

THE ^{119}Sn AND ^{15}N NMR SPECTRAL STUDY OF THE CHELATE FORMATION IN THE TRIPHENYLTIN(IV) OXINATEJaroslav HOLEČEK^a, Antonín LYČKA^b and Roland WAGENER^c^a Department of General and Inorganic Chemistry,
Institute of Chemical Technology, 532 10 Pardubice,^b Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví, Czechoslovakia and^c Sektion Chemie, Karl-Marx-Universität, 7010 Leipzig, G.D.R.

Received November 13th, 1985

Dedicated to Prof. Jaromír Horák on the occasion of his 60th birthday.

The ^{119}Sn and ^{15}N NMR spectra of triphenyltin(IV) oxinate and (therewith isoelectronic compound) 1-naphthoxide have been measured in the media of a non-coordinating solvent — deuteriochloroform — and two coordinating solvents — pyridine and hexamethylphosphoramide — in the temperature region from 240 to 370 K. The values of parameters of the ^{119}Sn and ^{15}N NMR spectra and their temperature dependences and comparison of the parameters of the ^{119}Sn NMR spectra of the two isoelectronic compounds indicate that, in the non-coordinating solvent (deuteriochloroform), the triphenyltin(IV) oxinate forms a chelate complex with bidentate function of the oxinate ligand and with *cis*-trigonally bipyramidal geometry around the penta-coordinated central tin atom, whereas the triphenyltin(IV) 1-naphthoxide forms a simple compound with pseudo-tetrahedral arrangement of the substituents around the tetra-coordinated central tin atom. In both coordinating solvents chemical reactions take place which produce complexes of triphenyltin(IV) compounds with one molecule of the solvent and with *trans*-trigonally bipyramidal structure around the penta-coordinated central tin atom. The temperature dependences of $\delta(^{119}\text{Sn})$ chemical shifts have been used for estimation of the basic thermodynamic parameters of formation of these complexes which confirm that the formation of the complexes with coordinating solvents is — in the case of triphenyltin(IV) oxinate — connected with an exchange equilibrium consuming the original *cis*-chelate complex (the coordination number 5 of the central atom does not change), whereas with the 1-naphthoxide the reaction consists in a simple formation of the complex with an increase in the coordination number of the central atom (from 4 to 5).

Our previous communication¹ compares some parameters of ^{13}C , ^{15}N , and ^{119}Sn NMR spectra of triphenyltin(IV) and tri(1-butyl)tin(IV) oxinates, and (therewith isoelectronic) 1-naphthoxides as well as those of 8-methoxyquinoline to provide a qualitative proof of the existence of the chelate connection $\text{Sn} \begin{matrix} \text{O} \\ \diagup \\ \text{N} \end{matrix}$ in triorganotin(IV) oxinates and its relative strength. Our purpose was to contribute thereby to elucidation of the conflict situation encountered in literature in the connection with formulating of the coordination number of the central tin atom and function of the oxinate group in the compounds of this type¹. The present communication brings more detailed

cular, no coordination changes at the central tin atom are observed. In the whole temperature interval, relatively large differences between their $\delta(^{119}\text{Sn})$ values also are retained (the differences in the temperature dependence are 96.9 to 98.1 ppm), which – in the light of our previous reports^{1,2} – indicates different coordination of the central tin atom in the two compounds. The characteristic values of $\delta(^{119}\text{Sn})$ chemical shifts correspond to pseudo-tetrahedral structure of compound *II* (the coordination number of central tin atom is equal to 4) and to *cis*-trigonally bipyramidal geometry of compound *I* with penta-coordinated tin atom². The relative temperature dependences of $\delta(^{119}\text{Sn})$ of the two compounds in deuteriochloroform solutions also indicate that no marked autoassociation of molecules of compound *II* takes place in the solution, in the case of compound *I* this fact represents – in our opinion – one of the proofs of relative strength of the $\text{Sn}\cdots\text{N}$ connection in the oxinate chelate complex. Slight upfield shifts (with increasing temperature) of the $\delta(^{119}\text{Sn})$ values of the two compounds are most likely ascribable to small specific changes caused by temperature to the $\delta(^{119}\text{Sn})$ chemical shifts of both the compound measured and the standard.

