Co-ordination Number, Symmetry of the Co-ordination Sphere of Tin(IV) and Oligomerization in Carbohydrate Complexes of Dibutyltin(IV)

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Dibutyltin(IV) complexes with 19 different carbohydrates were prepared and studied by Mössbauer spectroscopy. Comparison of the experimental quadrupole splitting values with those calculated on the basis of the partial quadrupole splitting concept revealed that the complexes are of four types: with the central tin(IV) atoms surrounded by donor atoms in a trigonal-bipyramidal, octahedral, both a trigonal-bipyramidal and octahedral or a tetrahedral arrangement. This procedure also distinguished between the different structural isomers of both trigonal-bipyramidal and octahedral complexes. Conclusions could therefore be drawn as to the factors determining which of the isomers is formed in the systems. The changes in the room-temperature Debye–Waller factors and the integral intensities of the Mössbauer doublets assigned to the tin(IV) in different surroundings reflected the oligomerization in the systems. The Mössbauer spectra revealed a temperature-dependent Goldanski–Karyagin effect.

The presence of carbohydrate ligands in organotin(IV) complexes modifies the biological properties of the organotin(IV) moiety[1] and is a reason for the increasing interest in the study of interactions between organotin(IV) compounds and carbohydrates.[2] Simple procedures have been elaborated for the preparation of carbohydrate complexes of dialkyltin(IV).[3,4] The carbohydrate hydroxy groups participating in the process have been identified,[5] and the stoichiometry of the compounds has been established as SnR_2L (R = alkyl, L = carbohydrate residue) by standard analytical procedures.[4] The co-ordination number, the symmetry of the tin(IV) co-ordination sphere and the degree of oligomerization in these compounds (if any) however have not been known until recently.

We earlier reported[4] the results of Mössbauer studies of carbohydrate complexes of diethyltin(IV). Experimental quadrupole splitting (q.s.) values were compared with those calculated on the basis of the partial q.s. (p.q.s.) concept, and the existence of three types of compounds was demonstrated, containing the central tin(IV) atoms in (*a*) a trigonal-bipyramidal environment, (*b*) an octahedral environment, or (*c*) both trigonal-bipyramidal and octahedral environments. The compounds of type (*c*) could be considered dimeric or oligomeric, but nothing was known about the intermolecular interactions of the former complexes.

For a better insight into the symmetry relations and structures of these complexes, dibutyltin(IV) complexes with 19 carbohydrates have been prepared and investigated. The results of Mössbauer studies on these are presented in this work.

Experimental

The dibutyltin(IV) carbohydrate complexes were prepared by reported methods[3,4] from components of analytical purity. The carbohydrate ligands (Reanal and Fluka) were purified by recrystallization from water. Dibutyltin(IV) oxide used for the preparation was also a Fluka product.

The compositions of the complexes were determined by standard analytical methods as presented in ref. 4. Elemental compositions calculated on the basis of 1 : 1 molar ratio of the dibutyltin(IV) moiety and the sugar residue were found to be in good agreement with the experimental data.

Infrared spectra recorded in the region 4000–400 cm^{-1} were in good agreement with the data in ref. 4 indicating the formation of well defined compounds of composition SnR_2L (R = Bu, L = carbohydrate residue).

The Mössbauer spectra were recorded at room temperature and at 77 K with an SM 2201 Mössbauer spectrometer (Nauc Pribor, St. Petersburg) with a ^{119}Sn-radiation source in a $CaSnO_3$ matrix with an activity of 0.1 GBq. The room-temperature measurements were carried out with a resonance scintillation detector (Mössbauer Technology Laboratory MÖSTEC, Rostov-on-Don). With the latter instrument absorption lines could be obtained even in organotin samples with very low Debye–Waller factors, since every conversion electron was registered due to the 4π geometry. The spectra were analysed as Lorentzian lines by least-squares fitting. To allow comparison of areas of the spectra of different samples all parameters of geometry and of surface density of tin(IV) were kept the same in the whole series of measurements. Each measured Mössbauer spectrum was fitted three or four times (using different input parameters) and the best fits have been chosen on the basis of the residual and standard deviations. The errors (twice the standard deviation) of the tabulated data are less than 5%. The isomer shifts (i.s.) are referred to SnO_2.

