Determination of the Coordination Number and Geometry of the Coordination Sphere of the Central Tin Atom in Stannatrane Complexes by Mössbauer Spectroscopy

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The Mössbauer isomer shift (IS) and quadrupole splitting (QS) values of 35 strannatrane complexes of $RSn(XCH_2CH_2)_3Y$, $R_2SN(XCH_2CH_2)_2Y$ and $R_2Sn(OCOCH_2)_2Y$ composition were determined (R = alkyl or aryl groups, X = O, N-Me or S, Y = N, N-R, O or S). On the basis of the partial quadrupole splitting concept QS values were calculated assuming different coordination numbers, and, in the case of pentacoordination, different configurations of the compounds. The comparison of experimental and calculated QS values leads to the determination of the coordination number of tin, and in the pentacoordinated compounds to that of the configuration of the complexes. The data reflected the effect of the functional groups and donor atoms on the structure of the strannatranes.

Introduction

Mössbauer spectroscopy is widely used for the determination of the coordination number of central metal ions (having Mössbauer active isotopes) in coordination compounds [1].

Herber *et al.* [2] used the ratio (ρ) of quadrupole splitting (QS) and of isomer shift (IS) for the determination of the coordination number of tin. According to these authors the coordination number of tin is higher than four, if this ratio is greater than 2.1, isomer shift being referred to tin dioxide.

A better possibility for the determination of the coordination number is the application of the method of partial quadrupole splittings (PQS) [3, 4]. The concept of PQS is based on the assumption that every ligand makes a definite PQS contribution to the experimentally determined quadrupole splitting of the molecule. The PQS values of the individual

ligands do not depend on the other ligands in the complex.

The additivity of the PQS values has been confirmed experimentally in low-spin iron(II) and tin(IV) complex systems [3, 5, 6]. Bancroft [4] drew attention to the fact that this additivity is to be expected only for those systems in which the contribution of the crystal field splitting to the electric field gradient is negligibly small, *i.e.*, for transition metals with filled or half filled d shells [*e.g.*, low-spin iron(II) or high-spin iron(III) complexes], or for main-group ions with empty s and p shells [*e.g.*, tin(IV) and antimony(V)].

It was originally assumed [3] the the PQS values of ligands are also independent of the coordination number in a complex. Bancroft *et al.* [7] have demonstrated that consistent PQS values can be obtained only in systems with the same coordination number. In accordance with this conclusion PQS values for ligands in tetrahedral or octahedral environments were determined; these values may differ significantly.

Bancroft [8] was the first to apply the PQS concept to the study of structural isomers of complexes with the same coordination number. His model systems were pentacoordinated tin organic complexes. We used his procedure for the study of a great series of stannatrane complexes.

These compounds are usually considered to be pentacoordinated. Recent investigations [9, 10] have called attention to the fact that the tin central atom in stannatranes may become hexacoordinated or tetracoordinated, and the pentacoordinated species may have different configurations. Our aim was to find out how Mössbauer spectroscopy reflects these differences. For this purpose 9 monoorgano- and 26 diorganostannatrane complexes were prepared. Their

TABLE I. Isomer Shift (IS), Experimental (QS_{exp}) and Calculated (QS_{C1}) Quadrupole Splitting Values of Monoorgano Stannatrane Complexes.

No.	Complex	IS $\mathrm{mm\ s^{-1}}$	QS_{exp} $\mathrm{mm\ s^{-1}}$	QS_{C1} $\mathrm{mm\ s^{-1}}$	ρ
1	$MeSn(OCH_2CH_2)_3N$	1.04	1.64	+1.29	1.58
2	$EtSn(OCH_2CH_2)_3N$	1.20	1.72	+1.29	1.43
3	$n\text{-}BuSn(OCH_2CH_2)_3N$	0.94	1.74	+1.29	1.91
4	$PhSn(OCH_2CH_2)_3N$	0.94	1.66	+1.19	1.77
5	$t\text{-}BuSn(OCH_2CH_2)_3N$	1.06	1.49	+1.29	1.04
6	$o\text{-}TolSn(OCH_2CH_2)_3N$	0.65	1.50	+1.19	2.31
7*	$t\text{-}BuSn(SCH_2CH_2)_3N$	−0.64	0.84	+0.84	1.31
8	$MeSn(OCOCH_2)_3N$	0.89	2.23	+2.73	2.50
9*	$MeSn(NMeCOCH_2)_3N$	0.97	1.44	+1.44	1.48

