

Double O,C,O-chelated diorganotin(IV) derivatives

Blanka Kašná^a, Roman Jambor^{a,*}, Libor Dostál^a, Ivana Císařová^b, Jaroslav Holeček^a

^a Department of General and Inorganic Chemistry, University of Pardubice, nám. Čs. legií 565, CZ-532 10, Pardubice, Czech Republic

^b Charles University in Prague, Faculty of Natural Science, Hlavova 2030, 128 40 Praha 2, Czech Republic

Received 9 December 2005; accepted 9 December 2005

Available online 19 January 2006

Abstract

Novel diorganotin(IV) compounds $(L^{1,2})_2SnCl_2$, where $L^{1,2}$ are O,C,O-chelating ligands (called the pincer ligands), 2,6-bis(alkoxy-methyl)phenyl-, 2,6-(ROCH₂)₂C₆H₃⁻, (L^1 , R = Me, L^2 , R = *t*-Bu), have been synthesized and characterized by ¹H, ¹³C and ¹¹⁹Sn NMR spectroscopy, MS-ESI spectrometry and elemental analysis. The structure of both compounds $(L^1)_2SnCl_2$ (**1**) and $(L^2)_2SnCl_2$ (**2**) was determined by X-ray crystallography. Determination of crystal structures reveals different shapes of coordination polyhedra. While deformed octahedron was found for **1**, tetrahedral geometry of the tin atom was determined for **2**. The NMR spectroscopy indicates a similar structural arrangement of **1** and **2** in solution. The reaction of **1** with silver salts of low nucleophilic anions X⁻ (X = OTf and 1-CB₁₁H₁₂) resulted in $(L^1)_2SnCl(OTf)$ (**3**), $(L^1)_2Sn(OTf)_2$ (**4**), and $(L^1)_2SnCl(CB_{11}H_{12})$ (**5**). The compounds **4** and **5** are of ionic nature both in solid state and in solution of CH₃CN.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Tin; NMR; Chelating ligand; X-ray structure

1. Introduction

The phenomenon of hypervalent or hypercoordinated organotin compounds is well known and such organotin compounds are interesting because of their unexpected structural aspects, biological activity and reactivity [1–4]. Introduction of Y,C,Y-chelating ligands (Y = donor atom) to organotin fragment is a possible way to achieve this hypercoordination. The first mention about organotin compounds with Y,C,Y-chelating ligand was published by van Koten in 1978 [5], where nitrogen donor atom was used for this purpose (Chart 1A) and these are studied so far.

On the other hand, only few examples of oxygen donor atom-containing ligands of Y,C,Y-type are known. In 1998, Jurkschat et al. reported synthesis of organotin compounds containing an O,C,O-pincer ligand (Chart 1B), in which the possibility of hypercoordination of the tin atom

through Sn–O interaction has been demonstrated [6]. This information led us to synthesise different O,C,O-chelating ligands (Chart 1C) and their tetra-, tri-, di- and monoorganotin derivatives [7]. It has been published that the presence of Y,C,Y-ligands together with an appropriate polar group in triorganotin compounds led to preparation of hypercoordinated organotin cations having two strong Sn–Y interactions [5,8]. Chemistry of organotin(IV) cations [9] is of current interest playing an important role in cytotoxic activity of organotin compounds [10] or in catalytic applications involving organic reactions such as esterification [11]. While triorganotin cations, $[R_3SnY_2]^+$ (Y = donor atom), possessing pentacoordinated tin atoms have been known since the 1960s (triorganotin cations containing Y,C,Y-ligand also represent this type of compounds) [12], diorganotin(IV) dications of $(R_2SnY_4)^{2+}$ type have been isolated in limited number only [13]. This fact prompts us to prepare diorganotin compounds with two O,C,O-chelating ligands having thus four oxygen donor atoms for stabilization of such diorganotin(IV) dications $(R_2SnY_4)^{2+}$.

* Corresponding author. Fax: +420 466037068.

E-mail address: roman.jambor@upce.cz (R. Jambor).

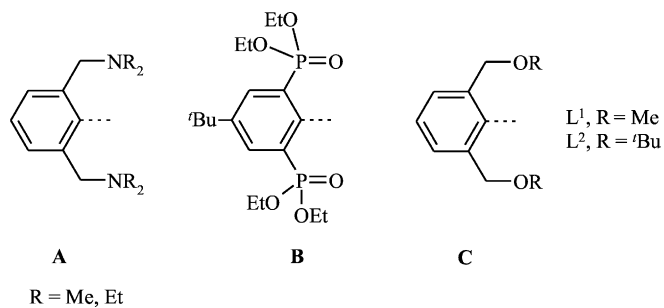


Chart 1.

This paper describes synthesis of diorganotin compounds $(L^{1-2})_2SnCl_2$ (**1** and **2**) with two O,C,O-chelating ligands 2,6- $[(CH_2OR)_2C_6H_3]^-$ (R = Me (**L**¹) and *t*-Bu (**L**²)) as well as reactivity of **1** towards silver salts of low nucleophilic anions X^- (X = OTf, $CB_{11}H_{12}$) leading to $(L^1)_2SnCl(OTf)$ (**3**), $(L^1)_2Sn(OTf)_2$ (**4**) and $(L^1)_2SnCl(CB_{11}H_{12})$ (**5**).

