Rigid five-coordinate diorganotin derivatives of oxalic acid diamides, studied by ^{119}Sn-NMR and X-ray structural analysis

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Dedicated to Professor Gerd Becker on the occasion of his 60th birthday

Abstract

Bis(2-hydroxy-3,5-di-*tert*-butyl-phenylanilido) oxalic acid reacts with diorganotin dichlorides, R_2SnCl_2, in the presence of triethylamine to give the polycyclic bis(diorganotin) derivatives **1**, in which the surroundings of each tin atom correspond to a distorted trigonal bipyramid with one nitrogen and two carbon atoms in the equatorial and two oxygen atoms in the axial positions. The solid state structure was established for **1a** (R = Me) by X-ray analysis, and the agreement between the [119]Sn chemical shift in the solid state and in solution suggests that this structure is retained in solution. It was possible for the first time to determine isotope-induced chemical shifts $^1\Delta^{12/13}C(^{119}Sn)$ for five-coordinate tin nuclei at natural abundance of ^{13}C. A positive sign of $^1\Delta^{12/13}C(^{119}Sn)$ was found for R = Me (**1a**), Bu (**1b**) and Ph (**1c**). © 2000 Elsevier Science S.A. All rights reserved.
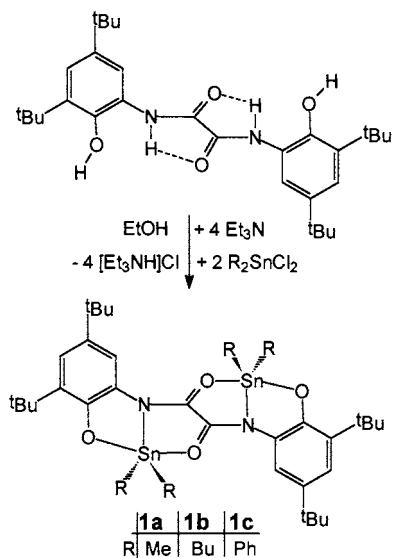
Keywords: Tin; Amides; NMR; Isotope effects; X-ray

1. Introduction

It is well documented that ^{119}Sn-NMR parameters, in particular chemical shifts $\delta\,^{119}Sn$ and coupling constants $^{2,3}J(^{119}Sn,\,^1H)$ and $^1J(^{119}Sn,\,^{13}C)$, indicate both the nature of the substituents linked to tin as well as its coordination number [1–3]. Other NMR parameters of considerable importance are isotope-induced chemical shifts which have been frequently reported for deuterium-enriched species [$^n\Delta^{1/2}H(^{119}Sn)$, where n denotes the number of bonds between tin and hydrogen] [4]; even Sn–^3H compounds have been studied in this respect [5]. The last generation of high-field NMR spectrometers provides sufficient sensitivity and resolution in order to measure isotope induced [119]Sn chemical shifts even for those rare spin-1/2-nuclei which are less

easy to enrich than ^2H and where the effects may be quite small. This was shown in an early study for $^1\Delta^{12/13}C(^{119}Sn)$ [6] and, more recently, in several reports even for $^1\Delta^{14/15}N(^{119}Sn)$ at natural abundance of ^{15}N [7]. In contrast with basic theory of isotope-induced nuclear shielding [8], it was found [6] that $^1\Delta^{12/13}C(^{119}Sn)$ can have a positive sign (the ^{119}Sn-NMR signal of the more heavy isotopomer is shifted to higher frequency). So far, all data for $^1\Delta^{12/13}C(^{119}Sn)$ have been determined for four-coordinate tin compounds, mainly for tetraorganotin compounds [6,9]. For an increase in the coordination number of tin more electronegative substituents are required. These may directly induce line broadening of the ^{119}Sn-NMR signals (e.g. for Cl, Br, I by unresolved [119]Sn–X scalar interactions) which makes the precise measurement of ^{13}C satellites difficult and time consuming. On the other hand, one frequently encounters equilibria in which several different tin coordination numbers (from 4 to 6 or 7) are involved, a situation which may arise in the case of organotin

Scheme 1.

