

Note

Solution and cross-polarization/magic angle spinning NMR investigation of intramolecular coordination Sn–N in some organotin(IV) C,N-chelates

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Abstract

An intramolecular donor/acceptor Sn–N bonding connection in a set of triphenyl- and diphenyl-(halogeno)tin(IV) C,N-chelates, Ph₂XSnL, where Ph = C₆H₅, X = Ph, Cl or Br and L¹ = 2-(dimethylaminomethyl)phenyl-, C₆H₄(CH₂NMe₂)-2, and L² = 2,6-bis-[(dimethylaminomethyl)phenyl]-, C₆H₃(CH₂NMe₂)₂-2,6, respectively, was studied by ¹¹⁹Sn, ¹⁵N, ¹³C and ¹H NMR spectroscopy in solution of non-coordinating solvent (CDCl₃) and by ¹¹⁹Sn cross-polarization/magic angle spinning NMR techniques in the solid-state. The existence of Sn–N coordination bonds was confirmed in studied compounds and their strengths were evaluated through the values of NMR spectra parameters of nuclei directly involved in Sn–N connection, namely by characteristic changes of chemical shifts δ (¹¹⁹Sn) and δ (¹⁵N) and values of J(¹¹⁹Sn, ¹³C) and J(¹¹⁹Sn, ¹⁵N) coupling constants. The set was extended by compound [2,6-C₆H₃(CH₂NMe₂)₂]PhSnCl₂ (**5a**), that is the decomposition product of compound [2,6-C₆H₃(CH₂NMe₂)₂]Ph_SnCl (**5**). This **5a** was characterized by NMR spectroscopy and its structure was estimated by X-ray diffraction techniques. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: C,N-chelates; NMR spectroscopy; Intramolecular interaction; X-ray diffraction

1. Introduction

The organometallic compounds with the potentially bi- or tridentate C,N-chelating ligands are extensively studied due to their potential biological activity [1], enhanced reactivity [2] and very interesting structures [2,3]. The central metal atom can interact with nitrogen donor centres from the other side(s) of ligand. The existence of this intramolecular interaction in organotin(IV) compounds in the solid-state has been proven by X-ray diffraction techniques on single crystals and indirectly confirmed also in solutions by ¹H NMR

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spectroscopy [4]. However, the direct and simple method for the confirmation of this interaction and the evaluation of its magnitude is missing. A new approach based on the measurements of NMR spectral parameters of nuclei directly involved in Sn–N coordination has been used in our department recently [5]. In this paper, we would like to show the possible way of donor/acceptor interaction Sn–N evaluation, in case of some C,N-chelates, using routine NMR measurements (in solution of non-coordinating solvent (CDCl₃) and in the solid-state using ¹¹⁹Sn, ¹⁵N, ¹³C and ¹H NMR and ¹¹⁹Sn cross-polarization/magic angle spinning (CP/MAS) NMR spectroscopy, respectively) on the set of some organotin(IV) compounds (see Fig. 1 and Table 1).

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2. Experimental

2.1. Syntheses

All experiments were carried out under anaerobic Dimethylaminomethylbenzene, conditions. 1.3-bis-(aminomethyl)benzene, 2,6-dimethylaniline, *n*-butyllithium, triphenyltin chloride, diphenyltin dichloride and diphenyltin dibromide were obtained from commercial sources (Sigma-Aldrich). Toluene, benzene, nhexane, *n*-pentane and diethylether were dried over and distilled from sodium wire, chloroform was dried over and distilled from P₂O₅ and LiAlH₄, respectively. The compounds 1, 2, 3 and 6 were prepared by standard methods [4] (e.g. ortho-lithiation of starting dimethylaminomethylbenzene and 1,3-bis[(dimethylamino)methyl]benzene (for 6), respectively, using *n*-butyllithium in diethylether/n-hexane solution). The resulting organolithium salts were filtered off, dissolved in benzene and added to solutions of appropriate organotin(IV) halides. The reaction mixtures were evaporated



Fig. 1. Structural (ligands L^1 and L^2) and numbering (compounds 2 and 4 as example) scheme.

| Table 1 | | |
|---------|-------------------------|-----------|
| Studied | $LSnR^{1}R^{2}R^{3} \\$ | compounds |

| Compound | La | \mathbb{R}^1 | R ² | R ³ |
|----------|-------|----------------|----------------|----------------|
| 1 | L^1 | Ph | Ph | Ph |
| 2 | L^1 | Ph | Ph | Cl |
| 3 | L^1 | Ph | Ph | Br |
| 4 | L^2 | Ph | Ph | Ph |
| 5 | L^2 | Ph | Ph | Cl |
| 5a | L^2 | Ph | Cl | Cl |
| 6 | L^2 | Ph | Ph | Br |

^a $L^1 = C_6H_4(CH_2NMe_2)-2$, and $L^2 = C_6H_3(CH_2NMe_2)_2-2$,6.

$$L^{2}Li + Ph_{2}SnCl_{2}$$
 $\overbrace{ii}^{i} 5_{ii}$

i) Ph₂SnCl₂, n-hexane, -40°C, 3 min.
ii) Ph₂SnCl₂, benzene, r.t., 30 min.