2. Experimental

2.1. General methods

Solvents were dried by standard methods and distilled prior to use. All moisture and air sensitive reactions were carried out in an argon atmosphere using standard Schlenk techniques. The reactions with silver salts were protected from light. The ¹H, ¹³C, and ¹¹⁹Sn NMR spectra were acquired on Bruker Avance500 spectrometer in CDCl₃ (range 300–210 K). Appropriate chemical shifts were calibrated on: ¹H-residual peak of CHCl₃ ($\delta = 7.25$ ppm), ¹³C-residual peak of CHCl₃ ($\delta = 77.23$ ppm), ¹¹⁹Sn-external tetramethylstannane ($\delta = 0.00$ ppm). Electrospray mass spectra (ESI-MS) were recorded in positive mode on an Esquire3000 ion trap analyzer (Bruker Daltonics) in the range 100–600 *m/z* and in the negative mode on the Platform quadrupole analyzer in the range 100–800 *m/z*. The samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 1–10 μ l/min. The IR spectra (cm^{-1}) were recorded on Perkin–Elmer 684 equipment as nujol suspensions or CH₃CN solutions. Starting compounds **L**¹Br and **L**²Li were prepared according to the literature [7].

2.2. Crystallography studies

Colorless crystals were obtained from layering of *n*-hexane onto a dichloromethane solution of **1** and **2**. The single crystal of compounds of **1** and **2** were mounted on glass fibre with epoxy cement and measured on four-circle diffractometer KappaCCD with CCD area detector by monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at 150(2) K. The crystallographic details are summarized in Table 1. The absorption correction was performed using a gaussian procedure from crystal shape [14a] or empirical absorption corrections (multiscan from symmetry-related measure-

Table 1
Crystal data and structure refinement for **1** and **2**

Compound	1	2
Empirical formula	C ₂₀ H ₂₅ Cl ₂ O ₄ Sn	C ₃₂ H ₅₀ Cl ₂ O ₄ Sn
Color	Colorless	Colorless
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbca</i>	<i>P2₁/c</i>
<i>a</i> (Å)	14.4470(2)	16.767(2)
<i>b</i> (Å)	13.0060(2)	11.2190(9)
<i>c</i> (Å)	23.0760(3)	19.7580(19)
β (°)		110.468(5)
<i>Z</i>	8	4
μ (mm ⁻¹)	1.447	0.918
D_{calc} (Mg m ⁻³)	1.593	1.313
Crystal size (mm)	0.35 × 0.075 × 0.02	0.3 × 0.3 × 0.15
Crystal shape	Bar	Prism
θ Range (°)	1–27.5	1–27.5
T_{min} , T_{max}	0.673, 0.938	0.735, 0.876
Number of reflections measured	71 947	48 792
Number of unique reflections, R_{int}	4969, 0.113	7962, 0.046
Number of observed reflections [$I > 2\sigma(I)$]	3462	6653
Number of parameters	248	364
S^a all data	1.071	1.060
Final R^b indices [$I > 2\sigma(I)$]	0.038	0.0295
wR_2^c indices (all data)	0.091	0.072
w_1/w_2^d	0.0415/3.0845	0.0310/2.2889
$\Delta\rho$ of maximum and minimum (e Å ⁻³)	0.875 and -1.422	0.879 and -0.711

$R_{int} = S|F_o^2 - F_o^2(\text{mean})|/SF_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged).

^{a-c} Definitions: $R(F) = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$, $wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{1/2}$, $S = [\sum (w(F_o^2 - F_c^2)^2) / (N_{refl} - N_{params})]^{1/2}$, Correction by SORTAV program.

^d Weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P]^{-1}$. $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

ments) [14b] for **1** and **2**, respectively. The structures were solved by the direct method (SIR-97) [15] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97) [16]. Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}(\text{pivot atom})$, for the methyl moiety multiple of 1.5 was chosen. The final difference maps displayed no peaks of chemical significance.

2.3. Synthesis of $(L^1)_2SnCl_2$ (**1**)

The 1 ml of hexane solution of BuLi (1.6 M, 1.6 mmol) was added to Et₂O (10 mL) solution of **L**¹Br (0.4 g, 1.6 mmol) at -78 °C and the solution stirred 2 h at this temperature. Then the toluene solution (20 ml) of SnCl₄ (0.21 g, 0.8 mmol) was added dropwise at -78 °C. The resulting suspension was stirred for 2 h at -78 °C, then for 5 days at room temperature. The solid was filtered off and the solvent was evaporated in vacuo. The residue was washed with pentane to afford **1** as a white solid. Yield: 0.40 g (95%); mp 125–128 °C. Anal. Calc.

for $C_{20}H_{26}Cl_2O_4Sn$ (MW 520.02): C, 46.19; H, 5.04. Found: C, 46.08; H, 5.00%. MW = 519. MS: m/z 485, 100% $[M-Cl]^+$; m/z 555, 100% $[M+Cl]^-$. 1H NMR ($CDCl_3$): δ (ppm) 3.26 (s, 12H, CH_3); 4.80 (s, 8H, CH_2 , $^nJ(^{119}Sn, ^1H) = 10.1$ Hz); 7.37–7.43 (complex pattern, 6H, SnC_6H_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 58.1 (CH_3); 74.1 (CH_2 , $^nJ(^{119}Sn, ^{13}C) = 40.3$ Hz); SnC_6H_3 : 140.3 (C(1)), 143.6, 127.3, 130.2; ^{119}Sn NMR ($CDCl_3$): δ (ppm) –242.0.