Fig. 2. 74.6 MHz ^{119}Sn CP/MAS NMR spectrum of **1a** (rotation 5.1 kHz; 90° pulse for [1]H 3 μs; contact time 1 ms; repetition rate 5 s; 5000 transients; Herzfeld–Berger tensor analysis of the spinning sidebands [20]: $\sigma_{11} = -244.9$, $\sigma_{22} = -68.0$, $\sigma_{33} = +563.8$). The isotropic δ [119]Sn value (determined by measurement of the spectrum at a different spinning rate; 7 kHz) is indicated.

carboxylates [10], and again, this may result in fairly broad ^{119}Sn-NMR signals for which the accurate measurements of the positions of ^{13}C satellites is hampered. In this work, we report on the synthesis (Scheme 1) of the compounds **1** [11] which have a rigid structure both in the solid state and in solution. This allows for precise measurements of the first $^1\Delta^{12/13}C(^{119}\mathrm{Sn})$ values for five-coordinate [119]Sn nuclei.

2. Results and discussion

2.1. X-ray structural analysis of 1a

The molecular structure of **1a** is shown in Fig. 1 and selected bond lengths and angles are given in the legend of Fig. 1. Each tin atom occupies the centre of a
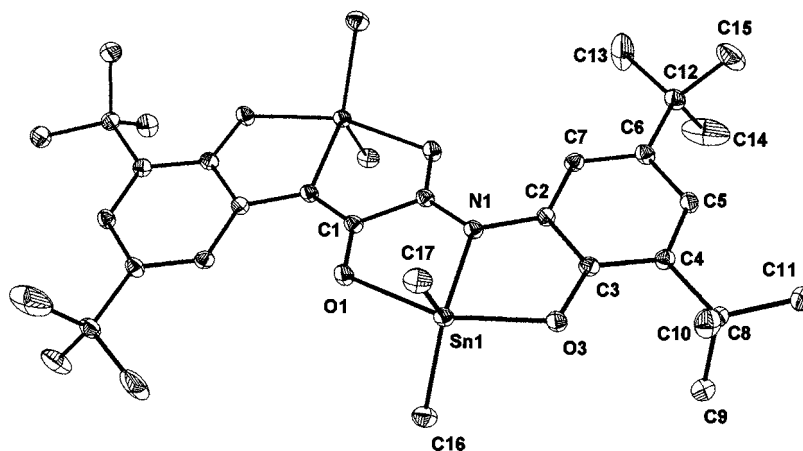
distorted trigonal bipyramid (e.g. O(3)Sn(1)O(1) 151.40(11)°; Sn(1)–O(1) 221.1(3) and Sn(1)–O(3) 205.9(3)), and there is only a small difference in the bond lengths of Sn–C. All other bond lengths and angles are also in the expected order of magnitude.

2.2. NMR spectroscopic results

2.2.1. Solid state CP/MAS NMR [119]Sn spectrum of 1a

The solid-state CP/MAS ^{119}Sn-NMR spectrum [12] of **1a** (Fig. 2) indicates that the bulk sample possesses a highly crystalline character without polymorphism. The single ^{119}Sn-NMR signal is in agreement with the presence of one molecule in the unit cell where the tin atoms are related by a centre of inversion. Most of the residual broadening of the ^{119}Sn-NMR signal can be attributed to unresolved scalar and dipolar interactions between [119]Sn and the neighbouring quadrupolar ^{14}N nucleus [13].

