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Stereochemistry of diorganotin(IV) bis(8-quinolinolate) and bis(8-quinolinethiolate) complexes in solution studied by NOE-difference spectroscopy

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Abstract

It was proved by ^1H NOE-difference spectroscopy that all diorganotin(IV) complexes of type $R_2Sn(oxin)_2$ and $R_2Sn(txin)_2$ (where oxin = 8-quinolinolate, txin = 8-quinolinethiolate, R = butyl, phenyl, benzyl and vinyl, respectively) in chloroform solution have a distorted *cis*-octahedral coordination at the metal centre. Two oxygen (sulphur) atoms occupy positions *trans* to each other, while the estimated bond angles O–Sn–O (S–Sn–S) are in the range 150–165°. Nitrogen atoms are *cis* to each other and the bond angles N–Sn–N are less than 90°. Intramolecular dynamic processes have to be taken into account.

Introduction

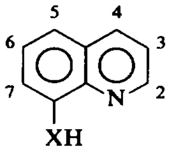
The structure of organotin(IV) complexes of 8-quinolinol (oxinH) [1–5] and 8-quinolinethiol (txinH) [6] has been studied by multinuclear NMR spectroscopy with a view to characterizing metal–ligand bonding and the influence of organic substituents on the strength of the Sn–N bond. These compounds form molecular chelates in the solid state [7] as well as in solutions of non-coordinating solvents.

Concerning the stereochemistry of diorganotin(IV) chelates a steric preference is known for the *cis* arrangement in the case of a chelating ligand of small bite size [8,9]. Utilizing the correlation [10,11] of tin–carbon $^1J(^{119}Sn, ^{13}C)$ coupling constants on the C–Sn–C bond angles it was proved that in all complexes of type $R_2Sn(oxin)_2$ and $R_2Sn(txin)_2$ studied substituents R occupy *cis* positions to each other [5,6,10]. The values of estimated C–Sn–C bond angles are in the range 120–136°, which indicate highly distorted (skewed) *cis*-octahedral geometry of the coordination polyhedra [5,6].

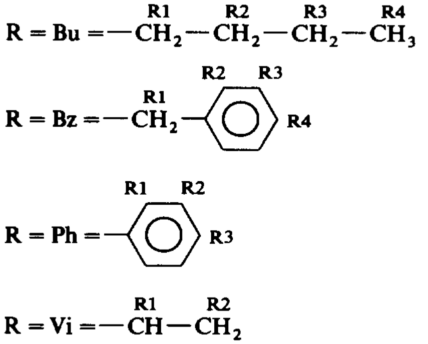
The aim of this study is to characterize the mutual arrangement of two chelating ligands in the coordination sphere of organotin(IV) oxinates $R_2Sn(oxin)_2$ and thiooxinates $R_2Sn(txin)_2$ in solution utilizing NOE-difference spectroscopy.

Experimental

In this paper, organotin(IV) oxinates and thiooxinates are marked and numbered in the following way:



X = O, S



$$R = Bu = \overset{R1}{-CH_2}-\overset{R2}{CH_2}-\overset{R3}{CH_2}-\overset{R4}{CH_3}$$

$$R = Vi = \overset{R1}{-CH}-\overset{R2}{CH_2}$$

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300 spectrometer operating at the frequencies of 300.13 and 75.45 MHz, respectively. For the measurement of ^1H relaxation times and NOE-difference spectra filtered deuteriochloroform solutions (1×10^{-2} mol dm^{-3}) were used. The required deoxygenation was realized by 40 min bubbling by argon and by perfect sealing fo the sample tube. The process of sample preparation was controlled by measuring the ^1H relaxation time of chloroform in order that $T_1 > 200$ s. All measurements were performed at 25 °C. As NOE-difference spectroscopy is a technique most sensitive to instrument instability, each sample was kept at constant temperature in the probe for 3 h prior to the start of the measurement to establish the thermal equilibrium.