The $\delta(^{119}\text{Sn})$ chemical shifts of both triphenyltin(IV) compounds in pyridine and hexamethylphosphoramide – in contrast to the solutions in deuteriochloroform –

TABLE I

The $\delta(^{119}\text{Sn})$ chemical shifts of triphenyltin(IV) oxinate (*I*) and 1-naphthoxide (*II*) in deuteriochloroform, pyridine, and hexamethylphosphoramide

Temperature K	$\delta(^{119}\text{Sn})$, ppm					
	Compound <i>I</i>			Compound <i>II</i>		
	C^2HCl_3^a	$\text{C}_6\text{H}_5\text{N}^b$	$[(\text{CH}_3)_2\text{N}]_3\text{PO}^c$	C^2HCl_3^d	$\text{C}_5\text{H}_5\text{N}^e$	$[(\text{CH}_3)_2\text{N}]_3\text{PO}^f$
240	-189.9	-264.2		-91.8	-254.7	
250		-250.0				
260	-190.1	-234.0		-91.9	-247.9	
280	-190.2	-218.1		-92.3	-243.9	
290			-266.7			
300	-190.2	-209.6	-263.2	-92.8	-237.7	-272.7
310			-255.8			
320	-190.2	-204.3	-248.5	-93.3	-230.9	-270.9
330			-239.9			
340		-200.3	-233.7		-217.5	-268.6
350			-227.4			
360		-198.0	-223.2		-202.8	-266.2
370			-218.9			

^{a-f} The concentrations of the solutions in molar fractions (10^{-2}): ^a 2.42; ^b 1.39; ^c 2.27; ^d 1.92; ^e 1.24; ^f 2.25.

exhibit much more distinct temperature dependences (Fig. 1). The temperature dependences of compound *I* in both coordinating solvents represent well-developed sigmoid curves. Their asymptotes are formed at one side by the $\delta(^{119}\text{Sn})$ value of compound *I* in deuteriochloroform solution (-190.2 ppm) and at the other side by the $\delta(^{119}\text{Sn})$ values calculated by extrapolation for the individual systems according to ref.⁴ (-285.0 ppm for the pyridine solution and -286.9 ppm for hexamethylphosphorami-

TABLE II

The $\delta(^{15}\text{N})$ chemical shifts and $J(^{119}\text{Sn}^{15}\text{N})$ coupling constants of triphenyltin(IV) oxinate in deuteriochloroform, pyridine, and hexamethylphosphoramide solutions

Temperature K	$\delta(^{15}\text{N})$, ppm			$J(^{119}\text{Sn}^{15}\text{N})^a$, Hz	
	C^2HCl_3^b	$\text{C}_5\text{H}_5\text{N}$	$[(\text{CH}_3)_2\text{N}]_3\text{PO}^c$	C^2HCl_3^b	$[(\text{CH}_3)_2\text{N}]_3\text{PO}^c$
240	-120.4	-124.3		97.6	
270	-117.6			96.4	
290			-117.8		78.1 ^d
300	-116.1		-117.5	96.4 ^d	79.5 ^d
310			-116.7		81.1
320			-116.1		83.5
330	-114.4		-115.3	96.4	
340			-114.5		87.8
350			-114.0		
360			-113.7		
370		-114.2			

^a Determined from the ^{119}Sn NMR spectra; ^{b-c} the concentrations of the solutions in molar fractions (10^{-2}); ^b 3.28; ^c 3.92; ^d determined from both ^{119}Sn and ^{15}N NMR spectra.