2.4. Synthesis of $(L^2)_2SnCl_2$ (2)

The hexane (10 ml) solution of L^2Li (0.26 g, 1 mmol) was added dropwise to a stirred toluene (10 ml) solution of $SnCl_4$ (0.13 g, 0.5 mmol) and Et_3N (0.03 g, 0.5 mmol). The suspension was stirred at room temperature for 5 days and the solid was filtered off. The solvent was evaporated in vacuo and the residue was washed with pentane to afford **2** as a white solid. Yield: 0.31 g (90%); mp 160–163 °C. Anal. Calc. for $C_{32}H_{50}Cl_2O_4Sn$ (MW 688.35): C, 55.84; H, 7.32. Found: C, 55.79; H, 7.29%. MW = 687. MS: m/z 653, 100% $[M-Cl]^+$; m/z , 100% $[M+Cl]^-$. 1H NMR ($CDCl_3$): δ (ppm) 1.04 (s, 36H, CH_3); 4.82 (s, 8H, CH_2 , $^nJ(^{119}Sn, ^1H) = 10.7$ Hz); 7.36–7.37 (complex pattern, 6H, SnC_6H_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 27.5 (CH_3); 64.7 (CH_2 , $^nJ(^{119}Sn, ^{13}C) = 43.4$ Hz); 75.6 ($OCMe_3$); SnC_6H_3 : 138.2 (C(1), $^nJ(^{119}Sn, ^{13}C) = 847.1$ Hz), 145.8, 126.3, 130.6. ^{119}Sn NMR ($CDCl_3$): δ (ppm) –175.5.

2.5. Synthesis of $(L^1)_2SnCl(OTf)$ (3)

The $AgOTf$ (0.21 g, 0.8 mmol) was added to a stirred solution of **1** (0.42 g, 0.8 mmol) in CH_2Cl_2 (10 mL). The suspension was stirred for 2 days at room temperature. The solid was filtered off and the solvent was evaporated in vacuo to give **3** as a white solid. Yield: 0.48 g (95%); mp 100–105 °C. Anal. Calc. for $C_{21}H_{26}ClF_3O_7SSn$ (MW 633.64): C, 39.81; H, 4.14. Found: C, 39.79; H, 4.08%. MW = 633. MS: m/z 149, 100% $[OTf]^-$; m/z 485, 100% $[M-OTf]^+$. 1H NMR ($CDCl_3$): δ (ppm) 3.40 (s, 12H, CH_3); 4.88 (s, 8H, CH_2 , $^nJ(^{119}Sn, ^1H) = 11.2$ Hz); 7.34 (d, 4H, ArH); 7.55 (t, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ (ppm) 59.4 (CH_3); 72.2 (CH_2 , $^nJ(^{119}Sn, ^{13}C) = 40.7$ Hz); 121.1 (q- CF_3 , $^nJ(^{19}F, ^{13}C) = 323.3$ Hz); SnC_6H_3 : 129.6 (C(1)), 141.6, 126.0, 132.1. ^{119}Sn NMR ($CDCl_3$): δ (ppm) –293.3. (CD_3CN): δ (ppm) –273.3. IR (nujol suspension) cm^{-1} : 1382(s), 1203 (s); (CH_3CN solution) cm^{-1} : 1266(s), 1170(s), 1031(vs).

2.6. Synthesis of $(L^1)_2Sn(OTf)_2$ (4)

Similar procedure to that for **3**. The reaction of **1** (0.55 g, 1.1 mmol) in CH_2Cl_2 (10 mL) and $AgOTf$ (0.56 g, 2.2 mmol) resulted in **4** as a white solid. Yield: 0.78 g (95%); mp 106–110 °C. Anal. Calc. for $C_{22}H_{26}F_6O_{10}SSn$ (MW 747.25): C, 35.36; H, 3.51. Found: C, 35.29; H, 3.49%. MW = 747. MS: m/z 599, 49% $[M-OTf]^+$; m/z 149, 100% $[OTf]^-$. 1H NMR (acetone- d_6): δ (ppm) 3.66 (s, 12H, CH_3); 5.21 (s, 8H, CH_2); 7.79 (t, 2H, ArH), 7.61 (d, 4H, ArH). ^{13}C NMR (acetone- d_6): δ (ppm) 60.2 (CH_3); 72.7 (CH_2 , $^nJ(^{119}Sn, ^{13}C) = 42.8$ Hz); 121.78 (q- CF_3 , $^nJ(^{19}F, ^{13}C) = 320.2$ Hz); SnC_6H_3 : 123.1 (C(1)), 143.5, 126.7, 133.9. ^{119}Sn NMR (acetone- d_6): δ (ppm) –403.5. (CD_3CN): δ (ppm) –398.4. IR (nujol suspension) cm^{-1} : 1378(s), 1233(vs), 1155(s), 1074(s), 1025(s); (CH_3CN solution): 1279(s), 1242(s), 1171(s), 1074(s), 1025(s).