The use of the pulse program NOEMULT with recycling irradiation of single lines of the multiplet has made it possible to achieve a high degree of saturation (90–95%) along with high selectivity $\gamma B_2 = 1.3$ Hz. The 400 ms soft pulses corresponding to 180° flip angle at a chosen decoupler power were applied. The total presaturation time equal to $5T_1$ of the longest T_1 value (i.e. 40–60 pulses) was used. The spin-lattice relaxation times were measured by the inversion–recovery method with 12–15 τ values. The T_1 values were determined by a three-parameter fit of integrated intensity variations. For the carbon relaxation time measurements the concentration of the complex in solution was increased to 2.5×10^{-2} mol dm^{-3}.

Results and discussion

Interligand distance determination by NOE

The basis of the NOE is the variation of the signal intensities of nuclei resulting from the direct dipole–dipole interaction with the nucleus, whose resonance transition is selectively presaturated [12]. As the contribution of dipolar interaction to the

Table 1

The ^{13}C spin-lattice relaxation time

Compound	$T_1(^{13}C)/s$									
	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(R1)	C(R2)	C(R3)	C(R4)
$Bu_2Sn(txin)_2$	1.00	1.02	0.91	0.93	1.02	1.01	1.07	1.75	2.20	3.23
$Bu_2Sn(oxin)_2$	0.89	0.95	0.81	0.86	0.91	0.95	1.47	1.93	2.08	3.46
$Bz_2Sn(txin)_2$	0.82	0.88	0.76	0.78	[a]	0.88	1.05	[a]	1.85	1.83
$Bz_2Sn(oxin)_2$	0.81	0.81	0.71	0.73	0.82	0.85	[b]	1.78	1.77	1.57
$Ph_2Sn(txin)_2$	0.88	0.94	0.79	0.77	0.94	0.91	2.50	2.47	0.77	
$Ph_2Sn(oxin)_2$	0.90	0.88	0.74	0.77	0.90	0.88	2.66	2.53	0.78	
$Vi_2Sn(txin)_2$	1.23	1.44	1.18	1.16	1.35	[a]	5.36	[a]		
$Vi_2Sn(oxin)_2$	1.10	1.23	1.11	1.10	1.13	1.20	6.24	1.20		

[a] Superimposed signals. [b] Signal broadening due to exchange process.

relaxation process is proportional to a factor, $1/r^6$, where r is the distance between the nuclei under consideration, NOE-difference spectroscopy provides valuable information about nuclei in close steric proximity. The values of the spin-lattice relaxation times must be known for the quantitative evaluation of NOE experiments.

Measured $T_1(^{13}C)$ values of individual carbon atoms of diorganotin(IV) complexes are summarized in Table 1. Required $T_1(^1H)$ values of proton H(7) are presented in Table 2. The NOE between protons of two chelating ligands bound to the same central atom is interesting from the stereochemical point of view. Such an effect can be observed between protons H(2) and H(7) (Fig. 1), because the direct dipolar interaction within the framework of one ligand is ineffective ($r_{2,7} = 0.67$ nm).

The transition probability between energy levels (zero, single, and double quantum) depends on the operating frequency of the spectrometer. However, the diorganotin(IV) complexes of type $R_2Sn(oxin)_2$ and $R_2Sn(txin)_2$ conform to the extreme narrowing condition ($\omega_0^2\tau_c^2 \ll 1$), where τ_c is a rotational correlation time. Under this condition frequency dependence vanishes and the formulae for the relaxation processes become much more simple.

Table 2

NOE data [a] of oxinates and thiooxinates

Compound	$10^{11} \times \tau_c/s$	$f_7(2)$	$f_2(7)$	$f_6(7)$	$T_1\{H(7)\}/s$	$r_{2,7'}/nm$
$Bu_2Sn(oxin)_2$	5.31	3.3	3.2	22.3	3.45	0.34
$Bz_2Sn(oxin)_2$	6.22	3.0	2.2	22.8	3.64	0.36
$Ph_2Sn(oxin)_2$	6.04	3.5	1.9	20.5	3.20	0.34
$Vi_2Sn(oxin)_2$	4.41	3.7	3.8	24.1	4.78	0.35
$Bu_2Sn(txin)_2$	4.79	0.0	0.0	18.6	4.12	?
$Bz_2Sn(txin)_2$	5.64	1.2	0.8	17.3	3.51	0.41
$Ph_2Sn(txin)_2$	5.50	1.2	[b]	18.2	3.50	0.41
$Vi_2Sn(txin)_2$	3.39	0.4	0.0	[c]	5.24	≈ 0.48

[a] $f_1(j)$ fractional enhancement of H(i) signal intensity (in %) due to H(j) signal saturation; T_1 spin-lattice correlation time; τ_c isotropic correlation time; $r_{2,7'}$ distance between protons H(2) and H(7′) of two ligands in one molecule. [b] Superimposed signals. [c] Higher order spin system.