TABLE II. Isomer Shift (IS), Experimental (QS_{exp}) and Calculated (QS_{Al} and QS_{Bl}) Quadrupole Splitting Values of the Diorganostannatrane Complexes, and Structure Suggestions.

No.	Complex	IS $\mathrm{mm\ s^{-1}}$	QS_{exp} $\mathrm{mm\ s^{-1}}$	QS_{Al} $\mathrm{mm\ s^{-1}}$	QS_{Bl} $\mathrm{mm\ s^{-1}}$	QS_{tetr}^{**} $\mathrm{mm\ s^{-1}}$	ρ	Suggested structure
10	$Me_2Sn(OCH_2CH_2)_2NMe$	1.33	3.08	+2.20	+1.625	1.87	2.32	hexacoordinated
10a	$Me_2Sn(OCH_2CH_2)_2N\text{-}t\text{-}Bu$	1.15	2.15	+2.20	+1.625	1.87	1.87	Al
11	$Et_2Sn(OCH_2CH_2)_2NEt$	0.96	2.16	+2.20	+1.625	1.87	2.25	Al
12*	$n\text{-}Bu_2Sn(OCH_2CH_2)_2NEt$	0.91	2.20	+2.20	+1.625	1.87	2.42	Al
13	$t\text{-}Bu_2Sn(OCH_2CH_2)_2NMe$	1.42	2.54	+2.20	+.1625	1.87	1.79	Al
14	$t\text{-}Bu_2Sn(OCH_2CH_2)_2N\text{-}i\text{-}Bu$	1.36	1.85	+2.20	+1.625	1.87	1.36	tetrahedral
15*	$t\text{-}Bu_2Sn(OCH_2CH_2)_2N\text{-}t\text{-}Bu$	1.37	1.87	+2.20	+1.625	1.87	1.36	tetrahedral
16	$t\text{-}BuPhSn(OCH_2CH_2)_2NMe$	1.29	1.91	+2.00	+.156***	1.53	1.48	Al
17	$Me_2Sn(OCOCH_2)_2NMe$	1.53	4.15	+3.29	+2.73	2.81	2.71	hexacoordinated
18	$Et_2SN(OCOCH_2)_2NMe$	1.67	4.19	+3.29	+2.73	2.81	2.50	hexacoordinated
19	$n\text{-}Bu_2Sn(OCOCH_2)_2NMe$	1.54	3.88	+3.29	+2.73	2.81	2.52	hexacoordinated
20	$t\text{-}Bu_2Sn(OCOCH_2)_2NMe$	1.68	2.98	+3.29	+2.73	2.81	1.77	Al or Bl
21	$t\text{-}Bu_2Sn(OCOCH_2CH_2)_2NMe$	1.76	3.24	+3.29	+2.73	2.81	1.86	Al
22	$Me_2Sn(SCH_2CH_2)_2NMe$	1.30	1.31	+1.86	+1.33	2.00	1.00	Bl
23	$t\text{-}Bu_2Sn(SCH_2CH_2)_2NMe$	1.63	1.90	+1.86	+1.33	2.00	1.16	Al or tetrahedral
24	$Me_2Sn(SCH_2CH_2)_2S$	1.53	1.81	+1.99	+1.186	2.00	1.18	Al or tetrahedral
25	$t\text{-}Bu_2Sn(SCH_2CH_2)_2S$	1.64	1.76	+1.99	+1.186	2.00	1.07	Al or tetrahedral
26*	$Cl_2Sn(SCH_2CH_2)_2S$	1.28	(−)1.18	−1.53	−1.18	−	0.92	Bl
27	$Me_2Sn(OCH_2CH_2)_2S$	1.21	2.44	+2.33	+1.52	1.87	2.02	Al
28	$n\text{-}Bu_2Sn(OCH_2CH_2)_2S$	1.16	2.08	+2.33	+1.52	1.87	1.79	Al
29	$t\text{-}Bu_2Sn(OCH_2CH_2)_2S$	1.47	1.96	+2.33	+1.52	1.87	1.33	tetrahedral