2.2.2. NMR spectra in solution

The δ [119]Sn value (-85.5) for **1a** in CDCl$_3$ solution is almost identical with the isotropic δ [119]Sn value for the solid sample (-83.6). Furthermore, the ^{119}Sn-NMR spectrum of the solution of **1a** shows [117]Sn satellites

Fig. 1. Molecular structure of **1a**. Selected bond lengths (pm) and angles (°): Sn(1)–O(3) 205.9(3), Sn(1)–O(1) 221.0(3), Sn(1)–N(1) 213.3(3), Sn(1)–C(16) 210.4(5), Sn(1)-C(17) 210.2(5); O(3)Sn(1)O(1) 151.40(11), N(1)Sn(1)O(1) 74.66(12), O(3)Sn(1)N(1) 77.32(12), O(3)Sn(1)C(17) 101.02(17), O(3)Sn(1)C(16) 98.81(17), C(16)Sn(1)O(1) 90.56(16), C(17)Sn(1)O(1) 94.09(17), C(17)Sn(1)N(1) 110.62(17), C(16)Sn(1)N(1) 120.50(17).
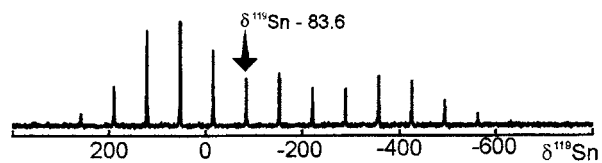
Table 1
^{13}C- and ^{119}Sn-NMR data [a] of compounds **1** and some other organotin compounds for comparison

	$\delta\,^{119}Sn\,\{^4J(Sn,\,Sn)\}$	$^1\Delta^{12/13}C(^{119}Sn)$	$\delta\,^{13}C\,[J(^{119}Sn,\,^{13}C)]$
1a	$-85.5\,\{40.8\}$	$+44.5$	0.8 [621.0] (SnMe$_2$); 35.9, 35.0, 32.4, 29.9 (^{t}Bu); 158.7 [54.0, 9.4] (C=O); 153.7 [23.5] (2), 137.4 [<1.5] (3), 136.5 [11.4] (5), 127.8 [45.8] (1), 122.0 [<1.5] (4), 115.2 [26.6] (2)
1b	$-122.5\,\{41.5\}$	$+35.0$	20.9 [577.3], 27.2 [28.0], 26.7 [88.0], 13.6 [<2.0] (SnBu$_2$); 35.2, 34.4, 31.7, 29.2 (^{t}Bu); 158.8 [45.0, 11.0] (C=O); 154.1 [23.0] (2), 137.0 [< 1.5] (3), 136.5 [10.0] (5), 128.2 [43.0] (1), 121.7 [<2.0] (4), 115.4 [22.8] (2)
1c	$-258.8\,\{51.8\}$	$+22.4$	137.8 [955.2] (i), 136.2 [55.8] (o), 129.0 [85.5] (m), 130.8 [17.5] (p) (SnPh$_2$); 35.4, 34.5, 31.7, 29.7 (^{t}Bu); 157.9 [54.5, 6.5] (C(O)); 153.5 [22.6] (2), 138.3 [1.3] (5), 137.2 [15.9] (3), 127.8 [48.8] (1), 122.6 [<1.5] (4), 115.7 [22.8] (6)
Me$_4$Sn	0	-18 [6]	-9.6 [336.6]
Bu$_4$Sn	-11.5	-20 [6]	9.1 [313.1], 29.6 [20.0], 27.6 [52.0], 14.0 [<2.0]
Ph$_4$Sn	-128.1	> -10 [6]	138.1 [530.8] 137.3 [37.5], 128.7 [52.0], 129.1 [11.7]

[a] In CDCl$_3$; coupling constants $^4J(^{119}Sn,\,^{117}Sn)\,\{\pm 1\,Hz\}$ are given in curved brackets and $J(^{119}Sn,\,^{13}C)\,[\pm 0.2\,Hz]$ are given in brackets; isotope induced chemical shifts $^1\Delta^{12/13}C(^{119}Sn)$ are given in ppb, and a positive sign denotes a shift to high frequency with respect to the lighter isotopomer.