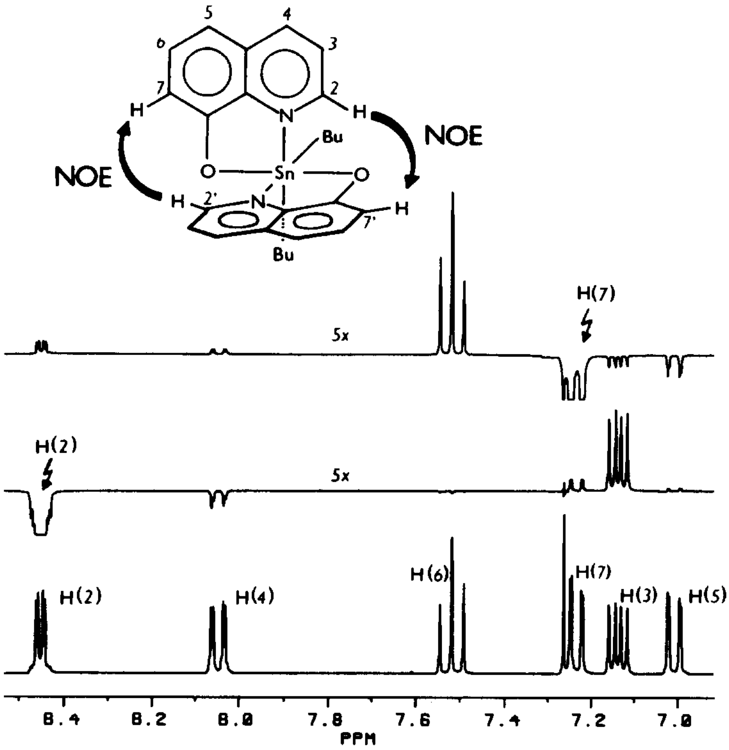


Fig. 1. The NOE-difference spectra of $Bu_2Sn(oxin)_2$: (a) Reference spectrum (aromatic part); (b) difference spectra, saturation of signal H(2); (c) saturation of signal H(7).

Provided that dipolar interaction is dominant, spin-lattice relaxation time of carbon nuclei is given thus [12]:

$$\frac{1}{T_1} = \frac{\mu_0^2\gamma_C^2\gamma_H^2\hbar^2\tau_c}{16\pi^2 r_{CH}^6} \tag{1}$$

$\mu_0 = 4\pi \times 10^{-7}$ H m^{-1} is the permeability of a vacuum, γ represents magnetogyric constants ($\gamma_H = 2.675 \times 10^8$ T^{-1} s^{-1}, $\gamma_C = 6.726 \times 10^7$ T^{-1} s^{-1}) and the bond length of directly bonded hydrogen atom to carbon atom is $r_{CH} = 0.108$ nm (the value published for pyridine [13]). Contributions from other protons may be neglected. Calculated isotropic rotational correlation times of complexes are given in Table 2. For the determination of τ_c, mean values of $T_1\{C(4)\}$ and $T_1\{C(5)\}$ were used, as they do not include torsional vibration of ligands round the C(8)–O (C(8)–S) bond. (For more detail see the paragraph concerning intramolecular dynamics).