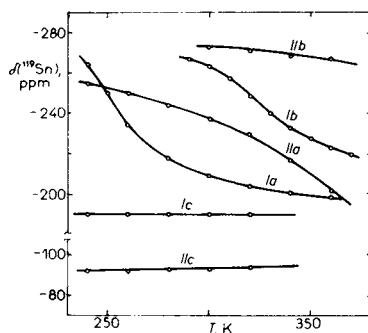


FIG. 1

The temperature dependence of the $\delta(^{119}\text{Sn})$ chemical shifts of triphenyltin(IV) oxinate (*I*) and 1-naphthoxide (*II*) in pyridine (*a*), hexamethylphosphoramide (*b*), and deuteriochloroform solution (*c*)

de solution). The temperature dependences of $\delta(^{119}\text{Sn})$ of compound *II* also, most likely, have the sigmoid form in the coordinating solvents, however, only parts of them are experimentally accessible (Fig. 1). It is likely that in this case one asymptote will be the value $\delta(^{119}\text{Sn})$ of about -92.5 ppm (the mean $\delta(^{119}\text{Sn})$ for the deuteriochloroform solution), the other values -259.3 ppm (pyridine) and -277.5 ppm (hexamethylphosphoramide) being again estimated by extrapolation according to ref.⁴. The sigmoid course limited by the respective asymptotes indicates that continuous changes take place in the systems with temperature, the original compounds *I* and *II* being gradually transformed into the corresponding complexes with one molecule of the coordinating solvent. The calculated (extrapolated) asymptotic $\delta(^{119}\text{Sn})$ values must be considered to be the characteristic values of chemical shifts of these complexes, the experimental points of the sigmoid dependences expressing the proportions of contributions of the original compounds and the complexes formed in the system as a consequence of the rapid exchanges in the NMR time scale and of rapidly established equilibria (*Aa, b*) and (*Ba, b*), resp.



(*S* denotes the molecule of coordinating solvent, pyridine (*a*) or hexamethylphosphoramide (*b*)). The values of extrapolated asymptotic $\delta(^{119}\text{Sn})$ for all the complexes (-259.3 to -286.9 ppm) are typical of *trans*-trigonally bipyramidal structure of the molecules with penta-coordinated tin atom.

The equilibria (*A*) and (*B*) differ in nature: whereas *B* only represents the formation of *trans*-trigonally bipyramidal complex from the originally tetrahedral molecule of the simple compound *II*, being thus characterized by a change of the coordination number of the central atom from 4 to 5, Eq. (*A*) describes an exchange equilibrium reaction connected with disappearance of the original chelate function of the oxinate group ($\text{Sn} \cdots \text{N}$ bond), and the *cis*-trigonally bipyramidal complex is (by action of a molecule of the coordinating solvent) changed to the *trans*-trigonally bipyramidal one in which the monodentate oxinate group and the solvent molecule occupy the axial positions. The coordination number of the central tin atom does not change in this reaction.

The Stability of Complexes

The courses of the $\delta(^{119}\text{Sn}) \sim T$ dependences and their mutual positions (and/or positions of their real or fictive inflection points) with regard to both the temperature axis and the $\delta(^{119}\text{Sn})$ axis (Fig. 1) express relative stabilities of the complexes, too. From the Fig. 1 it is clearly seen, *e.g.*, that at room temperature (300 K) and the given

experimental conditions the process of formation of the complexes of compound *II* with hexamethylphosphoramide or pyridine is completely or almost completely finished, whereas at the same conditions the solution of compound *I* in hexamethylphosphoramide contains about 25% molecules in the chelate complex form, the proportion of the chelate molecules being even as high as about 80% in the pyridine solutions. Generally, from the temperature dependences of $\delta(^{119}\text{Sn})$ it can be deduced that the *trans*-trigonally bipyramidal complexes with hexamethylphosphoramide are stronger than the corresponding complexes with pyridine and that the formation of both complexes of compound *II* is easier than that of compound *I*. Even better this can be seen from comparison of thermodynamic quantities of the reactions (*A*) and (*B*) which were calculated according to ref.⁴ and are presented in Table III (the values of K_x (molar fraction) and ΔG of the equilibrium (*Bb*) were estimated only very roughly, because only available for the calculation of K_x are the experimental data of final little part of the $\delta(^{119}\text{Sn}) \sim T$ dependence, where the process of formation of the complex is practically finished).