Fig. 2. Scheme of proposed reactions of lithium salt of L^2 with Ph_2SnCl_2 by different conditions ((a) and (b)).

in vacuo, and resulting solid materials were recrystallized from boiling toluene to give pure white solids. The compounds 3 and 6 have been previously reported, but the characterization was necessary, because of the different preparation methods. The compounds 5 and 5a were prepared from the same starting compounds (Fig. 2), compound 5 was obtained, when the starting lithium salt was added like a hexane suspension very quickly to the hexane solution of diphenyl tin(IV)dichloride at the low temperature (-40 °C) and the solvent was rapidly removed in vacuo, while when the reaction was carried out at the room temperature the compound 5a was obtained. We propose, from the ¹¹⁹Sn NMR shift value, that the compound **4** is a byproduct in this side reaction. After heating a solution of 5 to approximately 40 °C for 10 min the decomposition products 5a and 4 as well as a yet unidentified insoluble material were observed.

2.1.1. $Ph_3Sn(C_6H_4CH_2N(CH_3)_2)$ (1)

Yield 87%. m.p. 86–87 °C (Found: C, 66.86; H, 5.55; N, 2.84; Sn, 24.74. $C_{27}H_{27}NSn$ requires C, 66.97; H, 5.62; N, 2.89; Sn, 24.51.). ¹H NMR (CDCl₃): δ 7.60 (d, aryl-H, 6H), δ 7.28 (m, aryl-H, 10H), δ 7.14 (m, aryl-H, 3H), δ 3.31 (s, NCH₂-H, 2H), δ 1.52 (s, CH₃-H, 6H).

2.1.2. $Ph_2SnCl(C_6H_4CH_2N(CH_3)_2)$ (2)

Yield 79%. m.p. 218–220 °C (Found: C, 56.89; H, 5.06; N, 3.26; Cl, 8.14; Sn, 27.00. $C_{21}H_{22}NClSn$ requires C, 56.99; H, 5.01; N, 3.16; Cl, 8.01; Sn, 26.82.). ¹H NMR (CDCl₃): δ 8.53 (d, aryl-H, 1H), δ 7.73 (d, aryl-H, 4H), δ 7.46 (m, aryl-H, 2H), δ 7.42 (m, aryl-H, 6H), δ 7.22 (d, aryl-H, 1H), δ 3.56 (s, NCH₂-H, 2H), δ 1.89 (s, CH₃-H, 6H).

2.1.3. $Ph_2SnBr(C_6H_4CH_2N(CH_3)_2)$ (3)

Yield 74%. m.p. 238–240 °C (Found: C, 51.72; H, 4.51; N, 2.83; Br, 16.52; Sn, 24.42. $C_{21}H_{22}NBrSn$ requires C, 51.79; H, 4.55; N, 2.88; Br, 16.41; Sn, 24.37.). ¹H NMR (CDCl₃): δ 8.54 (d, aryl-H, 1H), δ 7.70 (d, aryl-H, 4H), δ 7.50 (m, aryl-H, 2H), δ 7.40 (m, aryl-H, 6H), δ 7.18 (d, aryl-H, 1H), δ 3.56 (s, NCH₂-H, 2H), δ 1.89 (s, CH₃-H, 6H).

2.1.4. $Ph_3Sn[C_6H_3(CH_2NMe_2)_2-2,6]$ (4)

The compound 4 was obtained by reaction of 2,6bis[(dimethylamino)methyl]phenyllithium (prepared by reaction of 2,6-bis[(dimethylamino)methyl]bromobenzene and *n*-butyllithium in diethylether solution at the room temperature) with triphenyltin chloride in diethylether solution. The reaction mixture was evaporated in vacuo, and arising solid material was dissolved in chloroform/hexane solution. The solution was set aside at -40 °C for 24 h and the observed crystalline solid material was filtered off and the stock liquor was evaporated in vacuo giving pure **4** as a white crystalline solid in 56% yield. m.p. 86–93 °C (Found: C, 66.9; H, 6.6; N, 4.9; Sn, 21.6. $C_{30}H_{34}N_2Sn$ requires C, 66.57; H, 6.33; N, 5.18; Sn, 21.93.). ¹H NMR (CDCl₃): δ 7.65 (d, aryl-H, 6H), δ 7.21 (m, aryl-H, 10H), δ 7.12 (d, aryl-H, 2H), δ 3.24 (s, NCH₂-H, 4H), δ 1.63 (s, CH₃-H, 12H).