The cross-relaxation between two protons of unknown distance is given thus [12]:

$$\sigma_{ds} = f_d(s)R_d + \sum_{j \neq d,s} \sigma_{dj} f_j(s) \tag{2}$$

where $f_d(s)$ is fractional enhancement of detected proton signal intensity while spin s is saturated, R_d is the total relaxation rate of spin d, σ_{dj} represents the cross-relaxation term with spins other than spin s, and $f_j(s)$ the fractional enhancement of signal intensity of proton j due to saturation of spin s. The values of σ_{dj} can be calculated from the correlation time and the known structure of rigid ligand according to the following expression [13]:

$$\sigma_{ij} = \frac{\mu_0^2 \gamma_H^4 \hbar^2 \tau_c}{32 \pi^2 r_{ij}^6} \tag{3}$$

The NOE between protons H(2) and H(7) can be observed provided that either proton H(2) or H(7) is saturated. The first alternative is advantageous considering the larger NOE enhancement on H(7), as the proton H(6) is the only neighbour in the proximity of H(7) for competitive relaxation. For the H(2) saturation the expression (2) is transformed as follows:

$$\sigma_{7',2} = f_{7'}(2)/T_1\{H(7)\} + \sigma_{7,6} f_{6'}(2) \tag{4}$$

where the prime differentiates two ligands in one complex. The term R_d in eq. 2 was substituted by experimental value $T_1\{H(7)\}$ which includes contributions of other relaxation paths. The term $f_{6'}(2)$ represents the three-spin effect and its substitution by the following term

$$f_{6'}(2) = -f_{7'}(2) f_6(7) \tag{5}$$

is sufficiently accurate. As a result of simple transformation of eqs. 1, 3–5 the final expression (eq. 6) for the distance between protons H(2) and H(7) is obtained:

$$r_{7,2} = \left\{ f_{7'}(2) \left[\left(\frac{\gamma_C}{\gamma_H} \right)^2 \frac{T_1\{C(4,5)\}}{T_1\{H(7)\}} \frac{2}{r_{CH}^6} - \frac{f_6(7)}{r_{6,7}^6} \right] \right\}^{-1/6} \tag{6}$$

Calculated distances are summarized in Table 2. Owing to rather weak enhancement of H(7) signal for $Vi_2Sn(txin)_2$, the calculated distance $r_{2,7'}$ must be regarded with suspicion.

A representative NOE-difference spectrum is given in Fig. 1. Saturation of proton H(2) results in a direct NOE on H(3) (fractional enhancement of signal intensity $f_3(2) = 23.3\%$), three-spin effect on H(4) ($f_4(2) = -4.5\%$), and in addition a four-spin effect on H(5) is observable ($f_5(2) = 0.9\%$).

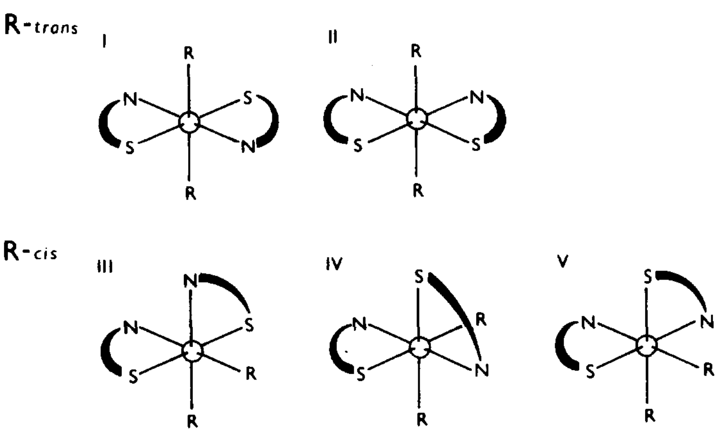
In spite of the very low r.f. power used for H(7) saturation, partial saturation of H(3) ($\approx 3\%$) occurs as a result of the frequency characteristic of orthogonal pulses. However, +3% NOE on H(2) can only be caused by direct cross-relaxation between protons H(7) and H(2) of two different ligands in one molecule of the complex.