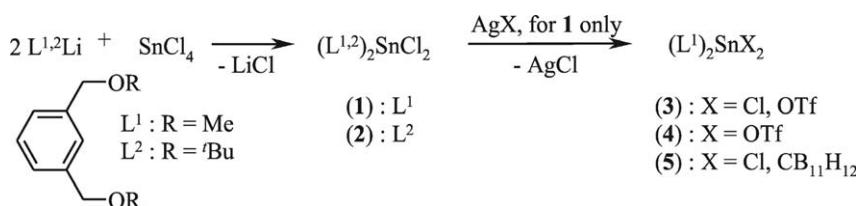
2.7. Synthesis of $(L^1)_2SnCl(CB_{11}H_{12})$ (5)

A similar procedure to that for **3**. The reaction of **1** (0.44 g, 0.85 mmol) in CH_2Cl_2 (10 mL) and $AgCB_{11}H_{12}$ (0.28 g, 0.85 mmol) resulted to **5** as a white powder. Yield: 0.51 g (96%); mp 163–166 °C. Anal. Calc. for $C_{21}H_{38}B_{11}ClO_4Sn$ (MW 627.61): C, 40.19; H, 6.10. Found: C, 40.25; H, 6.02%. MW = 628. MS: m/z 485, 100% $[M-CB_{11}H_{12}]^+$; m/z 143, 61% $[CB_{11}H_{12}]^-$. 1H NMR ($CDCl_3$): δ (ppm) 2.36 (s, CH - cage); 3.43 (s, 12H, CH_3); 4.89 (s, 8H, CH_2); 7.37 (d, 4H, ArH), 7.60 (t, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ (ppm) 59.8 (CH_3); 68.6 (CH - cage); 72.5 (CH_2 , $^nJ(^{119}Sn, ^{13}C) = 56.2$ Hz); SnC_6H_3 , 129.5 (C(1)), 141.5, 126.2, 132.3. ^{119}Sn NMR ($CDCl_3$): δ (ppm) –290.5. ^{11}B NMR ($CDCl_3$): δ (ppm) –0.1 (s, 1B, B(12)); –16.3 (s, 5B, B(7–11)); –20.6 (s, 5B, B(2–6)). IR (nujol suspension) cm^{-1} : $\nu(BH) = 2539$ (s).

3. Results and discussion

3.1. Synthetic aspects

Reaction of two equivalents of L^1Li with $SnCl_4$ at –78 °C gave the expected product $(L^1)_2SnCl_2$ (**1**) in form of a white stable compound. Since the reaction of L^2Li with $SnCl_4$ led to decomposition of ligand L^2 [7], the mixture of $SnCl_4$ and Et_3N (decrease of Lewis acidity $SnCl_4$) was used in the reaction with two equivalents of L^2Li resulting to $(L^2)_2SnCl_2$ (**2**) (Scheme 1). The reaction of **1** with silver



Scheme 1. The preparation and numbering of studied compounds.

salts of low nucleophilic anions (OTf, $\text{CB}_{11}\text{H}_{12}$) led to formation of compounds L_2SnX_2 ($\text{X} = \text{Cl}$, OTf (**3**), $\text{X} = \text{OTf}$ (**4**), $\text{X} = \text{Cl}$, $\text{CB}_{11}\text{H}_{12}$ (**5**)), characterized by NMR, IR spectroscopy and ESI-MS (Scheme 1).

3.2. Structural studies of prepared compounds 1–5

Molecular structures of **1** and **2** are depicted in Figs. 1 and 2. Crystallographic data are given in Table 1.

The shapes of the coordination polyhedra are rather different for both compounds. Geometry of **1** can be described as a deformed octahedron. Two values of Sn–O bond lengths ($\text{Sn}(1)\text{--O}(12) = 2.508(2) \text{ \AA}$ and $\text{Sn}(1)\text{--O}(21) = 2.343(2) \text{ \AA}$) are substantially smaller than the sum of the van der Waals radii of oxygen and tin (3.70 \AA) [17,18] in the studied compound, but larger than the sum of the covalent radii (2.066 \AA) [17], thus representing a strong and medium-strong Sn–O interaction. The remaining oxygen atoms are out of the primary tin coordination sphere. The tin atom together with coordinated oxygen atoms and both chlorine atoms form the equatorial plane of the deformed octahedron. Both carbon atoms occupy axial positions (Fig. 1). The coordinated oxygen and chlorine atoms are bound to the tin atom in *cis* position ($\text{O}(12)\text{--Sn}(1)\text{--O}(21) = 82.00(8)^\circ$ and $\text{Cl}(1)\text{--Sn}(1)\text{--Cl}(2) = 96.34(3)^\circ$), similarly to the diorganotin compound $\text{L}^1\text{PhSnCl}_2$ [7] but in contrast to the diorganotin dichloride containing $\text{C}_6\text{H}_2[\text{P}(\text{O})(\text{OEt})_2]_2\text{-1,3-}t\text{-Bu-5}$ as the different O,C,O-coordinating pincer ligand, where the oxygen atoms are bound to the tin atom in *trans* position [6].