2.1.5. $Ph_2SnCl[C_6H_3(CH_2NMe_2)_2-2,6]$ (5)

The compound 5 was prepared by rapid addition of a hexane suspension of 2,6-bis[(dimethylamino)methyl]phenyllithium into the hexane solution of diphenyltin dichloride at -40 °C. The obtained suspension was after 3 min of stirring rapidly evaporated in vacuo and the resulting white precipitate was washed with large volume of cold benzene. The filtrate was evaporated in vacuo to give a pure white solid in 12% yield. m.p. 80 °C with decomposition (Found: C, 57.29; H, 5.16; N, 5.26; Cl, 7.52; Sn, 24.77. C₂₄H₂₉N₂ClSn requires C, 57.69; H, 5.85; N, 5.61; Cl, 7.10; Sn, 23.75.). ¹H NMR (CDCl₃): δ 7.57 (d, aryl-H, 4H, ${}^{3}J({}^{119}Sn, {}^{1}H) = 67.0$ Hz), δ 7.34 (m, aryl-H, 7H), δ 7.11 (d, aryl-H, 2H), δ 3.69 (s, NCH₂-H, 4H), δ 1.97 (s, CH₃-H, 12H). ¹³C CP/MAS NMR (50.32 MHz, 300 K): δ 44.83(CH₃), 47.23(CH₃), 64.03(CH₂), 126.96(Ar), 128.47(Ar), 130.29(Ar), 132.87(Ar), 134.91(Ar), 135.65(Ar), 138.77(Ar), 143.40(Ar).

2.1.6. PhSnCl₂[C₆H₃(CH₂NMe₂)₂-2,6] (5a)

The compound **5a** was obtained from the reaction of 2,6-bis[(dimethylamino)methyl]phenyllithium with diphenyltin dichloride at the room temperature (see above). This compound is a pure white solid in 62% yield. m.p. 123–130 °C (Found: C, 47.16; H, 5.35; N, 6.04; Cl, 15.62; Sn, 25.85. C₁₈H₂₄N₂Cl₂Sn requires C, 47.21; H, 5.28; N, 6.12; Cl, 15.48; Sn, 25.91.). ¹H NMR (CDCl₃): δ 8.44 (d, aryl-H, 2H, ³J(¹¹⁹Sn, ¹H) = 120.74 Hz), δ 7.47 (m, aryl-H, 3H), δ 7.27 (t, aryl-H, 1H), δ 7.08 (d, aryl-H, 2H), δ 3.96 (s, NCH₂-H, 4H), δ 2.67 (s, CH₃-H, 12H).

2.1.7. $Ph_2SnBr[C_6H_3(CH_2NMe_2)_2-2,6]$ (6)

Yield 82%. m.p. 197–203 °C (Found: C, 52.79; H, 5.16; N, 5.26; Br, 14.42; Sn, 22.37. $C_{24}H_{29}N_2BrSn$ requires C, 52.98; H, 5.37; N, 5.15; Br, 14.69; Sn, 21.81.). ¹H NMR (CDCl₃): δ 7.65 (d, aryl-H, 4H), δ 7.58 (m, aryl-H, 7H), δ 4.01 (s, NCH₂-H, 4H), δ 2.26 (s, CH₃-H, 12H).

2.2. NMR experiments

The solution state ¹¹⁹Sn, ¹⁵N, ¹³C and ¹H NMR spectra were acquired at 134.28, 36.56, 90.56 and 360.13 MHz, respectively, on Bruker AMX 360 NMR spectrometer, using a 5 mm tuneable broad band probe at 300 K. The samples were obtained by dissolving of approximately 50–200 mg of each compound in 0.5 ml

of deuteriochloroform and in the case of compound 5, approximately 10 mg in 0.5 ml of benzene-d₆. Appropriate chemical shifts were calibrated on: ¹H-residual peak of CHCl₃ (δ = 7.25) or benzene (for 5) (δ = 7.16), ¹³C-residual peak of CHCl₃ (δ = 77.00 ppm) or benzene (for 5) (δ = 128.39), ¹⁵N-external nitromethane (δ = 0.00 ppm), ¹¹⁹Sn-external tetramethylstannane (δ = 0.00 ppm). The ⁿJ(¹¹⁹Sn, ¹⁵N) parameter was obtained from ¹⁵N NMR spectra.