according to $J(^{119}Sn,\,^{117}Sn) = 40.8$ Hz which proves unambiguously that the molecule contains two equivalent tin atoms. Thus, the prominent structural features of the solid state are retained in solution. The same situation can be safely assumed for **1b** and **1c** (solution state NMR data of **1a,b,c** are given in Table 1). The relationship between bond angles CSnC in dimethyltin derivatives and the magnitude of $|^1J(^{119}Sn,\,^{13}C)|$ [14] predicts for **1a** the angle C–Sn–C as 130.7° (between extremes of 119.2 and 143.4°) which is in reasonable agreement with the experimental value C(17)Sn-(1)C(16) = 127.97(19)°. The analogous relationship for dibutyltin compounds [15] predicts the angle C–Sn–C in **1b** as 132.3° (between extremes of 114.0 and 153.5°).

The solution state ^{119}Sn-NMR spectra are most efficiently recorded by using the refocused INEPT pulse sequence with ^1H decoupling [16]. This allows for convenient adjustment of repetition delays in order to minimise temperature gradients in the sample. Typically, the line widths of the ^{119}Sn-NMR signals were in the order of 3–5 Hz in the case of $B_0 = 11.5$ T or between 2–3 Hz for $B_0 = 6.9$ T. At higher field strength B_0 the ^{119}Sn nuclear spin relaxation becomes increasingly dominated by the contribution arising from chemical shift anisotropy ($\Delta\sigma$ ca. 900 ppm; cf. Fig. 2). In any case, the signals are fairly sharp and therefore, with both spectrometers, ^{13}C satellites are readily observed, and their positions with respect to the parent signal can be accurately determined (Fig. 3). All three isotope induced shifts $^1\Delta^{12/13}C(^{119}Sn)$ are positive [**1a**, +44.5 ppb (Me); **1b**, +35.0 ppb (Bu); **1c**, +22.4 ppb (Ph)], and the significance of these data becomes obvious by comparison with $^1\Delta^{12/13}C(^{119}Sn)$ for the respective tetraorganotin compounds [−18 ppb (Me), −18 ppb (Bu), > −10 ppb (Ph) [6]]. Although, the inversion of the sign from negative to positive for $^1\Delta^{12/13}C(^{119}Sn)$ has

been reported [6], the large positive values found in this work for the compounds **1** are without precedence. It appears that the crude relationship between $^1\Delta^{12/13}C(^{119}Sn)$ and the magnitude of $|^1J(^{119}Sn,\,^{13}C)|$ is further corroborated by the data for **1**. The largest set of data so far exists for SnMe derivatives [3,6,9] The sign inversion of $^1\Delta^{12/13}C(^{119}Sn)$ seems to take place when the magnitude of $|^1J(^{119}Sn,\,^{13}C_{Me})|$ approaches 400 Hz. In the case of **1a**, we find $|^1J(^{119}Sn,\,^{13}C_{Me})| = 621.0$ Hz, and this goes together with a significantly positive $^1\Delta^{12/13}C_{Me}(^{119}Sn)$ value. Similar relationships between $^1\Delta^{12/13}C_R(^{119}Sn)$ and $|^1J(^{119}Sn,\,^{13}C_R)|$ are expected for R = Bu or Ph.
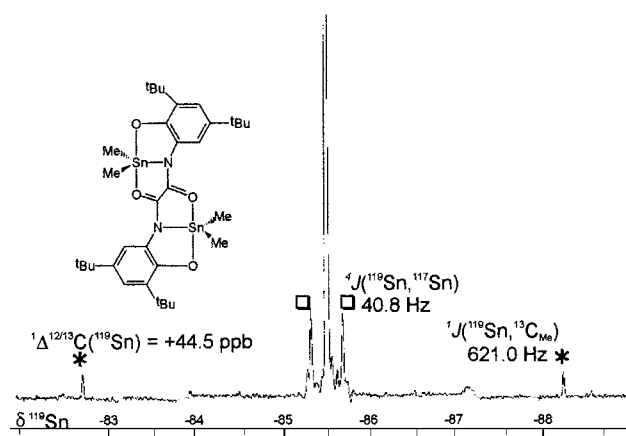