The K_x and/or ΔG values of Table III – first of all – confirm the qualitative conclusions about the strength of both the types of complexes (see the beginning of the previous paragraph). The generally more favourable values of these quantities for the complexes of compound *II* with both coordinating solvents, as compared with the complexes of compound *I*, agree with the idea that the simple formation of the complexes according to Eq. (*B*) is much easier than the exchange equilibrium (*A*), where the formation of *trans*-trigonally bipyramidal complex necessitates surmounting of the energy barrier represented by the relatively strong chelate complex. Thus the thermodynamic quantities of both reactions of compound *II* reflect the direct formation of its complexes with pyridine or hexamethylphosphoramide in the given medium and at given experimental conditions, whereas the same quantities for compound *I*

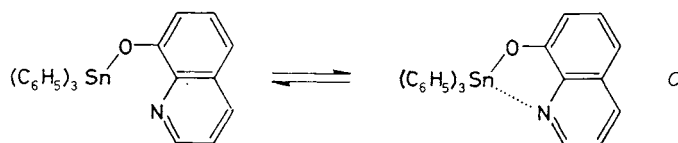
TABLE III

Thermodynamic quantities of formation of complexes of triphenyltin(IV) oxinate and 1-naphthoxide with pyridine and hexamethylphosphoramide at 300 K

Equilibrium	Complex	K_x mol. fraction	ΔK kJ mol ⁻¹	ΔH kJ mol ⁻¹	ΔS J mol ⁻¹ K ⁻¹
<i>Aa</i>	<i>I</i> . C ₅ H ₅ N	0.3 ± 0.1	+1.3 ± 1.3	-18.8 ± 1.1	-73 ± 4
<i>Ab</i>	<i>I</i> . [(CH ₃) ₂ N] ₃ PO	3.1 ± 0.5	-2.8 ± 0.4	-25.6 ± 0.6	-76 ± 2
<i>Ba</i>	<i>II</i> . C ₅ H ₅ N	6.6 ± 0.6	-4.7 ± 0.3	-16.7 ± 0.5	-40 ± 2
<i>Bb</i>	<i>II</i> . [(CH ₃) ₂ N] ₃ PO	(55)	(-10)		

represent overall quantities of two processes — decomposition of the chelate complex of oxinate and formation of the complex with a solvent molecule.

The oxinate and 1-naphthoxide groups are — in compounds *I* and *II* and in their complexes with a molecule of coordinating solvent — mutually isoelectronic and their geometrical dimensions (and, hence, their sterical effects, too) are almost identical. The close pK_a values of the conjugated acids (9.30 and 9.81 for 1-naphthol and 8-hydroxyquinoline, resp.)⁵ also indicate that there will be almost the same donor properties of the oxygen atom with respect to its partners. Hence, we shall make no serious mistake, if we replace, in our considerations about assessments of the rough value of stability constant of the chelate link $\text{Sn}\cdots\text{N}$ in compound *I*, *i.e.* of the equilibrium constant of reaction



and the corresponding ΔG value, the formally monodentate oxinate group at the left-hand side of the equation by the 1-naphthoxide group, and if we consider the measure of strength of the chelate link $\text{Sn}\cdots\text{N}$ to be expressed by the ΔG differences of the complexes of compounds *II* and *I* with the same solvent molecules and/or by the quotients of the corresponding K_x constants. The rough assessment in this sense seems to be also justified by the almost the same differences in the ΔG values thus obtained for pairs of the same triphenyltin(IV) compound with different solvent molecules:

$$\Delta G_{\text{I},((\text{CH}_3)_2\text{N})_3\text{PO}} - \Delta G_{\text{I},\text{C}_5\text{H}_5\text{N}} = -5.3 \text{ kJ mol}^{-1}$$

$$\Delta G_{\text{II},((\text{CH}_3)_2\text{N})_3\text{PO}} - \Delta G_{\text{II},\text{C}_5\text{H}_5\text{N}} = -5.9 \text{ kJ mol}^{-1}$$

which reflect the contribution of donor properties of the two coordinating solvents, *i.e.*, *e.g.* how much stronger are the complexes with hexamethylphosphoramide than the corresponding ones with pyridine. The difference in ΔG values for the pyridine complexes is

$$\Delta G_{\text{II},\text{C}_5\text{H}_5\text{N}} - \Delta G_{\text{I},\text{C}_5\text{H}_5\text{N}} = -7.8 \text{ kJ mol}^{-1}$$

and the corresponding difference for the hexamethylphosphoramide complexes is

$$\Delta G_{\text{II},((\text{CH}_3)_2\text{N})_3\text{PO}} - \Delta G_{\text{I},((\text{CH}_3)_2\text{N})_3\text{PO}} = -7.2 \text{ kJ mol}^{-1}.$$

