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^{13}C, ^{15}N AND ^{119}Sn NMR SPECTRAL EVIDENCE FOR TIN FIVE-COORDINATION IN TRIORGANOTIN(IV) OXINATES

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Summary

The ^{13}C and ^{119}Sn NMR spectra of tri(1-butyl)tin(IV) and triphenyltin(IV) oxinates and 1-naphthoxides in neat liquid and deuteriochloroform, pentadeuteriopyridine and hexamethylphosphortriamide solutions, and the ^{15}N NMR spectra of both the oxinates and 8-methoxyquinoline in deuteriochloroform have been recorded. From the comparison of chemical shifts $\delta(^{13}C)$, $\delta(^{15}N)$ and $\delta(^{119}Sn)$ and coupling constants $^nJ(^{119}Sn^{13}C)$ of the compounds it is concluded that the triorganotin(IV) oxinates, both as the neat liquid and in solution, form complexes containing five-coordinate tin atoms. In the neat liquid and in deuteriochloroform (a non-coordinating solvent) oxinates form chelate complexes with a *cis*-trigonal bipyramid arrangement. In coordinating solvents (pentadeuteriopyridine, hexamethylphosphortriamide) these are equilibria involving the formation of small amounts of oxinate complexes with one solvent molecule. These complexes have *trans*-trigonal bipyramid geometry with butyl or phenyl groups in equatorial plane and the monodentate oxinate group and a solvent molecule in axial positions.

Introduction

The bidentate behaviour of the oxine ligand has been well established in monoorganotin tris(oxinates) and in diorganotin bis(oxinates) [1–5]. The published information on triorganotin(IV) oxinates is conflicting. These compounds are sometimes formulated as chelate complexes involving five-coordinate tin atom [6–10] and sometimes as involving a four-coordinate tin atom and a monodentate oxinate molecule [11–13]. Recently an attempt was made to solve this problem using ^{119}Sn NMR spectra of triorganotin(IV) oxinates [14]; the $\delta(^{119}Sn)$ values were regarded as indicative of the presence of the four-coordinate tin atom but this interpretation is in

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conflict with our conclusions [15,16] reached by analysis of ^{119}Sn and ^{13}C NMR spectra of some triphenyltin(IV) and tri(1-butyl)tin(IV) compounds. The aim of this paper is to give some more evidence in support of our suggestion that triorganotin(IV) oxinates in neat liquid and in non-coordinating solvents solutions form five-coordinate chelate complexes.

Experimental

^{13}C, ^{15}N and ^{119}Sn NMR spectra were measured on a JEOL spectrometer JNM-FX 100 at 25.047, 10.095, or 37.14 MHz, respectively, at 300 K. Chemical shifts $\delta(^{119}\text{Sn})$ were measured in deuteriochloroform, pentadeuteriopyridine, and hexamethylphosphortriamide solutions at two concentrations (see Table 1), or as neat liquids. Chemical shifts $\delta(^{13}\text{C})$ and $\delta(^{15}\text{N})$ and coupling constants $^nJ(^{119}\text{Sn}^{13}\text{C})$ were obtained by use of more concentrated solutions. Chemical shifts $\delta(^{13}\text{C})$ were referred to a suitable solvent signal and converted to the δ-scale. A value of 13.50 ppm was assigned to the methyl carbon of the tri(1-butyl)tin group in the neat compounds **1a** and **1b**. $\delta(^{119}\text{Sn})$ values are related to external neat tetramethylstannane. ^{15}N NMR spectra were recorded in the presence of tris(acetylacetonato)chromium(III) (20 mg/1 ml); values of $\delta(^{15}\text{N})$ are referred to external neat nitromethane (25% ^{15}N). A more detailed description of the experimental conditions is given in refs. 15,16.

Tri(1-butyl)tin(IV) and triphenyltin(IV) oxinates (**1a** and **2a**) and 8-methoxyquinoline (**3**) were prepared by published methods [15–17].