TABLE II. *(continued)*

No.	Complex	IS mm s^{-1}	QS$_{exp}$ mm s^{-1}	QS$_{A1}$ mm s^{-1}	QS$_{B1}$ mm s^{-1}	QS$_{tetr}^{**}$ mm s^{-1}	ρ	Suggested structure
30	Me$_2$Sn(SCH$_2$CH$_2$)$_2$O	1.45	1.35	+1.75	+1.45	2.00	0.93	B1
31	t-Bu$_2$Sn(SCH$_2$CH$_2$)$_2$O	1.68	1.57	+1.75	+1.45	2.00	0.93	B1
32*	Cl$_2$Sn(SCH$_2$CH$_2$)$_2$O	0.85	1.78	−1.78	−0.91	−	1.18	A1
33	Me$_2$Sn(NMeCOCH$_2$)$_2$NMe	1.15	1.96	+2.75	+1.77	−	1.70	B1
34	t-Bu$_2$Sn(NMeCOCH$_2$)$_2$NMe	1.45	1.87	+2.75	+1.77	−	1.29	B1

*Compounds used for the calculation of new PQS values. **The sign of calculated QS$_{tetr}$ for A$_2$SnB$_2$ species is undetermined since $\eta = 1.00$.   ***The phenyl group is an axial position.

Mössbauer parameters were determined at liquid nitrogen temperature. The quadrupole splitting values were used for the calculations based on the PQS concept. Our results are presented in this paper.

Experimental

The 35 stannatrane complexes studied were prepared according to methods published in detail elsewhere [9, 11−15]. Their compositions were checked by elemental analysis. The measured carbon, hydrogen and nitrogen contents were found to be in good agreement with the calculated values. NMR and mass spectra were also used for the characterization of the compounds.

The Mössbauer spectra were recorded at liquid nitrogen temperature as described in our previous paper [16]. A computer evaluation method was used for the determination of the isomer shift (IS) and quadrupole splitting (QS) values. The reproducibility of these Mössbauer parameters was found to be better than ±0.03 mm/s in each measurement.

The experimentally determined Mössbauer parameters are shown in Tables I and II together with some calculated QS values, Herber's ρ values and the structure suggested on the basis of the calculations. (The IS values refer to that of SnO$_2$.) The calculations based on the PQS concept were performed assuming every possible configuration of the coordination sphere but the results of only those calculated QS values which belong to geometries having some chemical probability in this system are presented in the Tables. The PQS values used in the calculations are shown in Table III.

Results and Discussion

The composition of typical monoorganostannatrane and diorganostannatrane model compounds are shown in Figs. 1 and 2 respectively. The first question was whether the N atom is coordinated (structure A) or not (structure B) to the Sn central atom, i.e., whether these compounds contain penta or tetracoordinated Sn as central atom. Since the correlation between the quadrupole splitting of the compound and the PQS values of the ligands depends on the coordination number, and the PQS values of the same ligands also differ according to the symmetry of the compound, the PQS concept could be used for answering this question.