Calculations

To determine the steric arrangement of the co-ordination sphere in these tin(IV) compounds, q.s. values were calculated on the basis of a simple but general molecular orbital model, according to the p.q.s. concept,[6,7] for the possible symmetries of four-, five- and six-co-ordinated tin(IV) atoms binding two alkyl groups and two negatively charged (deprotonated) carbohydrate oxygen atoms, besides different numbers of non-deprotonated hydroxy oxygens.

The p.q.s. values of the different functional groups used in our

Table 1 Partial quadrupole splitting (p.q.s.) values of the functional groups, and calculated quadrupole splitting (q.s.) values for the tin(IV) co-ordination spheres in different stereochemical arrangements *

p.q.s./mm s^{-1}

$\{R\}^{tetr} = -1.37$	$\{\text{-O}^-\}^{tetr} = -0.37$	$\{\text{-OH}\}^{tetr} = -0.25$
$\{R\}^{tba} = -0.94$	$\{\text{-O}^-\}^{tba} = -0.21$	$\{\text{-OH}\}^{tba} = -0.13$
$\{R\}^{tbe} = -1.13$	$\{\text{-O}^-\}^{tbe} = -0.09$	$\{\text{-OH}\}^{tbe} = +0.02$
$\{R\}^{oct} = -1.03$	$\{\text{-O}^-\}^{oct} = -0.27$	$\{\text{-OH}\}^{oct} = -0.19$

q.s. (Calc.)/mm s^{-1}

Tetrahedral T_d	$R_2Sn(O^-)_2$	2.30
Trigonal-bipyramidal	*TBPY* 1	2.44
	TBPY 2	2.36
	TBPY 3	1.96
	TBPY 4	2.13
	TBPY 5	3.60
Octahedral	O_h 1	1.60
	O_h 2	1.36
	O_h 3	1.84
	O_h 4	3.20

* Deprotonated carbohydrate hydroxy groups represented by O$^-$, while OH represents non-deprotonated hydroxy groups in the co-ordination sphere; tetr represents tetrahedral symmetry, tba represents apical positions while tbe refers to equatorial positions in trigonal bipyramidal arrangements and oct represents octahedral symmetry.

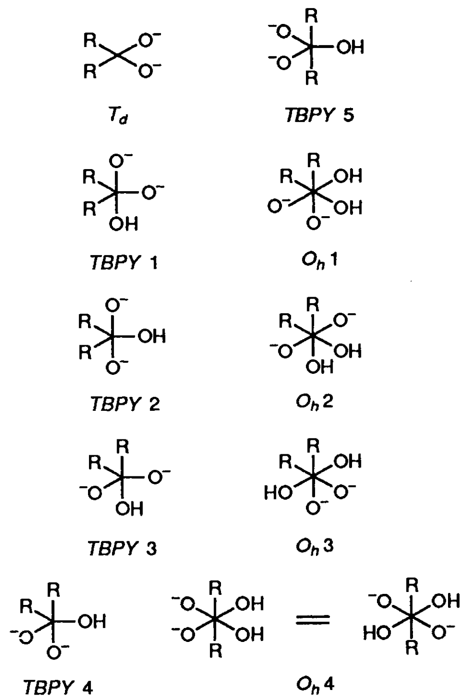

Fig. 1 Configurations of the tin(IV) co-ordination sphere used in the partial quadrupole splitting calculations

calculations, and the calculated q.s. values for tin(IV) in different stereochemical arrangements, are given in Table 1.