*Preparation of tri(1-butyl)tin(IV) 1-naphthoxide (**1b**)*

1-Naphthol (2.20 g) was dissolved in 50 ml of ethanol containing a stoichiometric quantity of sodium ethoxide. After addition of 4.82 g of tri(1-butyl)chlorstannane in ethanol (50 ml) the solution was stirred for 1 h at room temperature. The sodium chloride was filtered off and ethanol was evaporated from the filtrate at reduced pressure. The oily residue was diluted with n-hexane (50 ml) and refiltered, and the hexane was evaporated in vacuo. 5.15 g of oily product was obtained (79%).

Analysis: Found: C, 60.89; H, 7.80; Sn, 27.62. $C_{22}H_{34}OSn$ calcd.: C, 61.00; H, 7.91; Sn, 27.40%.

*Preparation of triphenyltin(IV) 1-naphthoxide (**2b**)*

Water was removed azeotropically from bis(triphenylstannyl)oxide (2.50 g) and 1-naphthol (1.0 g) in dry benzene (50 ml). The distillation residue was filtered and then concentrated under reduced pressure to ca. 10 ml. After addition of 25 ml hexane colourless crystals separated out, and then were filtered off, washed with cold pentane and dried in vacuo. The yield was 2.8 g (81%), m.p. 61–63°C. Analysis: Found: C, 68.01; H, 4.55; Sn, 24.20. $C_{28}H_{22}OSn$ calcd.: C, 68.19; H, 4.50; Sn, 24.07%. This compound was prepared as a "gum" by Poller and Ruddick [9].

Results and discussion

For triorganotin(IV) oxinates in the solid state Poller and Ruddick [9] established the *cis*-trigonal bipyramid structure with a chelating oxinate group. Their conclusions were reached on the basis of a comparison of the Mössbauer spectral data for triorganotin(IV) oxinates and isoelectronic 1-naphthoxides. We used a similar approach for judging the structures of oxinates in solutions, i.e. we compared the ^{13}C and ^{119}Sn NMR spectral data for tri(1-butyl)tin(IV) oxinate (**1a**) and triphenyltin(IV) oxinate (**2a**) with those for their 1-naphthoxide analogues (**1b** and **2b**), and also compared the chemical shifts $\delta(^{15}N)$ of both oxinates and of 8-methoxyquinoline (**3**). The ^{13}C, ^{15}N and ^{119}Sn NMR spectra parameters of the studied compounds as neat liquid and in solutions of various solvents are summarized in Tables 1 and 2.

Chemical shifts $\delta(^{119}Sn)$

Table 1 shows that the $\delta(^{119}Sn)$ values depend primarily on the type of substituent in the triorganotin(IV) group (1-butyl- or phenyl-), on the concentration, on the type of solvent, and on the character of the group bonded to the tin atom through oxygen (oxinate or 1-naphthoxide). If the effect of the triorganotin(IV) group substituent is neglected, the most significant differences in the $\delta(^{119}Sn)$ values are caused by change in the type of group which is bonded to the tin atom through oxygen. The compounds **1b** and **2b** show $\delta(^{119}Sn)$ values typical of tri(1-butyl)tin(IV) or triphenyltin(IV) compounds containing a four-coordinate tin atom in the neat liquid and in deuteriochloroform [15,16]. On the other hand, for compounds **1a** and **2a** under the same conditions $\delta(^{119}Sn)$ is shifted by ca. 85–100 ppm upfield. We assume that these differences cannot be explained by either steric or electronic (inductive or mesomeric) effects of the oxinate or 1-naphthoxide group. Steric effects of both the groups are comparable, and electronic effects can cause changes of only a few ppm as is evident from the existence of a linear correlation $\delta(^{119}Sn) \sim pK_a$ for conjugated acids in triphenyltin(IV) carboxylates ($\Delta\delta(^{119}Sn)/pK_a = 11.81$ ppm) [18] and from the similar values of pK_a of 1-naphthol (9.30) and 8-hydroxyquinoline (9.81) [19]. The observed differences in $\delta(^{119}Sn)$ chemical shifts between **1a** and **1b** or between **2a** and **2b** can thus be attributed to the five-coordinate tin atom in **1a** and **2a**.