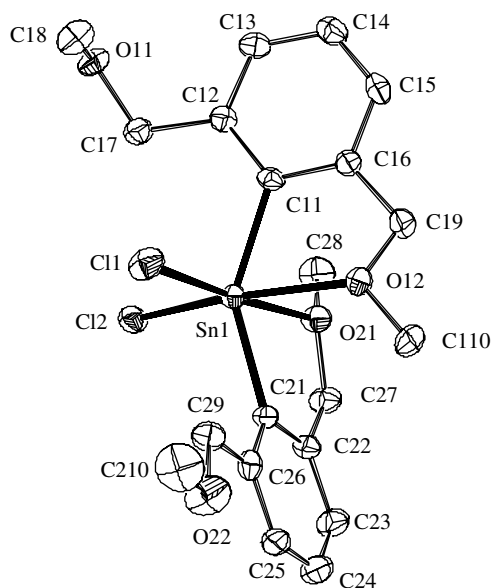


Fig. 1. View on the molecule of **1** with atom numbering scheme. Hydrogen atoms are omitted for clarity. The displacement ellipsoids are drawn on 50% probability level. Selected values of bonding lengths (\AA) and angles ($^\circ$): $\text{Sn}1\text{--C}11$ 2.155(3), $\text{Sn}1\text{--C}21$ 2.156(3), $\text{Sn}1\text{--O}21$ 2.343(2), $\text{Sn}1\text{--C}11$ 2.4232(9), $\text{Sn}1\text{--Cl}2$ 2.4242(9), $\text{Sn}1\text{--O}12$ 2.508(2), $\text{O}21\text{--Sn}1\text{--O}12$ $82.00(8)$, $\text{Cl}1\text{--Sn}1\text{--Cl}2$ $96.34(3)$, $\text{O}21\text{--Sn}1\text{--Cl}2$ $83.41(6)$, $\text{Cl}1\text{--Sn}1\text{--O}12$ $98.28(6)$, $\text{O}21\text{--Sn}1\text{--Cl}1$ $175.99(6)$, $\text{Cl}2\text{--Sn}1\text{--O}12$ $165.38(6)$, $\text{C}11\text{--Sn}1\text{--C}21$ $147.04(13)$.

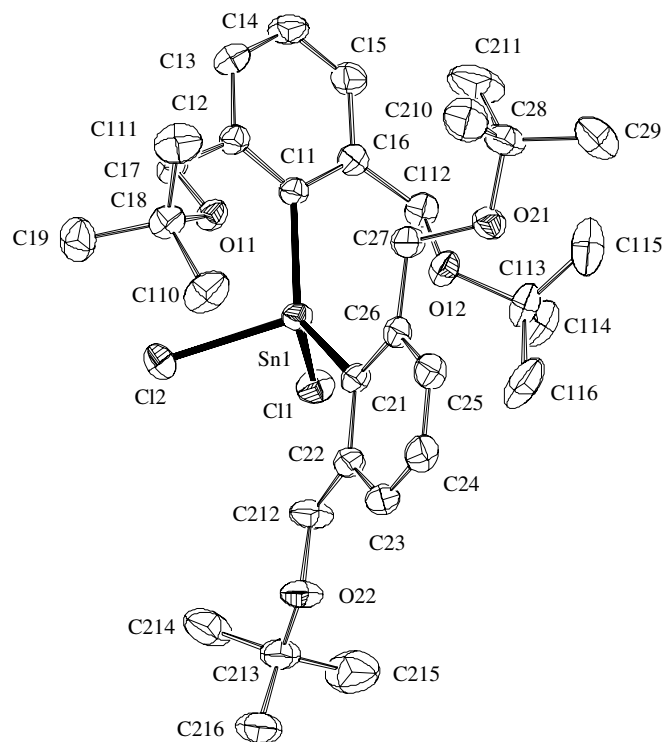


Fig. 2. View on the molecule of **2** with atom numbering scheme. Hydrogen atoms are omitted for clarity. The displacement ellipsoids are drawn on 50% probability level. Selected values of bonding lengths (\AA) and angles ($^\circ$): $\text{Sn}1\text{--C}11$ 2.1252(19), $\text{Sn}1\text{--C}21$ 2.1368(19), $\text{Sn}1\text{--C}11$ 2.3774(6), $\text{Sn}1\text{--Cl}2$ 2.3872(6), $\text{Sn}1\text{--O}11$ 3.0183(15), $\text{Sn}1\text{--O}12$ 2.7024(16), $\text{C}11\text{--Sn}1\text{--C}21$ $129.55(8)$, $\text{Cl}1\text{--Sn}1\text{--Cl}2$ $91.514(19)$, $\text{O}11\text{--Sn}1\text{--O}12$ $118.47(4)$.