Some p.q.s. values were taken from the literature.[6,7] The values of $\{O^-\}^{tetr}$ and $\{OH\}^{tetr}$ were calculated *via* equation (6) in ref. 8. The value of $\{OH\}^{tbe}$ was calculated as in ref. 9. The values of $\{O^-\}^{oct}$ and $\{OH\}^{oct}$ were determined on the basis of the correlation between the p.q.s. values of the octahedral and trigonal-bipyramidal apical positions, as detailed in ref. 6. The structural isomers for which the calculations were made are shown in Fig. 1.

Equations (1)–(10) were used to calculate the q.s. values assigned to the different structures.

$$\text{q.s.}(T_d) = 1.15(2\{R\}^{tetr} - 2\{O^-\}^{tetr}) \qquad (1)$$

$$\text{q.s.}(TBPY\ 1) = 7^{-\frac{1}{2}}[-7\{R\}^{tbe} + 4\{O^-\}^{tba} + 4\{OH\}^{tba} + \{O^-\}^{tbe}] \qquad (2)$$

$$\text{q.s.}(TBPY\,2) = 7^{-\frac{1}{2}}[-7\{R\}^{tbe} + 8\{O^-\}^{tba} + \{OH\}^{tbe}] \qquad (3)$$

$$\text{q.s.}(TBPY\,3) = 13^{-\frac{1}{2}}[-2\{R\}^{tba} - 5\{R\}^{tbe} + 8\{O^-\}^{tbe} - 2\{OH\}^{tba}] \qquad (4)$$

$$\text{q.s.}(TBPY\,4) = 13^{-\frac{1}{2}}[2\{R\}^{tba} - 5\{R\}^{tbe} - 2\{O^-\}^{tba} + 4\{O^-\}^{tbe} + 4\{OH\}^{tbe}] \qquad (5)$$

$$\text{q.s.}(TBPY\,5) = -4\{R\}^{tba} + 2\{O^-\}^{tbe} + \{OH\}^{tbe} \qquad (6)$$

$$\text{q.s.}(O_h\,1) = 2\{R\}^{oct} - \{O^-\}^{oct} - \{OH\}^{oct} \qquad (7)$$

$$\text{q.s.}(O_h\,2) = 2\{R\}^{oct} + 2\{OH\}^{oct} - 4\{O^-\}^{oct} \qquad (8)$$

$$\text{q.s.}(O_h\,3) = 2\{R\}^{oct} + 2\{O^-\}^{oct} - 4\{OH\}^{oct} \qquad (9)$$

$$\text{q.s.}(O_h\,4) = 4\{R\}^{oct} - 2\{O^-\}^{oct} - 2\{OH\}^{oct} \qquad (10)$$

Results and Discussion

The Mössbauer parameters determined by computer evaluation of the spectra measured at liquid-nitrogen temperature are presented in Tables 2 and 3. Some representative Mössbauer spectra are shown in Fig. 2. All spectra exhibited i.s. and q.s. which clearly indicate the presence of tin(IV) species. The Mössbauer spectra of compounds **1**–**6** comprised only one, well developed doublet, which suggests the presence of completely equivalent tin environments in these compounds. The suggested stereochemical arrangements of the tin(IV) in these complexes are also listed in Table 2.

The spectra of all the other complexes indicated the presence of two overlapping quadrupole doublets, the two outer and the two inner lines, respectively, being associated. The Mössbauer parameters of the decomposed spectra are presented in Table 3, together with the configurations suggested on the basis of the comparison of the experimental and calculated q.s. values.

The evaluation of the Mössbauer measurements on the basis of the p.q.s. concept shows, in agreement with previous X-ray structural investigations, that the tin(IV) in the studied complexes is present in either a trigonal-bipyramidal environment,[10,11] an octahedral environment, or in both.[4,12] Only one complex (compound **1**) was found to contain tetrahedrally co-ordinated tin(IV).