The quotients of the respective K_x constants are about 22 and 18. In spite of considerable simplification and limited exactness of the given reasoning, very favourable conditions follow from this analysis for the stability of the chelate combination (C). It is noteworthy that the assessed stability constant of the chelate connection in compound I ($K_x = 18$ and 22, resp.) is approximately three times greater than the stability constant of the II . C₅H₅N complex, which agrees with the generally accepted experience that the chelate complex is at least two times stronger than an analogous complex with two monodentate ligands⁶.

Another proof of the chelate function of oxinate group in compound I can be seen in the distinctly lower entropy value of formation of the I . C₅H₅N complex as compared with that of the II . C₅H₅N complex and, at the same time, in the small difference between ΔH values of the two reactions. The chelate formation is known^{6,7} to be connected (from the thermodynamic point of view) with increase in the reaction entropy and to be almost exclusively governed by the entropy term. The entropy decrease accompanying the formation of I . C₅H₅N complex, as compared with II . C₅H₅N complex (the same being probably true of the complexes with hexamethylphosphoramide), corresponds logically to decomposition of the chelate.

The $J(^{119}\text{Sn}^{15}\text{N})$ Coupling Constants

The $J(^{119}\text{Sn}^{15}\text{N})$ coupling constant (denoted by Blunden⁸ as $^1J(^{119}\text{Sn}^{15}\text{N})$; or it can also be denoted formally as $^4J(^{119}\text{Sn}^{15}\text{N})$) of compound I in deuteriochloroform undergoes practically no changes in the temperature interval from 240 to 330 K, and its value 96.4 Hz is comparable with the coupling constants ascribed⁹ to the Sn...N bond in a group of stannatranes. This value is clearly higher than that of the same compound in hexamethylphosphoramide solution, where the $J(^{119}\text{Sn}^{15}\text{N})$ exhibits a distinct temperature dependence which – with increasing temperature – asymptotically approaches the $J(^{119}\text{Sn}^{15}\text{N})$ value in the deuteriochloroform solutions (Fig. 2). The $J(^{119}\text{Sn}^{15}\text{N})$ value extrapolated to low-temperature region can be assessed to be about 73 Hz, and this value can be ascribed to the $^4J(^{119}\text{Sn}^{15}\text{N})$ coupling constants of the monodentate-bound oxinate ligand in accordance with refs⁸⁻¹⁰. The sigmoid course of the temperature dependence of $J(^{119}\text{Sn}^{15}\text{N})$ thus follows – in the same way – the exchange equilibrium between the original chelate complex of compound I and the *trans*-trigonally bipyramidal complex of the same compound with hexamethylphosphoramide and monodentate oxinate group as discussed above and as indicated also by the good linear dependence of the $\delta(^{119}\text{Sn})$ and $J(^{119}\text{Sn}^{15}\text{N})$ parameters in the hexamethylphosphoramide solution (Fig. 3). The absolute $J(^{119}\text{Sn}^{15}\text{N})$ values, their changes with the solvent type, and correlation with the $\delta(^{119}\text{Sn})$ values represent further direct evidence of the chelate function of the oxinate ligand in compound I.

The $\delta(^{15}\text{N})$ Chemical Shifts

As are the $J(^{119}\text{Sn}^{15}\text{N})$ coupling constants, so also are the $\delta(^{15}\text{N})$ chemical shifts of compound *I* (in hexamethylphosphoramide solutions) linearly dependent on the $\delta(^{119}\text{Sn})$ chemical shifts of the same system (Fig. 3). This fact thus confirms the mutual interdependence of the parameters of the ^{119}Sn and ^{15}N NMR spectra during formation and/or decomposition of the donor-acceptor $\text{Sn}\cdots\text{N}$ link in the chelate complex of compound *I*. The $\delta(^{15}\text{N})$ values found and especially their relatively small changes with both temperature and solvent type (Table II) allow no simple interpretation similar to that of $\delta(^{119}\text{Sn})$ and/or $J(^{119}\text{Sn}^{15}\text{N})$ parameters. This is obviously due to the fact that the shifts in $\delta(^{15}\text{N})$ values are caused, besides coordination, by other effects out of which a part are to a considerable extent mutually compensated and overlapped.