In recording NMR spectra of organotin(IV) compounds in solutions non-coordinating solvents are preferable to coordinating ones to preclude possible changes in the coordination number of the tin atom. On the other hand, if coordinating solvents are deliberately used it is possible to obtain further useful structural information. Thus, the values of $\delta(^{119}Sn)$ of **1b** and **2b** in coordinating solvents (pentadeuteriopyridine, hexamethylphosphortriamide) are shifted by 120–180 ppm upfield with respect to the values in deuteriochloroform, i.e. into the region of values typical of *trans*-trigonal bipyramidal tri(1-butyl)tin(IV) or triphenyltin(IV) complexes with one coordinated solvent molecule. The corresponding changes of $\delta(^{119}Sn)$ for compounds **1a** and **2a** are substantially lower, amounting only to 10–70 ppm. This can be attributed to the reversible displacement reaction [16] in which the chelated complex **1a** or **2a** gives small amount of a product containing one solvent molecule and a monodentate oxinate group.

From the variations of the $\delta(^{119}Sn)$ values for the compounds studied conclusions can be drawn about the position of the equilibrium and about the strength of the bond between the ligand and the central atom. The greater the difference between the values of $\delta(^{119}Sn)$ in deuteriochloroform and in the coordinating solvent, the further is the equilibrium shifted to the side of the products, and the more stable are the bonds formed. Our results confirm that **2a** is more stable than **1a** and that the complexes with hexamethylphosphortriamide are stronger than those with pyridine,

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TABLE 1

^{15}N AND ^{119}Sn NMR PARAMETERS OF COMPOUNDS **1–3**

No.	Compound	Solvent	$\delta(^{119}Sn)$ (ppm)		$^nJ(^{119}Sn^{13}C)$ (Hz)			$\delta(^{15}N)$ (ppm)
			a	*b*	$n=1$	$n=2$	$n=3$	
1a[c]	Bu_3Sn(oxinate)	neat	–	30.1	393.0	17.0	63.4	−99.0
		$CDCl_3$	38.2	37.6	390.6	18.3	68.4	−99.8
		py-d_5[d]	26.6	26.8	395.5	19.5	67.2	−100.1
		hmpta[e]	−16.7	−13.3	444.3	23.2	72.0	[f]
1b	Bu_3Sn(1-naphthoxide)	neat	–	115.8	354.0	20.4	61.0	–
		$CDCl_3$	123.7	123.0	354.0	20.2	62.3	–
		py-d_5	5.1	10.6	433.3	26.9	70.8	–
		hmpta	−56.0	−55.2	500.4	26.9	78.2	–
2a	Ph_3Sn(oxinate)	$CDCl_3$[g]	–	−190.1	633.1	47.8	62.5	−117.5
		py-d_5	−210.1	−209.4	666.0	47.8	62.6	−119.2
		hmpta	−260.9	−258.5	691.4	47.8	63.5	[f]
2b	Ph_3Sn(1-naphthoxide)	$CDCl_3$	−92.6	−92.4	631.1	46.4	63.4	–
		py-d_5	−244.2	−244.4[h]	805.6[h]	[i]	[i]	–
		hmpta	−273.1	−273.1	843.4	48.8	72.0	–
3	8-Methoxychinoline	$CDCl_3$	–	–	–	–	–	−82.5

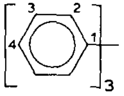
[a] Concentration ca. 50 mg of the sample for 1 ml of the solvent. [b] Concentration ca. 250 mg ml^{-1}. [c] Ref. 16. [d] py-d_5 = pentadeuteriopyridine. [e] Hmpta = hexamethylphosphortriamide. [f] Not found. [g] Ref. 15. [h] Saturated solution. [i] Overlapped.