Our first calculations have been carried out under the assumption of coordination number four (tetrahedral configuration) using the following equation

$$QS = 2\{R\}^{tetr} - 2\{X\}^{tetr}$$

for RSnX$_3$ compounds and

$$QS = (2\{R\}^{tetr} - 2\{X\}^{tetr}) \cdot 1.15$$
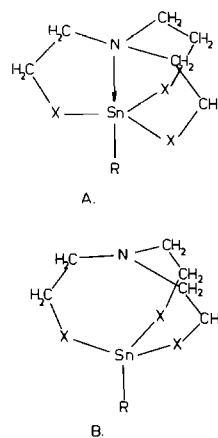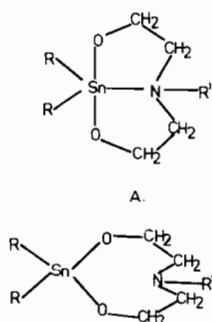
for R$_2$SnX$_2$ compounds

Fig. 1. Structure suggestions for RSn(XCH$_2$CH$_2$)$_3$N stannatrane complexes. A = pentacoordinated trigonal bipyramidal structure; B = distorted tetrahedral structure.

TABLE III. Partial Quadrupole Splitting Values of Ligands and Functional Groups in Complexes of Trigonal Bipyramidal (A) and Tetrahedral (B) Structure.

Ligand or group	A		B	Ref.
	in equatorial position	in apical position		
Cl^-	+0.20	±0.0		8
			±0.0	17, 24
Butyl	−1.13	−0.94		8
			−1.37	24
$-OCOCH_2$	+0.29	+0.075		18
			−0.15	24, 25
−Ph	−0.98	−0.89		8
			−1.26	17, 24
$-OCH_2CH_2$	−0.189	−0.287		Table II, No. 12
			−0.55	Table II, No. 15
$-SCH_2CH_2$	−0.34	−0.40		Table I, No. 7
			−0.50	26
N−R	+0.206	+0.01		8
S	+0.55	+0.267		Table II, No. 26
−NMeCO	−0.14			Table I, No. 9
−O	−0.09	−0.21		Table II, No. 32

Fig. 2. Structure suggestions for $R_2Sn(OCH_2CH_2)_2NR'$ stannatrane complexes. A = pentacoordinated trigonal bipyramidal structure; B = distorted tetrahedral structure.

Fig. 3. A trigonal bipyramidal tin complex. A ligands are situated in equatorial, B in apical position.
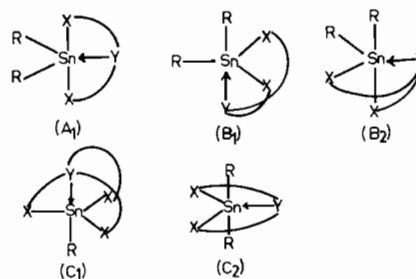
Fig. 4. Supposed configurations of pentacoordinated stannatrane complexes.

where $\{\ \}^{tetr}$ denotes the partial quadrupole splitting (PQS) values of the ligand in tetrahedral species, X denotes the O donor atom in OC_2H_4 group, and R the alkyl or aryl substituent. PQS values were taken for this purpose from the corresponding literature [17]. The data permitted the calculation of a PQS value for tetrahedral OCH_2CH_2. The results refuted in most cases the assumption of tetracoordination. (Only compound 14 was found to be unambiguously of tetrahedral structure, and in the case of compounds 23—25 the PQS calculation did not make possible the distinction between tetra and pentacoordination.)

Pentacoordination may result in the formation of trigonal bipyramidal or square pyramidal structures. The probability of the latter one in tin organic sys-

tems is negligibly small. The coordination sites in a trigonal bipyramid are the equatorial (A) and apical (B) ones (Fig. 3).

Figure 4 shows the possible structural isomers of our stannatrane complexes of $RSnX_3Y$ and R_2SnX_2Y composition, where X_3Y represents the $(OC_2H_4)_3N$ type ligand and X_2Y the $(OC_2H_4)_2N$ ligand in which O could be substituted by N, N−R and S, N could be substituted by N−R, S and O. The following formulae [8] were used for the calculation of the

quadrupole splitting values assuming the presence of these isomers:

$$QS_{A1} \approx \frac{-7\{R\}^{tbe} + 8\{X\}^{tba} + \{Y\}^{tbe}}{\sqrt{7}}$$

$$QS_{B1} \approx \frac{-2\{R\}^{tba} - 5\{R\}^{tbe} - 2\{Y\}^{tba} + 8\{X\}^{tbe}}{\sqrt{13}}$$