Fig. 3. 111.9 MHz ^{119}Sn-NMR spectrum of **1a** (in CDCl$_3$ at 22°C) recorded by the refocused INEPT pulse sequence with ^1H decoupling [16b–d] [based on $^2J(^{119}Sn,\,^1H_{Me}) = 77.0$ Hz; aquisition time 3 s; repetition time 8 s; result of 1024 transients]. The satellites due to $^1J(^{119}Sn,\,^{13}C_{Me})$ and $^2J(^{119}Sn,\,^{117}Sn)$ are marked; close to the bottom of the parent signal a number of other ^{13}C satellites can be seen which correspond to the various long range coupling constants $^nJ(^{119}Sn,\,^{13}C)$ which are also measured in the ^{13}C-NMR spectrum (see Table 1).

The change in the sign of $^1\Delta^{12/13}C(^{119}Sn)$ is still a puzzling fact. The fairly large range of $^1\Delta^{12/13}C(^{119}Sn)$ invites one to collect a larger data set, including more extreme bonding situations in organotin compounds. Thus, other penta- or hexa-coordinate tin compounds, monomeric tin(II) compounds such as diorganostannylenes or three-coordinate anionic species such as $[R_3Sn]^-$ might be of interest with respect to $^1\Delta^{12/13}C(^{119}Sn)$. In the latter cases, the influence of the free pair of electrons can be evaluated. Sign changes $^1\Delta^{12/13}C(X)$ have also been observed for other heavy nuclei (e.g. for $^1\Delta^{12/13}C(^{207}Pb)$ [6] or $^1\Delta^{12/13}C(^{199}Hg)$ [17]), and there are indications that $^1\Delta^{12/13}C(^{29}Si)$ data may have either sign [6,18]. A suggestion [19] that the assumption of an increasingly positive charge at the site of the nucleus in question could help to explain this is questionable, although it has been noted that the $^1\Delta^{1/2}H(^{119}Sn)$ values for solvated ionic species $[SnH_3]^-$ are large and negative [4a] whereas those for $[SnH_3]^+$ are small and negative [4b].

3. Conclusions

The agreement between ^{119}Sn chemical shifts in solution and in the solid state indicates that the rigid structure of the five-coordinate tin compounds of type **1** is retained in solution. This made it possible to measure precise isotope-induced chemical shifts $^1\Delta^{12/13}C(^{119}Sn)$ for the first time for five-coordinate organotin compounds. The rather large positive values $^1\Delta^{12/13}C(^{119}Sn)$ (in contrast to mainly negative values for tetraorganotin compounds) show that such data deserve more attention since they contain information on the bonding situation of the tin atom. The relationship between $^1\Delta^{12/13}C(^{119}Sn)$ values and the magnitude of $\left| ^1J(^{119}Sn, {}^{13}C) \right|$ is another interesting aspect of isotope-induced chemical shifts.

4. Experimental

4.1. General

All preparative work and the handling of compounds were carried out by observing necessary precautions to exclude air and moisture. Starting materials were commercial products and used without further purification.

EI mass spectra (20 eV) were obtained with a HP 5958 spectrometer. NMR spectra were recorded by using Bruker MSL 200 (solide state NMR; double bearing probehead; the compound was packed into a 5 mm ZrO_2 rotor), and Bruker DRX 300 and DRX 500 instruments, all equipped with multinuclear units. The compounds were dissolved in $CDCl_3$ (ca. 30–40 mg in 0.5 ml) in 5 mm (o.d.) tubes and measured at $22 \pm 1°C$.

Chemical shifts are given with respect to solvent signals $[\delta\,^1H\,(CHCl_3 \text{ in } CDCl_3) = 7.24; \delta\,^{13}C\,(CDCl_3) = 77.0]$ and external references for $\delta\,^{119}Sn\,(Me_4Sn) = 0$, $\Xi\,^{119}Sn = 37.290665$ MHz]. ^{119}Sn-NMR spectra of solutions were measured by the refocused INEPT pulse sequence with ^1H decoupling [12], based on $^{2,3}J(^{119}Sn, {}^1H)$ (see the legend of Fig. 3 for typical conditions).