TABLE 2

CHEMICAL SHIFTS $\delta(^{13}C)$ OF COMPOUNDS 1 AND 2

Compound No.[b]	Solvent	$\delta(^{13}C)$[a] (ppm)				
		C(1)	C(2)	C(3)	C(4)	Others (oxinate or 1-naphthoxide)
1a	neat	19.79	28.12	27.00	13.50	157.81, 143.33, 139.73, 136.46, 129.05, 128.76, 120.57, 113.85, 113.41
	$CDCl_3$	19.93	28.12	27.14	13.64	157.61, 143.72, 139.77, 136.70, 129.15, 128.91, 120.86, 113.80, 113.80
	py-d_5	20.55	28.69	27.62	14.04	158.67, 144.95, 140.45, 137.42, 129.92, 129.48, 121.73, 114.37, 114.37
	hmpta	20.21	27.76	26.64	13.19	158.96, 144.20, 140.25, 136.35, 129.18, 127.82, 120.90, 113.30, 112.71
1b	neat	15.89	27.78	26.95	13.50	158.83, 135.39, 129.25, 127.80, 126.18, 125.45, 123.60, 123.30, 117.50, 110.83
	$CDCl_3$	16.13	27.78	27.00	13.50	158.44, 135.14, 128.90, 127.35, 126.27, 125.64, 123.93, 122.96, 117.70, 111.21
	py-d_5	17.92	28.84	27.62	14.12	160.82, 136.40, 130.26, 127.68, 127.08, 126.21, 124.56, 124.07, 116.61, 111.15
	hmpta	18.50	27.86	26.74	13.24	161.11, 135.18, 129.62, 126.50, 126.36, 124,36, 123.63, 121.78, 113.35, 109.25
2a	$CDCl_3$	145.03	136.06	128.22	128.69	155.99, 144.24, 138.32, 137.93, 129.51, 128.00, 121.24, 114.00, 113.53
	py-d_5	146.63	136.84	128.89	129.24	156.92, 145.14, 138.71, 136.90, 130.13, 129.54, 122.10, 114.54, 113.84
	hmpta	148.13	135.85	127.23	127.43	156.63, 143.76, 138.58, 137.53, 129.18, 128.91, 121.42, 112.50, 112.18
2b	$CDCl_3$	137.43	136.46	129.10	130.37	157.61, 135.04, 128.56, 127.39,3 126.13, 125.88, 124.32, 123.10, 118.47, 111.70
	py-d_5[c]	142.64	137.33	129.14	129.87	160.83, 127.90, 127.34, 123.34, 115.78, 112.13[d]
	hmpta	143.95	136.06	127.43	127.87	160.23, 134.89, 129.43, 128.06, 125.97, 124.26, 123.77, 121.92, 113.39, 110.71

[a] $[C^4H_3 \cdot C^3H_2 \cdot C^2H_2 \cdot C^1H_2]_3SnX$ or



, X = oxinate (a) or 1-naphthoxide (b), [b] See Table 1. [c] Saturated solution, [d] Other chemical shifts are overlapped by signals of the solvent.

in keeping with the values of the donor numbers [20]. From small changes in $\delta(^{119}Sn)$ for both oxinates in pyridine solutions conclusions can also be drawn about the relative strengths of the chelate complexes, in which the nitrogen atom of the chelate group is evidently at least as a strong donor as the nitrogen atom of the pyridine molecule. This is also confirmed by the $\delta(^{15}N)$ values of species **1a** and **2a** in deuteriochloroform and pentadeuteriopyridine (see later).

Small concentration dependences of $\delta(^{119}Sn)$ can be explained in terms of association equilibrium, or of displacement reactions [16], or of variations in the magnetic susceptibilities of the solutions.