The solid-state ¹³C and ¹¹⁹Sn spectra of studied compounds were recorded on Bruker DSX 200 spectrometer equipped with a double-bearing CP/MAS probe at the room temperature. The compounds were packed in standard 4-mm ZrO₂ rotor. The ¹¹⁹Sn Hartmann-Hahn cross-polarization match was set with tetracyclohexyltin using a ¹H 90° pulse of 4 µs. Ramped (RAMP)/CP/ MAS [6,7] experiments were used with repetition delay of 10 s and contact time was set to 2 ms. In each case at least two spinning rates (4.5-9 kHz) were used to identify the isotropic chemical shift. The number of scans varied between 200 and 4000. The ¹³C and ¹¹⁹Sn chemical shifts were calibrated indirectly by external glycine (carbonyl signal $\delta = 176.03$ ppm) and tetracyclohexyltin ($\delta = -97.35$ ppm), respectively. The ¹¹⁹Sn NMR chemical shift was allocated approximately to the centre of gravity of the signal.

2.3. Crystallography

Measured single crystal was obtained by vapour diffusion of *n*-hexane into the 5% dichloromethane solution of compound 5a. Crystal data for 5a: $C_{18}H_{24}N_2Cl_2Sn$, M = 457.98, monoclinic, space group $P2_1/c$ (no. 14), a = 16.3570(1), b = 59.876(1), c =7.9330(3) Å, $\beta = 98.2060(6)^\circ$, U = 7690.0(3) Å³, Z = 16, T = 150(2) K, $\mu = 1.608$ mm⁻¹, graphite-monochromated Mo K α radiation $\lambda = 0.71073$ Å, colourless bar with dimensions approximately $0.22 \times 0.18 \times 0.13$ mm³, crystal mounted with epoxy glue on a glass fibre and measured on Nonius Kappa CDD diffractometer, θ range for data collection 1.1-26.7°, empirical absorption correction applied (multiscan from symmetry-related measurements), 12910 unique diffractions of 25 847 collected, 9747 diffractions with $I > 2\sigma(I)$ were regarded as observed, 12910 diffractions used in refinement of 429 parameters via full-matrix least-squares on F^2 , final R indices for observed data: R = 0.076, $R_w =$ 0.197, for all data R = 0.103, $R_w = 0.217$, goodness-offit = 1.067, largest residual peaks 2.965 and -1.596 e Å ^{- 3}.

The structure was solved by direct methods (SIR93 [8]) and refined by full-matrix least-squares on F^2 (SHELXL97 [9]). Only heavy atoms (Sn and Cl) were refined anisotropically, N and C isotropically and hydrogens were fixed in their calculated positions. The crystal data are given in Table 3.

Table 2

Relevant parameters of ¹¹⁹Sn, ¹⁵N and ¹³C NMR spectra of compounds 1-6 in deuteriochloroform and in the solid-state in the case of ¹¹⁹Sn at 300 K

| Compound | $\delta({}^{15}N)$ (ppm); (${}^{n}J({}^{119}Sn, {}^{15}N)$ (Hz)) | $\delta(^{119}\text{Sn})^{a}$ (ppm) | δ (¹¹⁹ Sn) _{iso} (ppm) | $\delta(^{1}\text{H(CH}_{2}))$ (ppm) | $\delta({}^{13}C)$ (ppm); ("J({}^{119}Sn, {}^{13}C) (Hz)) | | | |
|-------------------------|---|--|---|---|---|-----------------|-------------------------------|-------------------------------|
| | | | | | CH ₂ | CH ₃ | C(1) | C'(1) |
| L ¹ H | -353.0 | | | 3.27 | 63.61 | 44.54 | 128.15 | |
| 1 | -351.0 (23.6) | -163.3 | -159.3 | 3.31 | 65.25 (20.1) | 44.86 | 138.37 (577.8) | 141.94 (545.9) |
| 2 | $-347.6(^{b})$ | -177.1 | -191.7 | 3.56 | 64.68 (29.1) | 45.67 | 137.32 (796.2) | 141.36 (772.0) |
| 3 | -347.2 (69.36) | -180.8 | -196.5 | 3.56 | 64.74 (27.7) | 45.77 | 136.69 (774.0) | 141.75 (758.8) |
| L ² H | -353.7 | | | 3.38 | 64.22 | 45.26 | 129.81 | |
| 4 | -349.6(18.0) | -201.9 | -211.3 | 3.24 | 65.50 (24.5) | 44.72 | 139.29 (640.9) | 145.29 (547.9) |
| 5 ^{c,d} | ^b (^b) | -193.4 | -72.6 | 3.69 | 63.08 (^b) | 47.59 | ^b (^b) | ^b (^b) |
| 5a | -345.5 (^b) | -257.5 | -260.0 | 3.96 | 62.13 (65.1) | 46.71 | ^b (^b) | ^b (^b) |
| 6 | -347.2 (^b) | -69.10 | -71.6 | 4.01 | 64.24 (35.2) | 46.81 | 130.10 (696.4) | 133.40 (688.7) |

^a CDCl₃.