In contrast to **1**, the shape of tin coordination polyhedron in **2** can be described as a deformed [4+2] bicapped tetrahedron. The greatest deviations from ideal tetrahedral shape are found for $\text{C}(11)\text{--Sn}(1)\text{--C}(21)$ ($129.55(8)^\circ$) and $\text{Cl}(1)\text{--Sn}(1)\text{--Cl}(2)$ ($91.51(2)^\circ$). The values of both Sn–O bond lengths ($\text{Sn}(1)\text{--O}(11) = 3.0183(15) \text{ \AA}$ and $\text{Sn}(1)\text{--O}(12) = 2.7024(16) \text{ \AA}$) indicate relatively weak intramolecular interactions comparable to those found in diorganotin compound $\text{L}^2\text{PhSnCl}_2$ [7]. The remaining oxygen atoms are out of the primary tin coordination sphere, where Sn–O bond lengths ($\text{Sn}(1)\text{--O}(21) = 4.5173(17) \text{ \AA}$ and $\text{Sn}(1)\text{--O}(22) = 4.7311(15) \text{ \AA}$) are even longer than the sum of van der Waals radii of oxygen and tin. The value of $\text{O}(11)\text{--Sn}(1)\text{--O}(12)$ being $118.47(4)^\circ$ indicates both coordinated oxygen atoms are bound to the tin atom in *cis* position in **2** similarly to **1**.

In addition to the different shapes and the strength of Sn–O interaction, there are other interesting differences in the molecule structures of **1** and **2**. While each oxygen donor atom O(12) and O(21) bound to the tin atom comes from different L^1 ligand in **1**, both oxygen atoms O(11) and O(12) weakly coordinated to the tin atom originate from one L^2 ligand in **2**. Both crystals are purely molecular, without any intermolecular contact significantly shorter than sum of van der Waals radii.

NMR data indicate the structure found in the solid state is retained in solution of CDCl_3 of **1** and **2**. The values of $\delta(^{119}\text{Sn})$ correspond to hexacoordinated tin atom in **1** and [4+2] coordination in **2** [19]. The low-temperature ^1H NMR spectra have not revealed decoalescence of the signals indicating fast dynamic process in solution even at 170 K.

NMR studies of **3–5** indicate similar results found for **1**. The values of $\delta(^{119}\text{Sn})$ indicate hexacoordinated tin atom in CDCl_3 or $\text{MeCN}-d_3$ solutions of **3–5** (-293.3 , -273.3 for **3**, -403.5 , -398.4 for **4** and -290.5 for **5**) [20] and ^1H NMR spectra revealed fast dynamic process (no decoalescence of the signals) in CDCl_3 solutions of **3–5** at 200 K. Since the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **5** showing three distinct 1:5:5 resonance is typical for the free $[\text{1-CB}_{11}\text{H}_{12}]^-$ anion [21], we can predict the compound **5** is ionic in solution. However, the answer if **3** and **4** are also ionic is missing. The question whether the triflate anions are coordinated to the tin atom in **3** and **4** may be answered by IR spectroscopy [22]. IR spectrum of **3** (nujol suspension) has shown two absorptions in the range of asymmetric stretching vibrations $\nu_{\text{as}}(\text{SO}_3)$ at 1382 and 1203 cm^{-1} assigned to covalently bound triflate anion [20]. IR spectrum of CH_3CN or CHCl_3 solution of **3** revealed only one $\nu_{\text{as}}(\text{SO}_3)$ at 1266 attributed to the presence of non-coordinated triflate anion (C_{3v} symmetry, cf. with appropriate IR vibration in Bu_4NOTf ; $\nu_{\text{as}}(\text{SO}_3)$ at 1273 cm^{-1}) [23]. IR spectrum of **4** both in nujol suspension and CH_3CN solution has shown three vibrations $\nu_{\text{as}}(\text{SO}_3)$ at 1378 and 1155 (assigned to covalently bound triflate anion) and 1233 cm^{-1} (assigned to ionic triflate group) (1279, 1171 and 1242 in CH_3CN), respectively, indicating different coordination modes of triflate anions both in the solid state and solution. Conductivity measurements coincide with these results and conductivity measurements ($c = 5 \text{ mmol L}^{-1}$) of **3** (518 $\mu\text{S cm}^{-1}$, molar conductivity $\Lambda = 103.6 \text{ S cm}^{-2} \text{ mol}^{-1}$), **4** (1101 $\mu\text{S cm}^{-1}$, $\Lambda = 220.2 \text{ S cm}^{-2} \text{ mol}^{-1}$) and **5** (618 $\mu\text{S cm}^{-1}$, $\Lambda = 123.6 \text{ S cm}^{-2} \text{ mol}^{-1}$) confirm the electrolytic dissociation of **3–5** into charged species in CH_3CN [20]. ESI-MS has also shown the existence of ionic forms in CH_3CN solutions of **3–5**, proving the existence of cationic forms: $m/z = 485$ $[\text{L}_2^1\text{SnCl}]^+$ for **3**, $m/z = 599$ $[\text{L}_2^1\text{SnOTf}]^+$ for **4** and $m/z = 485$ $[\text{L}_2^1\text{SnCl}]^+$ for **5**. In conclusion we can predict the prepared compounds **4** and **5** are ionic both in solid state and in solutions ($[\text{L}_2^1\text{SnOTf}]^+[\text{OTf}]^-$ and $[\text{L}_2^1\text{SnCl}]^+[\text{1-CB}_{11}\text{H}_{12}]^-$), while compound **3** is of molecular nature in solid state ($\text{L}_2^1\text{SnCl}(\text{OTf})$) but it ionized in CH_3CN solution ($[\text{L}_2^1\text{SnCl}]^+[\text{OTf}]^-$).