$$QS_{B2} \approx$$

$$\frac{-2\{R\}^{tba} - 5\{R\}^{tbe} - 2\{X\}^{tba} + 4\{X\}^{tbe} + 4\{Y\}^{tbe}}{\sqrt{13}}$$

$$QS_{C1} \approx -2\{R\}^{tba} - 2\{Y\}^{tba} + 3\{X\}^{tbe}$$

$$QS_{C2} \approx -4\{R\}^{tba} + 2\{X\}^{tbe} + \{Y\}^{tbe}$$

where { } denotes the partial quadrupole splitting (PQS) values; { }^{tbe} PQS of the ligand in equatorial position { }^{tba} PQS of the ligand in apical position.

It was shown by many examples that [8]

$$3\{X\}^{tbe} - 4\{X\}^{tba} \approx 0.58 \text{ mm/s}$$

The PQS values used for the calculations have been taken partly from the literature [8, 18], others had to be calculated using the experimental QS values of some of our compounds. The PQS value of trigonal bipyramidal (equatorial) OCH_2CH_2 has been estimated previously by Bancroft *et al.* [8] from the QS data of our compounds No. 1–4 in Table I (published in our previous paper [16]). However, recent NMR and molecular weight measurement indicated intermolecular association leading to hexacoordination of these compounds [9, 14]. Therefore new PQS values had to be calculated for OCH_2CH_2 from the QS of compound 12, shown by X-ray measurements [10] to have a A1 trigonal bipyramidal structure. Recent X-ray structural investigations of compounds 7 and 26 performed by M. Dräger [10, 23] made possible the direct calculation of the PQS values for trigonal bipyramidal SCH_2CH_2 and S groups. The complexes used for the PQS calculations are marked by * in Tables I and II. The PQS values used in the calculations and their origin are presented in Table III. The experimental and calculated QS values are compared in Tables I and II.

The experimental QS data in Table I do not show a good agreement with those calculated on the basis of Cl pentacoordinated configuration assumed earlier. This is understandable on consideration of recent NMR and molecular weight measurements [9, 14] showing hexacoordination due to intermolecular association even in solutions. This interaction is not observed in the case of compound 5 in accordance

with its QS value indicating pentacoordination. The greater space requirement of the bulky t-butyl group seems to hinder the association leading to hexacoordination.

According to the data in Table II most of the diorganostannatrane compounds have either an A1 or a B1 trigonal bipyramidal structure. The formation of C2 or B2 structures is less probable because of steric reasons (ring strain). (The Mössbauer data are not compatible with these configurations.)

Previous calculations [8] for compound 11 and two similar complexes have indicated B1 structures. The PQS value of OCH_2CH_2 used in those calculations was derived however from QS values of compounds shown recently to be hexacoordinated [9, 14]. We had therefore to calculate a new PQS value for the OCH_2CH_2 group from the QS of compound 12, which proved to have an A1 structure by X-ray studies [10]. The QS values calculated with the help of this new PQS value indicated the A1 structure of compounds 10a, 11, 13 and 16.

The data of four compounds (10, 17–19) suggested hexacoordination which might be due to intermolecular association in the solid substance through bridging oxygen donor atoms. Such interactions could also be shown in related systems by X-ray structural investigations [19, 20].

In the case of compounds 14 and 15 the comparison of the experimental and calculated QS values (see Table II) indicated clearly a tetrahedral coordination sphere. This is in agreement with the results of ^{119}Sn NMR measurements [15]. The Mössbauer data of $Me_2ClSn(S_2C\text{-}NMe_2)$ and $Me_3Sn(S_2C\text{-}NMe_2)$ taken from the literature [21, 22] as having QS values of 2.80 and 2.33 respectively present a similar example. The former compound was shown by X-ray analysis to have a pentacoordinated A1, the latter a strongly distorted tetrahedral configuration. Using the experimental QS value of $Me_2ClSn(S_2C\text{-}NMe_2)$ we have calculated the PQS value of the dithiocarbamate moiety, and with the help of the latter one the QS value of $Me_3Sn(S_2C\text{-}NMe_2)$. The result excluded the possibility of pentacoordination in accordance with the X-ray data.