^b Not found.

^c Explained in text.

^d Measured in benzene-d₆.

The lower accuracy of structure parameters is caused by unfavourable crystal properties. Due to very large lattice parameter, the high number of diffraction should be excluded, because of their overlapping. Also all four symmetrically independent molecules are disordered (especially in dimethylamino moieties), therefore, temperature factors are rather high for low temperature measurement. Regardless of these difficulties, the structure determination shows main features of molecular geometry.

3. Results and discussion

The relevant parameters of ¹¹⁹Sn, ¹⁵N, ¹³C and ¹H NMR spectra of compounds 1-6 are collected in Table 2. Compared to the free amines L¹H and L²H, respectively, data for compounds 1-6 show, that introduction of organotin(IV) substituents provides a downfield shift of $\delta({}^{1}H(CH_{2}))$ and $\delta({}^{1}H(CH_{3}))$ NMR resonances of the $CH_2N(CH_3)_2$ groups and also downfield shift of $\delta(^{15}N)$ values. The $\delta(^{119}\text{Sn})$ chemical shift values of all compounds 1-6 are significantly more highfield than those of unsubstituted analoga tetraphenylstannane (-128.1ppm) [10], triphenyltinchloride (-44.7 ppm) [10], triphenyltin bromide (-59.8 ppm) [10] and diphenyltin dichloride (-26.7 ppm) [11]. Furthermore, the differences in δ ⁽¹¹⁹Sn) and δ ⁽¹⁵N) chemical shift values of substituted and unsubstituted analoga generally increase with increasing Lewis acidity of the tin centre (excluding compound 6—see later). On the basis of these facts, it can be concluded, that there is some interaction of one (or two) CH₂N(CH₃)₂ donor substituent(s) with central tin atom in the compounds

studied. These conclusions are also confirmed by the existence of relatively high values of $J(^{119}\text{Sn}, ^{15}\text{N})$ and by increase of $J(^{119}\text{Sn}, ^{15}\text{N})$, $J(^{119}\text{Sn}, ^{13}\text{C}(\text{CH}_2))$, $^{1}J(^{119}\text{Sn}, ^{13}\text{C}(1))$ and $^{1}J(^{119}\text{Sn}, ^{13}\text{C}(1'))$ coupling constants, respectively, with increasing Lewis acidity of tin centre.

In Table 2, there are listed solid-state ¹¹⁹Sn NMR data for the compounds 1–6. All compounds display one central signal consistent with the presence of only one type of organotin(IV) particles in asymmetric units. The very small $\Delta\delta$ (¹¹⁹Sn) values (compared to solution spectra) of approximately 5–15 ppm for 1–6 (except 5) are clear indication that their solid-state structure is retained in deuteriochloroform solution.

The coordination geometry of central tin atom in compound 1 is slightly distorted tetrahedron with bonding angles C(1)-Sn-C(1) and C(1)-Sn-C(1') being approximately 110° and 107°, respectively (calculated according to the literature [12] from coupling constants ${}^{1}J({}^{119}Sn, {}^{13}C(1))$ and ${}^{1}J({}^{119}Sn, {}^{13}C(1')))$. The Sn–N intramolecular interaction is probably very weak as follows from values of $\Delta \delta$ ⁽¹⁵N) = 2.7 ppm ($\Delta \delta$ ⁽¹⁵N) means the differences between $\delta(^{15}N)$ of appropriate compound and the free ligand), $J(^{119}Sn, ^{15}N) = 23.6$ Hz and $J(^{119}\text{Sn}, ^{13}\text{C(CH}_2)) = 20.1$ Hz. The isotropic ^{119}Sn chemical shift of **1** in the solid-state, $\delta_{iso} = 159.3$ ppm, indicates there is no difference between the solution and solid-state structures. An unsymmetrical shape of the central signal δ (¹¹⁹Sn)_{iso} is observed in ¹¹⁹Sn CP/MAS NMR of compound 1. It probably corresponds to the two overlapping signals with 1:2 ratio of their relative intensities as a result of residual quadrupolar coupling due to ${}^{14}N$ (I = 1) [13].