In the previous communication¹ the formation of the donor-acceptor $\text{Sn}\cdots\text{N}$ link of the triorganotin(IV) oxinates was ascribed to the marked upfield shift of $\delta(^{15}\text{N})$ of these compounds in deuteriochloroform solutions as compared with the model compound – 8-methoxyquinoline in the same solvent. This interpretation quite agrees with the finding¹¹ that the $\delta(^{15}\text{N})$ values of free azine molecules always show down field shift as compared with $\delta(^{15}\text{N})$ of the same compound whose nitrogen atom (by its free electron pair) is bound by a donor-acceptor bond with an acceptor partner. This reverse effect (an upfield shift of $\delta(^{15}\text{N})$ connected with decreasing electron density at the nitrogen atom), which is frequently encountered especially in the classes of aromatic and heterocyclic nitrogen compounds containing carbon–nitrogen or

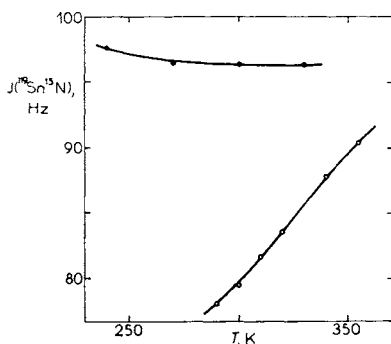


FIG. 2

The temperature dependence of the $J(^{119}\text{Sn}^{15}\text{N})$ coupling constant of triphenyltin(IV) oxinate in deuteriochloroform (●) and hexamethylphosphoramide solution (○)

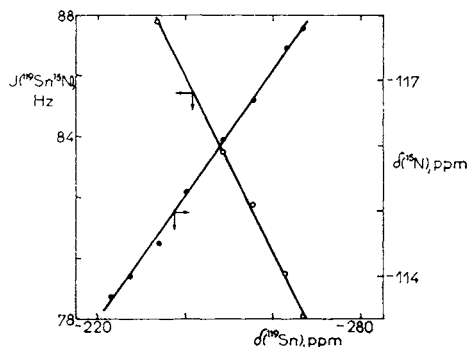
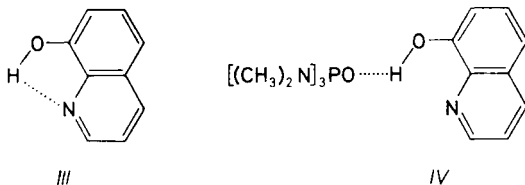


FIG. 3

The mutual interdependence of the parameters of ^{15}N and ^{119}Sn NMR spectra of triphenyltin(IV) oxinate in hexamethylphosphoramide solution

nitrogen–nitrogen multiple bonds¹¹, stands in accordance with our further finding that the $\delta(^{15}\text{N})$ value of 8-hydroxyquinoline in deuteriochloroform (-93.0 ppm) is, due to formation of the intramolecular hydrogen bond *III*,