Coupling constants $^nJ(^{119}Sn^{13}C)$

The $^nJ(^{119}Sn^{13}C)$ values for compounds **1** and **2** and their dependence upon the solvent character are also consistent with the change of compounds coordination and configuration. Values of $^1J(^{119}Sn^{13}C)$ for **1a** and **1b**, like those of **2a** and **2b** differ only slightly in neat liquid and in deuteriochloroform. This is consistent with the assumption that in both of the four-coordinate triorganotin(IV) compounds and in their *cis*-trigonal bipyramidal five-coordinate chelates, hybrid orbitals sp^3 [15,16] participate in the Sn–C bond. The striking increase in $^1J(^{119}Sn^{13}C)$ for compounds **1b** and **2b** in pentadeuteriopyridine, and especially in hexamethylphosphortriamide, is due to the formation of *trans*-trigonal bipyramide complexes, where the triorganotin(IV) groups forms the equatorial plane (using sp^2-hybrid orbitals of the tin atom) and one solvent molecule and 1-naphthoxide group occupy the axial positions. Substantially smaller changes in values of $^1J(^{119}Sn^{13}C)$ of compounds **1a** and **2a** due to the both coordination solvents result from the fast reversible displacements discussed earlier. Similar but smaller effects can be observed also in ^2J $(^{119}Sn^{13}C)$ and, more particularly, in $^3J(^{119}Sn^{13}C)$.

Chemical shifts $\delta(^{13}C)$

In the ^{13}C NMR spectra of the compounds studied (except for **2b** in pentadeuteriopyridine in which there is overlapping of signals by the solvent resonances) the number of the signals found corresponds with the presence of magnetically non-equivalent carbon atoms. This, along with the $\delta(^{13}C)$ values for individual carbon atoms, is a clear proof of the identity of the compounds studied (see Table 2). Values of $\delta(^{13}C(1))$ also support the conclusions about the coordination and configuration of compounds in solution. In agreement with the conclusions in refs. 15,16 the formation of *trans*-trigonal bipyramidal triorganotin(IV) complexes is associated with a slight downfield shift of $\delta(^{13}C(1))$. The ready formation of such complexes of compounds **1b** and **2b** in pentadeuteriopyridine, or hexamethylphosphortriamide causes an increase of $\delta(^{13}C(1))$ by 2–6 ppm as compared with the value in deuteriochloroform. A substantially smaller change of $\delta(^{13}C(1))$ in compounds **1a** and **2a** (under the same conditions 0.5–3 ppm) indicates the reluctance of the chelate complexes to form *trans*-trigonal bipyramidal complexes with the monodentate oxinate ligand and one molecule of the coordinating solvent.

Chemical shifts $\delta(^{15}N)$

The $\delta(^{15}N)$ values for compounds **1a** and **2a** are markedly shifted upfield by 17–35 ppm compared those for 8-methoxyquinoline (**3**), which we use as a model, in which the quinolinyl group is bonded through the oxygen atom, as in compounds **1a** and **2a**, but in which because of the absence of the acceptor centre, coordination is impossible. The direction of the shifts caused by the coordination and the differences in $\delta(^{15}N)$ values are in good agreement with the values found for coordinated and non-coordinated silatranes [21] and stannatranes [22,23] and a number of other donor-acceptor complexes involving the donor nitrogen atom [24]. The same effect can be observed with 8-hydroxyquinoline itself, which, because of the hydrogen bond O–H ··· N (in combination with the substitution shift of the OH group) shows an upfield shift of $\delta(^{15}N)$ $(-95 \pm 4$ ppm) [25] with respect to both compound **3** and quinoline $(-72 \pm 3$ ppm) [24]. All these facts are in agreement with a "reverse" trend [26] in ^{15}N NMR spectroscopy, i.e. electron-withdrawing substituents induce upfield ^{15}N shifts.