The four-coordinated tin in compound 4 is indicated by ${}^{1}J({}^{119}Sn, {}^{13}C(1))$ and ${}^{1}J({}^{119}Sn, {}^{13}C(1'))$ coupling constants (640.9 and 547.9 Hz, respectively). The moderate upfield δ ⁽¹¹⁹Sn) chemical shift (vide supra) and slightly increased ${}^{1}J({}^{119}Sn, {}^{13}C(1))$ coupling constant with respect to the values found for Ph₄Sn (531 Hz [12]) allowing one to conclude that the weak Sn-N interaction is present in CDCl₃ solution of 4. This fact is confirmed by small value of $\Delta \delta(^{15}N) = 4.1$ ppm and by magnitude of $J(^{119}\text{Sn}, ^{15}\text{N})$ and $J(^{119}\text{Sn}, ^{13}\text{C(CH}_2))$ coupling constants (18.0 and 24.5 Hz, respectively). The geometry of central tin atom was assigned as a distorted (capped or dicapped) tetrahedron with bonding angles C(1)-Sn-C(1') and C(1)-Sn-C(1) 107° and 113° [10], respectively, analogous C-Sn-C' angles, obtained from X-ray diffraction analysis on single crystal, in compound $(Me_3Sn)_2\{C_6[CH_2N(Me)_2]_4-2,3,5,6\}$ with similar vicinity of central tin atom are 108.45°, 94.85° and 109.28° (average 104.2°), those of C-Sn-C are 113.36°, 120.51° and 107.27° (average 113.7°) [14]. The ¹¹⁹Sn CP/MAS NMR spectrum of 4 consists of a broad nearly symmetrical central signal without distinct splitting. The fact that only a few spinning sidebands of very low intensity are observed for 4, indicates there is an almost tetrahedral geometry around tin in the solidstate [15].

The value of $\delta(^{119}\text{Sn}) = -177.1$ ppm for compound **2** in the CDCl₃ solution corresponds to the five-coordinated triphenyltin(IV) compounds [10] with trigonal bipyramidal geometry. The magnitude of calculated bonding angles (C(1)-Sn-C(1) and C(1)-Sn-C(1') are 123° and 121°, respectively) [12] shows, that the tin atom coordination polyhedra is *trans*-trigonal bipyramide with the carbon atoms C(1) and C(1') in the equatorial plane and more electronegative chlorine and nitrogen atoms in the axial positions. The change in the coordination and in the geometry going from **1** to **2** is reflected also in the increase of $J(^{119}\text{Sn}, ^{13}\text{C(CH}_2))$



Fig. 3. ¹¹⁹Sn RAMP CP/MAS NMR spectrum of compound **6** and detail of the central signal its (1:4:4).

coupling constant and higher increase of the $\delta(^{15}N)$ value $(\Delta \delta({}^{15}N) = 5.4 \text{ ppm})$ [5]. The $J({}^{119}Sn, {}^{15}N)$ was not detected because of relatively low solubility of 2. The central signal pattern of ¹¹⁹Sn CP/MAS NMR spectrum is six-line signal pattern with relative intensity of each line of 1:2:1:2:2:4 in compound 2, which is typically for compounds containing tin atom bonded to two different quadrupolar nuclei (14N and 35,37Cl with I = 1 and 3/2, respectively) [16]. According to these results of this analysis we can assume the trans-trigonal bipyramidal geometry of tin atom in single crystals of the compound 2 (see X-ray results for: chloro[2-(dimethylaminomethyl)phenyl]dimethyltin [4, 17],bromo[2-(dimethylaminomethyl)phenyl]methyl-phenyltin [18] and bromo[2-(dimethylaminomethyl)phenyl]dimethyltin [19]) and solution (as mentioned above).

The ¹¹⁹Sn, ¹⁵N and ¹³C NMR spectra parameters for compound **3** are analogous to the same values for compound **2** and also the coordination geometry is probably the same. The value of $J(^{119}Sn, ^{15}N) = 69.4$ Hz is clear evidence of the Sn–N coordination bond. The coordination geometry of compound **3** was proven by X-ray diffraction [18]. Only unresolved broad signal (without distinct splitting suitable for any analysis) is obtained in ¹¹⁹Sn CP/MAS NMR spectrum for **3**, which is probably caused due to the effective decoupling by fast ^{79,81}Br relaxation (as explained by Harris [15] splitting due to ¹¹⁹Sn–^{79,81}Br interaction can only be observed, when the and ^{79,81}Br relaxation is sufficiently slow).