Interligand distance in model structures

For the octahedral coordination of bis-chelates of type $R_2Sn(oxin)_2$ five stereoisomers are possible with regard to symmetry (Scheme 1). In addition, *cis*-stereoisomers have their optical antipodes which are, however, not directly distinguishable by NMR. The X-ray diffraction data [14] of $Bu_2Sn(oxin)_2$ were used to calculate [15] the distance between H(2) and H(7′) in model stereoisomers. The bond angles N–Sn–N and/or O–Sn–O were assumed to be equal to 90 or 180° for *cis* and *trans* coordination, respectively. Calculated distances $r_{2,7'}$ of possible stereoisomers are as follows

$r_{2,7'}(\mathrm{I}) = 0.50$ nm

$r_{2,7'}(\mathrm{III}) = 0.48$ nm



Scheme 1.

$r_{2,7'}(\text{IV}) = 0.68$ nm

$r_{2,7'}(\text{V}) = 0.64$ nm $\quad r_{7,2'}(\text{V}) = 0.79$ nm

For steric reasons the stereoisomer II is absolutely unsuitable. The two ligands of stereoisomer V are magnetically nonequivalent. With respect to the experimentally determined H(2)–H(7′) distance only stereoisomers I and III come into consideration. Regarding symmetry requirements there is no type of distortion of the coordination polyhedron, which should decrease the H(2)–H(7′) distance in stereoisomer I.

Consequently the stereoisomer III with N-donor atoms in *cis* and O-donor atoms in *trans* positions to each other is the only acceptable stereoisomer for given experimental conditions (in $CDCl_3$ solution). This type of ligand arrangement is characteristic also for analogous complexes in the solid state: $Me_2Sn(oxin)_2$ [16], $Bu_2Sn(oxin)_2$ [14] and (*p*-Cl-Ph)(*p*-totyl)Sn(oxin)$_2$ [17]. It is also in accord with our previous NMR results on $^1J(^{119}Sn, ^{13}C)$ [5,6] which unambiguously confirm the *cis* arrangement of R-substituents in the oxinates and thiooxinates under study.

In addition, preference for this type of stereoisomer results from the calculation of ^1H chemical shifts of coordinated oxinate and thiooxinate ligands employing $\Delta\delta(^1H)$ increments for a given character of ligand to metal bonding [18] and for different mutual arrangements of ligands [19].

The distance between H(2) and H(7′) has been calculated on the basis that bond angles N–Sn–N and O–Sn–O were 90° and 180°, respectively. However, the distance $r_{2,7'}$ is strongly dependent on these angles. Moreover, the strength of the Sn–N bond and consequently the averaged Sn–N bond distance depends on the type of R substituent. For this reason the dependences of mutual distance of H(2) and H(7′) were calculated as a function of O–Sn–O angle of oxinates and S–Sn–S angle of thiooxinates for a set of Sn–N distances ranging from 0.21 to 0.28 nm (Figs. 2 and 3). The minimal distance 0.21 nm is equal to the sum of the covalent radii of tin and nitrogen. The distance between H(2) and H(7′) were calculated on the condition that the angle N–Sn–N was 90° and at the same time that both ligands were magnetically equivalent (C_2 symmetry). Only one set of signals for two ligands is observed in ^1H and ^{13}C NMR spectra. Figure 4 depicts the dependence of

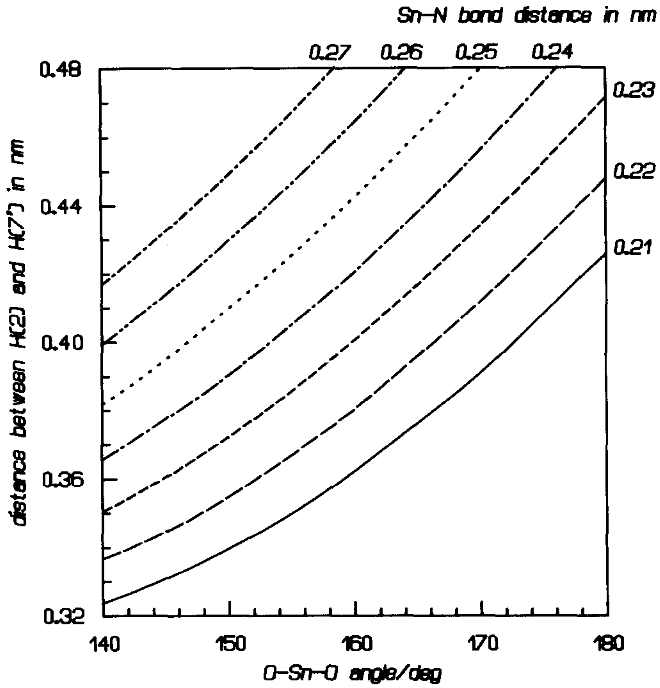


Fig. 2. The calculated dependence of the distance between protons H(2) and H(7) of two ligands in one molecule on the O–Sn–O angle for a set of Sn–N bond lengths in the model structure of $R_2Sn(oxin)_2$.