4. Conclusion

Novel diorganotin(IV) compounds **1** and **2** have been synthesized and characterized. The structure of both compounds (L^1) $_2\text{SnCl}_2$ (**1**) and (L^2) $_2\text{SnCl}_2$ (**2**) was studied by X-ray crystallography. Determination of crystal structures

reveals different shapes of coordination polyhedra. While deformed octahedron was found in **1**, tetrahedral geometry of the tin atom was determined for **2**. The reaction of **1** with silver salts of low nucleophilic anions resulted in **3–5** being ionic in solutions and in solid state (**4–5**), based on IR spectroscopy and conductivity measurement.

5. Supplementary data

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 290336 and 290337 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

The authors thank the Grant Agency of the Czech Republic (Grant No. 204/04/0223) and the Ministry of Education of the Czech Republic (VZ 0021627501 and LC523) for financial support.

References

- [1] (a) M. Nath, R. Yadav, G. Eng, P. Musingarimi, *Appl. Organomet. Chem.* 13 (1999) 29, and references therein; (b) A.J. Crowe, in: B.K. Keppler (Ed.), *Metal Complexes in Cancer Chemotherapy*, VCH, Weinheim, 1993, pp. 369–379; (c) M. Gielen, P. Lelieveld, D. de Vos, R. Willem, in: M. Gielen (Ed.), *Metal-based Antitumor Drugs*, vol. 2, Freund Publishing House, Tel Aviv, Israel, 1992, pp. 29–54.
- [2] (a) N. Pieper, C. Klaus-Mrestani, M. Schürmann, K. Jurkschat, M. Biesemans, I. Verbruggen, J.C. Martins, R. Willem, *Organometallics* 16 (1997) 1043; (b) U. Kolb, M. Dräger, M. Dargatz, K. Jurkschat, *Organometallics* 14 (1995) 2827; (c) D. Dakternieks, G. Dyson, K. Jurkschat, R. Tozer, E.R.T. Tiekink, *J. Organomet. Chem.* 458 (1993) 29.
- [3] T.J. Pinnavaia, *Science* 220 (1983) 4595.
- [4] (a) K. Akiba (Ed.), *Chemistry of Hypervalent Compounds*, Wiley-VCH, Weinheim, 1999, and references therein; (b) J.T.B.H. Jastrzebski, J. Boersma, P.M. Esch, G. van Koten, *Organometallics* 10 (1991) 930; (c) N.W. Mitzel, U. Losehand, A. Richardson, *Organometallics* 18 (1999) 2610; (d) M.A. Buntine, F.J. Kosovel, R.T. Tiekink, *Phosphorus, Sulfur Silicon Relat. Elem.* 150–151 (1999) 261, and references therein; (e) K. Jurkschat, N. Pieper, S. Seemeyer, M. Schürmann, M. Biesemans, I. Verbruggen, R. Willem, *Organometallics* 20 (2001) 868.
- [5] G. van Koten, J.T.B.H. Jastrzebski, J.G. Notes, A.L. Spek, J.C. Schoone, *J. Organomet. Chem.* 8 (1978) 233.
- [6] M. Mehring, M. Schürmann, K. Jurkschat, *Organometallics* 17 (1998) 1227.
- [7] R. Jambor, L. Dostál, A. Růžička, I. Císařová, J. Brus, J. Holeček, *Organometallics* 19 (2002) 3996.
- [8] (a) J.T.B.H. Jastrzebski, P.A. van der Schaaf, J. Boersma, G. van Koten, M. de Wit, Y.D. Wang, Y.D. Heijdenrijk, C.H. Stam, *J. Organomet. Chem.* 407 (1991) 301; (b) K. Peveling, M. Henn, C. Löw, M. Mehring, M. Schürmann, B. Costisella, K. Jurkschat, *Organometallics* 23 (2004) 1501;