The δ ⁽¹¹⁹Sn) chemical shift of compound 6 (-69.1 ppm) indicates the four-coordinated tin atom in this compound. On the other hand, ${}^{1}J({}^{119}Sn, {}^{13}C(1))$ and ${}^{1}J({}^{119}Sn, {}^{13}C(1'))$ coupling constant values (694.4 and 688.7 Hz, respectively) and values of bonding angles C(1)-Sn-C(1) and C(1)-Sn-C(1') (117° and 116°, respectively) are in agreement with trigonal bipyramidal configuration. The similar situation is found in quasiplanar triorganotin(IV) cations solvated or coordinated more or less strongly with two donor particles from both side of C₃Sn plane completing thus deformed trans-trigonal bipvramide structure [20]. Both NMR parameters are agree with trans-trigonal bipyramidal configuration of cation [Ph₂SnL²]⁺ (compensed by simple anion Br⁻) that was determined by X-ray diffraction in similar compounds [4]. The $J(^{119}\text{Sn}, ^{15}\text{N})$ coupling constant was not determined, due to a very broad signal in ¹⁵N NMR spectrum in CDCl₃ solution. In ¹¹⁹Sn CP/MAS NMR spectra, there is splitting of central signal into triplet (Fig. 3). This splitting have a 1:4:4 integral pattern [13], with the same distances between the neighbouring signals of the central signal (138 Hz). This pattern results from the dipolar interaction and Zeeman's effect of the ¹¹⁹Sn nucleus with 2



Fig. 4. Proposed structure of 5 in solution ((A) and (A')) and in the solid-state (B).

equiv. quadrupolar ¹⁴N nuclei. This pattern, is the direct proof of the ionic character of **6**. The structure of **6** was proven by X-ray diffraction techniques [21].

The compound 5 is unstable at higher temperature (above 30 °C) in almost all solvent. The NMR spectra were obtained from low concentration (compound 5 is rather insoluble) benzene-d₆ sample. The ¹H NMR spectrum (300 K) reveals one set of signals for 5. The upfield shift of δ (¹¹⁹Sn) (-193.38 ppm—narrow peak) is typical for five-coordinated triphenyl compounds and it signalises the similar structure with compound 2 in CDCl₃ (fluxional process—one nitrogen atom is bonded to the tin atom while the second nitrogen atom from ligand is out of the coordination sphere of tin atom; Fig. 4(A)). However, in ¹¹⁹Sn CP/MAS NMR spectra, there is the same 1:4:4 tree-line pattern with equidistant differences between neighbouring signals approximately 108 Hz and this indicates the same ionic structure $[Ph_2SnL^2]^+Cl^-$ as in compound 6. Also δ ⁽¹¹⁹Sn) chemical shift value of the compound **6** is strikingly downfield shifted (-72.6 ppm). On the basis of these facts and known structure of **6**, we can predict, that the structure of **5** is analogous to compound **6** in the solid-state (Fig. 4(B)). We propose, that Sn–N interaction is weaken and one of the nitrogen atoms goes out of the tin coordination sphere and is replaced by chlorine atom in solution. We assume fluxional processes (changing of both N(CH₃)₂ and Cl groups) in solution, analogously to literature [22], which can be, by our opinion, the main reason of thermal unstability of **5**, which undergoes to compound **5a** in almost all solution.

In compound **5a** the tin atom is five or 4 + 2-coordinated $(\delta)^{(119}\text{Sn}) = -257.5 \text{ ppm})$, due to relative strong Sn-N interaction. The increase of the intramolecular Sn-N interaction strength is also confirmed by the relative high value of coupling constant ${}^{n}J({}^{119}Sn,$ $^{13}C(CH_2)$) (65.1 Hz) and by the downfield shift of the $\delta(^{15}N) (\Delta \delta(^{15}N) = 5.5 \text{ ppm})$. The shape of coordination polyhedra of central tin atom neighbourhood is either trans-trigonal bipyramide with only one nitrogen atom bounded to the tin centre (alternatively-only one set of signals was found in ¹⁵N, ¹³C and ¹H NMR spectra for both dimethylaminomethyl groups due to fast exchange-on the NMR time scale) or distorted octahedron. Only unresolved broad signal (without distinct splitting suitable for any analysis) is obtained in ¹¹⁹Sn CP/MAS NMR spectrum for 5a, which is probably caused due to the effective decoupling by fast ^{35,37}Cl relaxation.



Fig. 5. View of four symmetrically independent molecules of 5a (PLATON [23], 30% probability ellipsoids).