the H(2)–H(7') distance on N–Sn–N angle for the selected values of O–Sn–O angles at a constant Sn–N bond distance (0.24 nm).

Stereochemistry of oxinates and thiooxinates

An estimation of the Sn–N bond distance is necessary for determination of the degree of octahedron distortion. The Sn–N bond distance of $Me_2Sn(oxin)_2$, $Bu_2Sn(oxin)_2$ and (*p*-ClPh)(*p*-totyl)Sn(oxin)$_2$ in the solid state ranges from 0.231 to 0.238 nm [14,16,17]. With respect to small differences in ^{15}N chemical shifts of oxinates studied in this paper their Sn–N bond distance is estimated as 0.235 nm.

The Sn–N bond distance in crystalline $Ph_3Sn(txin)$ is 0.260 nm [20]. If one uses this value and the Sn–N distance equal to the sum of covalent nuclei and correlates them with the NMR data of tri- and diorganotin(IV) thiooxinates [6] and protonated ligand [21], then the estimated values of the Sn–N bond distances are as follows: 0.245 nm for $Bz_2Sn(txin)_2$ and $Ph_2Sn(txin)_2$, 0.255 nm for $Vi_2Sn(txin)_2$, 0.265 nm for $Bu_2Sn(txin)_2$.

Model calculations for estimated Sn–N bond distances of oxinates as well as for thiooxinates give greater values of $r_{2,7'}$ as are the values $r_{2,7'}$ determined from NOE experiments (Table 2) over the whole range of O–Sn–O and S–Sn–S angles. Further decreases of O–Sn–O or S–Sn–S angles below 140°, which means greater distortion of the coordination polyhedron, is prevented by the steric hindrance between the two oxinate or thiooxinate ligands in the coordination sphere of tin. However, the decrease in N–Sn–N angle brings about a further decrease of the H(2)–H(7')

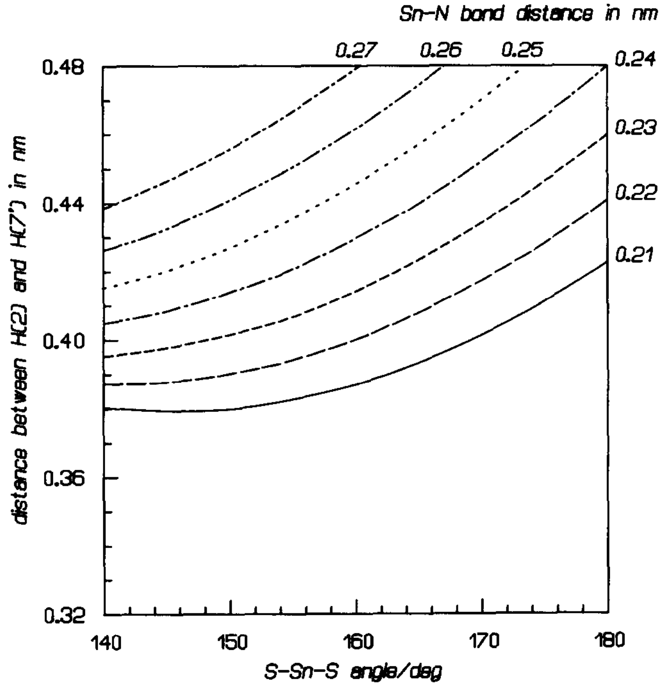


Fig. 3. The calculated dependence of the distance between protons H(2) and H(7) of two ligands in one molecule on the S–Sn–S angle for a set of Sn–N bond lengths in the model structure of $R_2Sn(txin)_2$.