- (c) B. Kašná, R. Jambor, L. Dostál, A. Růžicka, I. Císařová, J. Holeček, *Organometallics* 23 (2004) 5300.
- [9] (a) E.G. Rochow, D. Seyferth, *J. Am. Chem. Soc.* 75 (1953) 2877, and references therein;
(b) R. Okawara, E.G. Rochow, *J. Am. Chem. Soc.* 82 (1960) 3285;
(c) M.M. McGrady, R.S. Tobias, *Inorg. Chem.* 3 (1964) 1157;
(d) M. Wada, R. Okawara, *J. Organomet. Chem.* 4 (1965) 487;
(e) H.C. Clark, J.R. O'Brien, *Inorg. Chem.* 2 (1965) 740;
(f) H.C. Clark, R.J. O'Brien, A.L. Pickard, *J. Organomet. Chem.* 4 (1965) 43;
(g) B. Wrackmeyer, C. Kehr, R. Boese, *Angew. Chem., Int. Ed. Engl.* 30 (1991) 1370;
(h) B. Wrackmeyer, G. Kehr, A. Sebald, J. Kümmeler, *Chem. Ber.* 125 (1992) 1597;
(i) For recent studies on triorganotin cationic species in solution, see: T. Birchall, V. Manivannan, *J. Chem. Soc., Dalton Trans.* 2671 (1985);
(j) J.B. Lambert, B. Kuhlmann, *J. Chem. Soc., Chem. Commun.* 931 (1992);
(k) J.B. Lambert, S.M. Ciro, C.L. Stern, *J. Organomet. Chem.* 499 (1995) 49.
- [10] L. Pellerito, L. Nagy, *Coord. Chem. Rev.* 224 (2002) 111.
- [11] (a) K. Sakamoto, Y. Hamada, H. Akashi, A. Orita, J. Otera, *Organometallics* 18 (1999) 3555;
(b) S. Durand, K. Sakamoto, T. Fukuyama, A. Orita, J. Otera, A. Duthie, D. Dakternieks, M. Schulte, K. Jurkschat, *Organometallics* 19 (2000) 3220.
- [12] (a) R.S. Tobias, *Organomet. Chem. Rev.* 1 (1966) 93, and references therein;
(b) M. Wada, R. Okawara, *J. Organomet. Chem.* 1 4 (1965) 487.
- [13] (a) E.G. Martinez, A.S. Gonzalez, J.S. Casas, J. Sordo, U. Casellato, R. Graziani, *Inorg. Chim. Acta* 191 (1992) 75;
(b) E.C. Constable, F.K. Khan, J. Lewis, M.C. Liptrot, P.R. Raithby, *J. Chem. Soc., Dalton Trans.* 333 (1985);
(c) A. Wirth, O. Moers, P.G. Jones, A. Blaschette, *Acta Crystallogr., Sect. C* 55 (1999) 2033;
(d) A. Wirth, O. Moers, A. Blaschette, P.G. Jones, *Z. Anorg. Allg. Chem.* 625 (1999) 982;
- (e) A. Wirth, A. Blaschette, P.G. Jones, *Main Group Met. Chem.* 21 (1998) 309;
(f) A. Wirth, O. Moers, A. Blaschette, P.G. Jones, *Z. Anorg. Allg. Chem.* 626 (2000) 529;
(g) A. Blaschette, I. Hippel, J. Krahl, E. Wieland, P.G. Jones, A. Sebald, *J. Organomet. Chem.* 437 (1992) 279;
(h) I. Hippel, P.G. Jones, A. Blaschette, *J. Organomet. Chem.* 448 (1993) 63;
(i) I. Lange, J. Krahl, P.G. Jones, A. Blaschette, *J. Organomet. Chem.* 474 (1994) 97;
(j) V. Chandrasekhar, R. Boomishankar, S. Singh, A. Steiner, S. Zacchini, *Organometallics* 21 (2002) 4575;
(k) R. Shankar, M. Kumar, S.P. Narula, R.K. Chadha, *J. Organomet. Chem.* 671 (2003) 35;
(l) J.S. Casas, E. Garcia-Martinez, A.S. Gonzalez, J. Sordo, U. Casellato, R. Graziani, U. Russo, *J. Organomet. Chem.* 493 (1995) 107.
- [14] (a) P. Coppens, in: F.R. Ahmed, S.R. Hall, C.P. Huber (Eds.), *Crystallographic Computing*, Munksgaard, Copenhagen, 1970, pp. 255–270;
R.H. Blessing, *Sortav*, *J. Appl. Crystallogr.* 30 (1997) 421;
(b) A.L. Spek, *PLATON*, *J. Appl. Crystallogr.* 36 (2003) 7.
- [15] A. Altomare, G. Casciarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* 27 (1994) 435.
- [16] G.M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, 1997.
- [17] A. Bondi, *J. Phys. Chem.* 68 (1964) 441.
- [18] J. Emsley, *Die Elemente*, Walter de Gruyter, Berlin, 1994.
- [19] J. Holeček, M. Nádvorník, K. Handlír, A. Lyčka, *J. Organomet. Chem.* 241 (1983) 177.
- [20] J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, *Dalton Trans.* (2003) 3258.
- [21] (a) W.H. Knoth, *J. Am. Chem. Soc.* 89 (1967) 1274;
(b) W.H. Knoth, *Inorg. Chem.* 10 (1971) 598;
(c) J. Plešek, T. Jelínek, E. Drdákova, S. Heřmánek, B. Štíbr, *Collect. Czech. Chem. Commun.* 49 (1984) 1559.
- [22] G.A. Lawrence, *Chem. Rev.* 86 (1986) 17.
- [23] D.H. Johnston, D.F. Shriver, *Inorg. Chem.* 32 (1993) 1045.