Table 3

Selected bond distances (Å) and bond angles (°) and dihedral angles φ (°) of aromatic planes for four symmetrically independent molecules of **5a**

Bond lengths, angles n (Å, °)

| | 1 | 2 | 3 | 4 |
|--|------------|------------|-----------|-----------|
| $\overline{\mathrm{Sn}(n)-\mathrm{C}(n1)}$ | 2.092(10) | 2.099(9) | 2.088(9) | 2.090(10) |
| Sn(n)-C(n1') | 2.143(9) | 2.144(8) | 2.139(9) | 2.144(10) |
| Sn(n)-N(n2) | 2.402(8) | 2.391(8) | 2.420(9) | 2.426(10) |
| Sn(n)-N(n1) | 2.404(10) | 2.426(8) | 2.432(8) | 2.407(11) |
| Sn(n)- $Cl(n2)$ | 2.548(3) | 2.543(3) | 2.537(2) | 2.544(2) |
| Sn(n)- $Cl(n1)$ | 2.538(3) | 2.560(3) | 2.547(2) | 2.551(3) |
| C(n1)- $Sn(n)$ - $C(n1')$ | 176.8(4) | 177.0(3) | 177.6(4) | 179.1(4) |
| C(n1)- $Sn(n)$ - $N(n2)$ | 76.9(3) | 77.0(3) | 76.5(3) | 77.3(4) |
| C(n1')- $Sn(n)$ - $N(n2)$ | 105.2(3) | 100.1(3) | 102.1(3) | 101.9(4) |
| C(n1)- $Sn(n)$ - $N(n1)$ | 76.7(4) | 76.3(3) | 76.0(3) | 76.9(4) |
| C(n1')- $Sn(n)$ - $N(n1)$ | 101.1(3) | 106.7(3) | 105.4(3) | 103.9(4) |
| N(n2)-Sn(n)-N(n1) | 153.7(3) | 153.2(3) | 152.4(3) | 154.2(3) |
| C(n1)-Sn (n) -Cl $(n2)$ | 85.6(3) | 88.2(3) | 91.0(3) | 89.2(3) |
| C(n1')- $Sn(n)$ - $Cl(n2)$ | 92.2(3) | 91.9(2) | 90.9(2) | 90.4(3) |
| N(n2)- $Sn(n)$ - $Cl(n2)$ | 89.2(3) | 89.8(2) | 86.6(2) | 92.9(2) |
| N(n1)-Sn(n)-Cl(n2) | 89.5(3) | 88.4(2) | 91.47(18) | 85.6(2) |
| C(n1)- $Sn(n)$ - $Cl(n1)$ | 90.7(3) | 88.1(3) | 88.2(3) | 88.8(3) |
| C(n1')- $Sn(n)$ - $Cl(n1)$ | 91.5(3) | 91.9(2) | 90.0(2) | 91.6(3) |
| N(n2)-Sn(n)-Cl(n1) | 89.6(2) | 91.6(2) | 95.8(2) | 86.9(3) |
| N(n1)-Sn(n)-Cl(n1) | 89.9(3) | 88.5(2) | 85.74(18) | 93.8(3) |
| Cl(n1)- $Sn(n)$ - $Cl(n2)$ | 176.30(10) | 175.60(10) | 177.21(9) | 178.02(9) |
| $\varphi(n)$ | 75.4(4) | 73.6(3) | 42.2(4) | 74.3(3) |

The second from both structure possibilities of compound 5 was confirmed by single crystal X-ray diffraction. The coordination sphere of tin atom in compound 5a (Fig. 5) is occupied by two carbon and two chlorine atoms in equatorial *trans*-positions and two nitrogen atoms in axial positions, resulting polyhedron is closed to octahedron. From the comparison of four symmetrically independent molecules (Fig. 5) is most remarkable difference in the mutual positions of phenyl moieties for one molecule, as can be seen from dihedral angles (φ) subtended by least-square planes C(*n*1)–C(*n*6) and C(*n*1')–C(*n*6'), where *n* is number of molecule in Table 3. The crystal appears to be molecular, without significant π - π interactions.

4. Conclusions

The existence of coordination bonds in studied compounds were confirmed and their strengths were evaluated by the help of NMR spectra parameters of nuclei directly involved in Sn–N connection. The structures of studied compounds and the coordination geometry of central tin atoms are the same in solution of non-coordinating solvent (CDCl₃) and in the solid-state, except the compound **5**, which is unstable and probably due to dynamic processes in solution decomposes to diorganotin(IV) compound **5a**.

5. Supplementary material

A full list of crystallographic data and parameters including fractional coordinates is deposited under CCDC No. 156543 at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc. cam.ac.uk).

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