distinctly shifted upfield as compared with the $\delta(^{15}\text{N})$ in hexamethylphosphoramide (-75.9 ppm) where – with respect to the solvent basicity – it can be justifiably presumed that the hydrogen atom is predominantly bound by intermolecular interaction with the oxygen atom of the solvent (*IV*). From these findings it was deduced that the $\delta(^{15}\text{N})$ values of compound *I* in pyridine and hexamethylphosphoramide would exhibit down field shifts with decreasing temperature (*i.e.* with increasing content of *trans*-trigonally bipyramidal *I* · $\text{C}_5\text{H}_5\text{N}$ or *I* · $((\text{CH}_3)_2\text{N})_3\text{PO}$ complexes and decreasing amount of the chelate *I*) and that thus the slope of the dependence of $\delta(^{15}\text{N})$ vs $\delta(^{119}\text{Sn})$ (Fig. 3) would have opposite sign and also a steeper course. Of course, it must not be overlooked that the reverse effect does not represent any completely general property of the ^{15}N NMR spectroscopy (*e.g.*, the dependence of the $\delta(^{15}\text{N})$ chemical shifts on the electron density at the nitrogen atom of substituted anilines^{12,13} is just opposite to that of substituted nitrobenzenes¹⁴) and, moreover, the $\delta(^{15}\text{N})$ values can be distinctly affected by further effects out of which the most significant are: *a*) the effect of solvent type (the $\delta(^{15}\text{N})$ chemical shifts of quinoline¹⁵ and pyridine¹⁶ exhibit differences of 20–25 ppm depending on the solvent character), *b*) specific temperature dependence of $\delta(^{15}\text{N})$ (*cf.* the large temperature dependence of $\delta(^{15}\text{N})$ of compound *I* in deuteriochloroform (Table II) and the slight temperature dependence of $\delta(^{119}\text{Sn})$ of the same system (Table I)), and *c*) a different character of the substitution chemical shift of the $(\text{C}_6\text{H}_5)_3\text{SnO}-$ group as compared with $(\text{C}_6\text{H}_5)_3\text{Sn}\cdots\text{N}\langle\text{O}-$. All these effects can compensate the effects of coordination to a considerable extent, or they can even overlap it, and thus they can distinctly affect not only the temperature dependence of $\delta(^{15}\text{N})$ but also the slope and steepness of the dependence of $\delta(^{15}\text{N})$ vs $\delta(^{119}\text{Sn})$.

REFERENCES

1. Lyčka A., Holeček J., Nádvořník M., Handlíř K.: *J. Organometal. Chem.* **280**, 323 (1985) and the references quoted therein.
2. Holeček J., Nádvořník M., Handlíř K., Lyčka A.: *J. Organometal. Chem.* **241**, 299 (1983).

3. Skraup Z. H. in the book: *Forschrifte der Teerfarbenfabrikation* (P. Friedlander, Ed.), p. 178. Springer, Berlin 1888.
4. Holeček J., Handlíř K., Černý V., Nádvorník M., Lyčka A.: Polyhedron, in press.
5. Kortüm G., Vogel W., Andrussov K.: *Dissociation Constants of Organic Acids in Aqueous Solution*. Butterworth, London 1961.
6. Basolo F., Pearson R. G.: *Mechanism of Inorganic Reactions*, p. 31, Mir, Moscow 1971.
7. Rossotti F. J. C. in the book: *Modern Coordination Chemistry* (J. Lewis, R. G. Wilkinson, Eds), p. 20. Interscience Publishers Inc., New York 1960.
8. Blunden S. I., Cusack P. A., Gillies D. G.: *J. Magn. Reson.* **60**, 114 (1984).
9. Jurkschat K., Mügge G., Tzschach A., Zschunke A., Engelhardt G., Lippmaa E., Mägi N., Larin M. F., Petsunovich V. A., Voronkov M. G.: *J. Organometal. Chem.* **171**, 301 (1979).
10. Swisher R. G., Day R. P., Holmes R. R.: *Inorg. Chem.* **22**, 3692 (1983).
11. Witanowski M., Stefaniak L., Januszewski H. in the book: *Nitrogen NMR* (M. Witanowski, G. A. Webb, Eds), Chap. 4, p. 226. Plenum Press, London—New York 1973 and the references quoted therein.
12. Dorie J., Mechin B., Martin G.: *Org. Magn. Reson.* **12**, 229 (1979).
13. Axenrod T., Pregosin P. S., Wieder M. J., Becker E. D., Bradley R. B., Milne G. W.: *J. Amer. Chem. Soc.* **93**, 6536 (1971).
14. Craig D. J., Levy G. C., Brownlee R. T. C.: *J. Org. Chem.* **48**, 1601 (1983).
15. Paolillo L., Becker E. D.: *J. Magn. Reson.* **2**, 168 (1970).
16. Duthaler R. O., Roberts J. D.: *J. Amer. Chem. Soc.* **100**, 4969 (1978).

Translated by J. Panchartek.