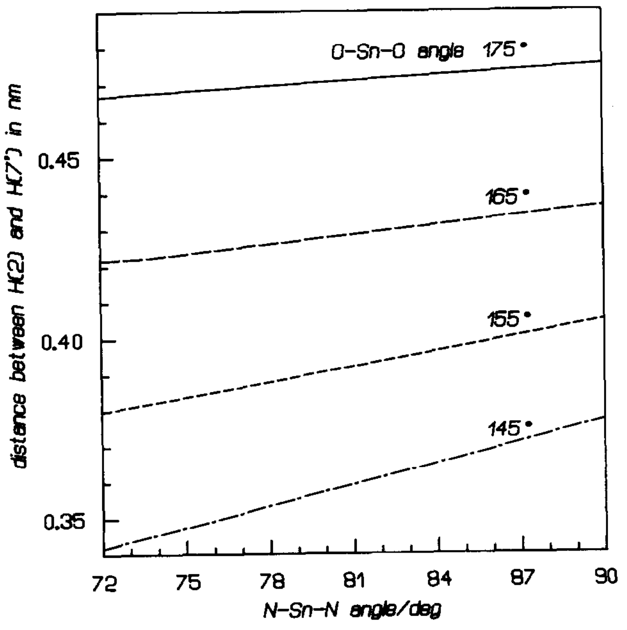


Fig. 4. The calculated dependence of the distance between protons H(2) and H(7) on the N–Sn–N angle for a set of O–Sn–O angles (bond length Sn–N equal to 0.24 nm).

distance (Fig. 4). This type of distortion is in accord with the solid state structure of analogous complexes in which the N–Sn–N angles range from 75 to 80° [14,16,17].

In spite of considerable distortion of the *cis*-octahedral structure the calculated distances $r_{2,7'}$ are still greater than those determined from NOE experiments. This difference may be explained if an internal motion of ligands is taken into account. The results in Table 2 concerning $r_{2,7'}$ distances are only valid for a rigid molecular structure. Without consideration of internal thermal motion, the calculated values $r_{2,7'}$ overestimate the shorter distances as a result of averaging based on $(\langle r_{2,7'}^{-6}\rangle)^{-1/6}$. Incorporation of the thermal motion with an amplitude equal to 10% of the time-averaged value of H(2)–H(7′) distance is sufficient to obtain the common solution for the $r_{2,7'}$ distances determined from NOE experiments and calculated for model structures.

Intramolecular dynamic processes

From relaxation measurements and NOE experiments it follows that there are intramolecular dynamic process, in addition to the tumbling which is expected of complex molecules in solution. As already mentioned T_1 values of C(4) and C(5) are shorter than those of the other protonated carbons of the ligands (Table 1). Torsional vibration of the ligand around the C(8)–O (C(8)–S) bond with respect to the metal centre does not contribute to C(4) and C(5) relaxation rate, because their dominant relaxation vectors are parallel to the torsional axis. The experimental T_1 values of the carbons in corresponding positions are inversely proportional to the molecular weights in accordance to the theory, nevertheless, they are shorter for oxinates than for thiooxinates. This can be explained by a higher flexibility of thiooxinate complexes relative to oxinates, due to weaker Sn–N bonding.

Spin-lattice relaxation of R substituents gives valuable informations about thermal internal motion and mobility (Table 1). Contrary to the $T_1(^{13}C)$ values of ligands, the $T_1(^{13}C)$ values of R substituents are greater for oxinates than those for thiooxinates. This higher mobility of R substituents in oxinates relative to the bis-chelate skeleton is in agreement with the greater values of C(R1)–Sn–C(R1′) angles [5,6]. As can be expected in butyl derivatives the mobility of the chain increases from metal centre to the outer end of chain (increase in T_1). The T_1 values of phenyl derivatives confirm torsional vibrations or hindered rotation of phenyl ring round Sn–C(R1) bond. In comparison, the benzyl group has two degrees of freedom for internal motion which is demonstrated by small differences in the T_1 values of phenyl ring of benzyl. This is supported also by the ^{1}H NMR spectra of CH_2 group in which the signals of magnetically nonequivalent protons are averaged due to dynamic processes. The lower coalescence temperature of thiooxinates corresponds to higher flexibility of these molecules relative to oxinates.