4.2. General procedure for the synthesis of **1**

The oxalic acid bis(amide) (0.5 g; 1 mmol) and triethylamine (0.5 ml; 4 mmol) were dissolved in ethanol (10 ml). A solution of dimethyltin dichloride (0.45 g; 2 mmol) in ethanol (5 ml) was added dropwise at room temperature. A solid was formed immediately, and after 10 min the solid (0.77 g; 98%) was filtered off and washed with hexane. The compound was recrystallized from $EtOH/CH_2Cl_2$ to give the pure product **1a** (m.p. 382–384°C). Single crystals were grown from $CDCl_3$ solutions: Anal. Calc. for $C_{34}H_{52}N_2O_4Sn_2 \cdot 1/8$ $CDCl_3$: C, 51.7; H, 6.6; N, 3.54. Found: C, 50.92; H, 6.34; N, 4.48%. MS (EI, 20 eV): $m/e = 791$ (M^+).

1a: ^1H-NMR (500.13 MHz; $CDCl_3$): $\delta\,^1H\,[J(^{119}Sn, {}^1H)] = 8.39$ d $^4J(H, H) = 2.4$ Hz, 7.19 d $^4J(H, H) = 2.4$ Hz (4H, C_6H_2); 1.43 s, 1.35 s (36H, ^tBu); 0.84 [77.0] s (12H, $SnMe_2$).

1b: m.p. 168–170°C; ^1H-NMR (500.13 MHz; $CDCl_3$): $\delta\,^1H = 8.53$ d $^4J(H, H) = 2.4$ Hz, 7.18 d $^4J(H, H) = 2.4$ Hz (4H, C_6H_2); 1.45 s, 1.36 s (36H, ^tBu); 1.74 m, 1.54 m, 1.43 m, 0.93 t $^3J(H, H) = 7.4$ Hz (36H, $SnBu_2$).

1c: m.p. 366–368°C; ^1H-NMR (500.13 MHz; $CDCl_3$): $\delta\,^1H\,[J(^{119}Sn, {}^1H)] = 8.69$ d $^4J(H, H) = 2.4$ Hz, 7.35 d $^4J(H, H) = 2.4$ Hz (4H, C_6H_2); 7.91 [84.0] m (8H, $SnPh_2(o)$); 7.40 m (12H, $SnPh_2(m, p)$); 1.65 s, 1.48 s (36H, ^tBu).

4.3. X-ray structural analysis of **1a**

$C_{36}H_{52}N_2O_4Sn_2 \cdot 2CHCl_3$, orange, rectangular crystal (mounted on a glass fibre) of dimensions $0.62 \times 0.28 \times 0.28$ mm crystallises in the triclinic space group $P\bar{1}$ with the lattice parameters: $a = 983.8(2)$, $b = 1051.5(2)$, $c = 1171.4(2)$ pm, $\alpha = 70.00(3)°$, $\beta = 87.34(3)°$, $\gamma = 82.59(3)°$, $V = 1129.2(4)$ 10^6 pm^3, $Z = 1$, $\mu = 1.497$ mm^{-1}; $F(000) = 518$; diffractometer: Enraf-Nonius (Mo-K_α with $\lambda = 71.073$ pm); 4209 reflections collected at 193 K in the range $5.52 \leq 2\theta \leq 51.94°$, 4209 reflections independent, 3614 assigned to be observed $[F > 4\sigma(F)]$, semi-empirical absorption correction, max./min. transmission 0.6793/0.4590; solution by heavy-atom-method; full-matrix least-squares refinement (SHELXL) against F^2 with 234 parameters converged at R_1/w_2-values of 0.0392/0.1019; the max./min. residual electron density was $1.099/-1.137 \times 10^{-6}$ e pm^{-3}.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 142217 for **1a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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