In the case of compounds 23–25 the Mössbauer data did not permit a distinction between pentacoordinated A1 or tetrahedral structure. This must be due to the decreased interaction between Y and tin. This phenomenon was shown also by the X-ray measurement [10] in compound 24.

Other compounds (7, 26 and 32) have also undergone X-ray structural investigations [23]. The Mössbauer and X-ray data are in good agreement in all cases except one. Only the Mössbauer study of compound 32 reflected a different configuration from that derived from X-ray investigations (A1 instead of B1). This anomaly might be due either to the difference in the structure between a mono-

crystal and the X-ray amorphous Mössbauer probe, or to the difference in the interaction at room and liquid nitrogen temperature. To answer this question the X-ray and Mössbauer studies of the same sample have to be performed at the same temperature. (The comparison of the experimental IS and QS values of compounds 26 and 32 clearly indicates their different configuration. The structure suggestion of the former one (B1) given in Table II is in agreement with that derived from X-ray measurements).

Besides the comparison of the experimental and calculated QS values the primary QS and isomer shift values are also of interest for the coordination chemist. The data in the Tables indicate the effect of different R groups and that of the change in the donor atom in analogous systems on the electronic density at the central tin atom and on the symmetry of the coordination sphere of the compound. It is to be seen that neither the space requirement of R groups, nor the electronic density on a donor group alone, but both together determine the structure of the compound. The exchange of one methyl group by one butyl may have an effect not smaller than the exchange of an oxygen or nitrogen donor by sulphur. Both changes may result in the change of the coordination number (see compounds 10 and 13, 17 and 20, or 10 and 22 respectively) or in the change of the configuration (see e.g. compounds 22 and 23). The exchange of the OCH_2CH_2 group by $OCOCH_2$ favours intermolecular association resulting in hexacoordination of tin (see compounds 8 and 17–19). This association is very probably due to the presence of carboxyl oxygens which can coordinate the tin atom of a neighbour molecule. The increase of the space requirement of R organic groups decreases the possibility of such interactions (compare compound 20 with 17–19). The exchange of oxygen by sulphur donor atoms in otherwise analogous complexes results in the increase of the isomer shift (IS) values indicating an increased electron density at the place of the tin nucleus and in the decrease of the quadrupole splitting (QS) values, reflecting the increased symmetry of the electronic shell round the tin central atom (compare compounds 23, 24 and 25 with 13, 27, and 29 respectively). The Mössbauer parameters and the configuration reflected by them seem to be sensitive also to the space requirement of the substituent on the N atom of the ligand (see compound 13 and 14 or 15).

The Mössbauer measurements have been made naturally with solid samples. Thus their results reflect the coordination number of tin and the geometry of the molecules in the solid state. Nevertheless most of the results are in good agreement with those of NMR and IR investigations made in solutions indicating that solid state effects play only a secondary role in the determination of the structure of these compounds.

Minor but nevertheless significant differences between the Mössbauer parameters of compounds showing analogous configuration (see e.g. compounds 1–3, 10a–13, 17–19 etc.) may reflect small distortions or weak intermolecular interactions in the solid samples due to specific effects of the differing functional groups (in the case of compounds 1–3 e.g. that of the methyl-, ethyl and n-butyl groups). Their quantitative evaluation with the help of PQS calculations only is however not possible.

The last columns in Tables I and II show that Herber's ρ values cannot be used in this system for the characterization of the coordination number of tin(IV). The good agreement between the structural suggestions made on the basis of the partial quadrupole splitting (PQS) concept with those made on the basis of independent studies (e.g. NMR and even X-ray structural investigations) proved the applicability of the PQS calculation for the determination of coordination number and configuration in such complex tin(IV) organic systems.

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