Conclusions

NOE-difference spectroscopy unambiguously identifies one sole type of stereoisomer for all the complexes $R_2Sn(oxin)_2$ and $R_2Sn(txin)_2$ studied in $CDCl_3$ solution, at least on the NMR time scale. The *cis*-octahedral geometry relative to the R substituent is in agreement with the NMR results on $^1J(^{119}Sn, ^{13}C)$ coupling constants [5,6]. The oxygen (sulphur) atoms accupy *trans*, and nitrogen atoms *cis*, positions to each other. This stereochemical arrangement is consistent with theoretical predictions based on the minimization of the total repulsion energy [9]. Negatively charged oxygen (sulphur) donors of the asymmetric oxinate (thiooxinate) ligand favour the more strongly bonding sites which are *cis* to both R substituents.

The *cis*-octahedral structure has considerable angular distortion. The estimated range of the bond angles O–Sn–O (S–Sn–S) is from 150 to 165° while the N–Sn–N angle is less than 90°. In addition, flexibility of these molecules and internal motion must be taken into account for a plausible interpretation of NOE-difference data.

Detailed information concerning these intramolecular dynamic processes can be obtained from $T_1(^{13}C)$ data.

References

1 H.C. Clark, V.K. Jain, I.J. Mc Mahon and R.C. Mehrotra, J. Organomet. Chem., 243 (1983) 299.
2 V.K. Jain, J. Mason, B.S. Saraswat and R.C. Mehrotra, Polyhedron, 4 (1985) 2089.
3 A. Lyčka, J. Holeček, M. Nádvorník and K. Handlíř, J. Organomet. Chem., 280 (1985) 323.
4 J. Holeček, A. Lyčka and R. Wagner, Collect. Czech. Chem. Commun., 51 (1986) 211.
5 A. Lyčka, J. Holeček and M. Nádvorník, Main Group Met. Chem., 12 (1989) 171.
6 A. Lyčka, J. Jirman, J. Holeček and I. Tkáč, J. Organomet. Chem., 372 (1989) 327.
7 A. Lyčka, J. Holeček, B. Schneider and J. Straka, J. Organomet. Chem., 389 (1990) 29.
8 D.L. Kepert, Inorg. Chem. 12 (1977) 1.
9 D.L. Kepert, in S.J. Lippard (Ed.), Progr. Inorg. Chem., 23 (1977) 1.
10 W.F. Howard, R.W. Crecely and W.H. Nelson, Inorg. Chem., 24 (1985) 2204.
11 J. Holeček and A. Lyčka, Inorg. Chim. Acta, 118 (1986) L15.
12 J.H. Nogle and R.E. Schirmer, The Nuclear Overhauser Effect; Chemical applications, Academic Press, New York, 1971.
13 M.D. Harmony, V.W. Laurie, R.C. Kuczkowski, R.H. Schwendeman, D.A. Ramsay, S.J. Lovas, W.J. Lafferty and A.G. Maki, J. Phys. Chem. Reference Data, 8 (1979) 619.
14 D. Shi, S.Z. Hu, J. Struct. Chem., 7 (1988) 111.
15 P. Ugliengo, G. Borzani and D. Viterbo, J. Appl. Cryst., 21 (1988) 75.
16 E.O. Schlemper, Inorg. Chem., 6 (1967) 2012.
17 W. Chen, W.K. Ng, V.G. Kumar Das, G.B. Jameson and R.J. Butcher, Acta Crystallogr., Sect. C, 45 (1989) 861.
18 C.B. Baker and D.T. Sawyer, Anal. Chem., 40 (1968) 1945.
19 J.L. Nieto and A.M. Gutierrez, Polyhedron, 2 (1983) 987.
20 N.G. Furmanova, Yu.T. Strutchov, E.M. Rokhlina and D.N. Kravcov, Zh. Struct. Khim., 21 (1980) 87.
21 G.C. Levy and R.L. Lichter, Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy, Wiley, New York, 1979.