Higher upfield shifts of $\delta(^{15}N)$ in compound **2a**, in comparison with **1a**, is in agreement with the conception of generally stronger triphenyltin(IV) complexes. The relative independence of $\delta(^{15}N)$ values upon the solvent type is consistent with the previously discussed strength of the chelate arrangement of oxinate ligands in both compounds. Our attempt to measure $\delta(^{15}N)$ values for compounds **1a** and **2a** in hexamethylphosphortriamide using our spectrometer (at 10.095 MHz, with 10 mm tube) was unsuccessful.

References

1 E.O. Schlemper, Inorg. Chem., 2 (1963) 243.
2 K. Kawakami, Y. Kawasaki and R. Okawara, Bull. Chem. Soc., Japan, 40 (1967) 2693.
3 W. McFarlane, J. Maire and M. Delmas, J. Chem. Soc., Dalton Trans., (1972) 1862.
4 J. Otera, T. Hinoishi and R. Okawara, J. Organomet. Chem., 202 (1980) C93.
5 J. Otera, T. Hinoishi, Y. Kawabe and R. Okawara, Chem. Lett., (1981) 273.
6 M. Wada, K. Kawakami and R. Okawara, J. Organomet. Chem., 4 (1965) 159.
7 K. Kawakami and R. Okawara, J. Organomet. Chem., 6 (1966) 249.
8 Y. Kawasaki, Org. Magn. Reson., 2 (1970) 165.
9 R.C. Poller and J.N.R. Ruddick, J. Organomet. Chem., 39 (1972) 121.
10 Y. Kawasaki, Bull. Chem. Soc., Japan, 49 (1976) 2319.
11 R. Barbieri, G. Faraglia, M. Giustiniani and L. Roncucci, J. Inorg. Nucl. Chem., 26 (1964) 203.
12 L. Roncucci, G. Faraglia and R. Barbieri, J. Organomet. Chem., 1 (1964) 427.
13 L. Roncucci, G. Faraglia and R. Barbieri, J. Organomet. Chem., 6 (1966) 278.
14 H.C. Clark, V.K. Jain, I.J. McMahon and R.C. Mehrotra, J. Organomet. Chem., 243 (1983) 299.
15 J. Holeček, M. Nádvorník, K. Handlíř and A. Lyčka, J. Organomet. Chem., 241 (1983) 177.
16 M. Nádvorník, J. Holeček, K. Handlíř and A. Lyčka, J. Organomet. Chem., 275 (1984) 43.
17 A. Kaufmann and E. Rothlin, Chem. Ber., 49 (1916) 581.
18 J. Holeček, K. Handlíř, M. Nádvorník and A. Lyčka, J. Organomet. Chem., 258 (1983) 147.
19 G. Kortüm, W. Vogel and K. Andrussov, Dissociation Constants of Organic Acids in Aqueous Solution, Butterworth, London, 1961.
20 V. Gutmann and E. Wychera, Inorg. Nucl. Chem. Lett., 2 (1966) 257.
21 V.A. Pestunovich, S.N. Tandura, B.Z. Shterenberg, V.P. Baryshok and M.G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2159.
22 K. Jurkschat, C. Mügge, A. Tzschach, A. Zschunke, G. Engelhardt, E. Lippmaa, M. Mägi, M.F. Larin, V.A. Pestunovich and M.G. Voronkov, J. Organomet. Chem., 171 (1979) 301.
23 E.E. Liepinsh, I.S. Birgele, G.I. Zelchan and E. Lukevits, Zh. Obshch, Khim., 49 (1979) 1537.
24 M. Witanowski, L. Stefanik and H. Januszewski, in M. Witanovski and G.A. Webb (Eds.), Nitrogen NMR, Plenum Press, London, 1973, Chapter 4.
25 P. Hampson and A. Mathias, Chem. Commun., (1967) 371.
26 D.J. Craik, G.C. Levy and R.T.C. Brownlee, J. Org. Chem., 48 (1983) 1601.