium is shifted to monomer adduct with solvent