The configurations given in Tables 2 and 3 reveal that in the compounds studied (except for **1** and **3**) one of the tin(IV) moieties is bonded to two butyl groups in *trans* positions. The preferred configurations among the trigonal-bipyramidal isomers are *TBPY* 5 (thirteen compounds) and *TBPY* 1 (nine compounds), while that among the octahedral isomers is O_h 4 (seven compounds). The configurations O_h 1, O_h 2 and O_h 3 were not observed, and all other configurations were present in at most two cases each.

For all systems, the Mössbauer spectra were recorded at both liquid-nitrogen- and room-temperature. The line intensities for the individual complexes proved to be different, with very large differences in the room-temperature spectra. The percentage absorptions are shown in Table 4. The absorptions relating to the different components are proportional to the Debye–Waller factor (f), which can be approximated as the product of two factors, equation (11), where f_M is connected with the vibration

$$f = f_M f_K \qquad (11)$$

Table 2 Experimental ^{119}Sn Mössbauer parameters of dibutyltin(IV) carbohydrates, and suggested configurations of tin(IV)[a]

Compound	Carbohydrate	i.s./mm s^{-1}	q.s./mm s^{-1}	Configuration
1	Mannitol	1.06	2.23	T_h
2	Maltose[b]	1.24	3.06	O_h4
3	Raffinose[c]	1.05	2.21	*TBPY*4
4	Lactobionic acid[d]	1.31	3.27	O_h4
5	D-Galacturonic acid	1.43	3.76	*TBPY*5
6	D-Gluconic acid γ-lactone	1.31	3.25	O_h4

[a] The spectra were recorded at liquid-nitrogen temperature. [b] 4-*O*-α-D-Glucopyranosyl-D-glucose. [c] *O*-α-D-Galactopyranosyl-(1→6)-α-D-glucopyranosyl β-D-fructofuranoside. [d] 4-*O*-β-Galactopyranosyl-D-gluconic acid.

Table 3 Mössbauer parameters (i.s., q.s.) of dibutyltin(IV) carbohydrate complexes at 77 K after decomposition of their spectra, suggested configurations of tin(IV), and ratios (R_A) of areas assigned to the two doublets

		i.s.$_1$	q.s.$_1$		i.s.$_2$	q.s.$_2$		
Compound	Carbohydrate	mm s^{-1}		Configuration	mm s^{-1}		Configuration	R_A
7	D-Glucose	1.25	2.92	O_h4	1.43	3.73	*TBPY*5	5:2
8	D-Ribose	1.22	2.56	*TBPY*1	1.33	3.78	*TBPY*5	4:2
9	D-Arabinose	1.26	2.93	O_h4	1.50	3.69	*TBPY*5	3:2
10	L-Arabinose	1.23	2.65	*TBPY*1	1.37	3.73	*TBPY*5	3:2
11	D-Xylose	1.22	2.58	*TBPY*1	1.36	3.68	*TBPY*5	2:2
12	D-Galactose	1.33	3.58	*TBPY*5	1.19	2.40	*TBPY*1	2:2
13	D-Mannose	1.21	2.54	*TBPY*1	1.35	3.72	*TBPY*5	3:2
14	L-Rhamnose[a]	1.25	2.60	*TBPY*1	1.36	3.75	*TBPY*5	3:2
15	D-Fructose	1.10	2.69	*TBPY*1	1.47	3.26	O_h4	2:5
16	L-Sorbose	1.23	2.60	*TBPY*1	1.34	3.74	*TBPY*5	4:2
17	Sorbitol[b]	1.11	2.29	*TBPY*2	1.30	3.53	*TBPY*5	5:2
18	Maltitol[c]	1.20	2.38	*TBPY*2	1.30	3.48	*TBPY*5	3:2
19	D-Gluconic acid δ-lactone	1.30	3.14	O_h4	1.47	4.16	*TBPY*5	7:2

[a] 6-Deoxy-L-mannose. [b] D-Glucitol. [c] 4-*O*-α-D-Glucopyranosyl-D-glucitol.

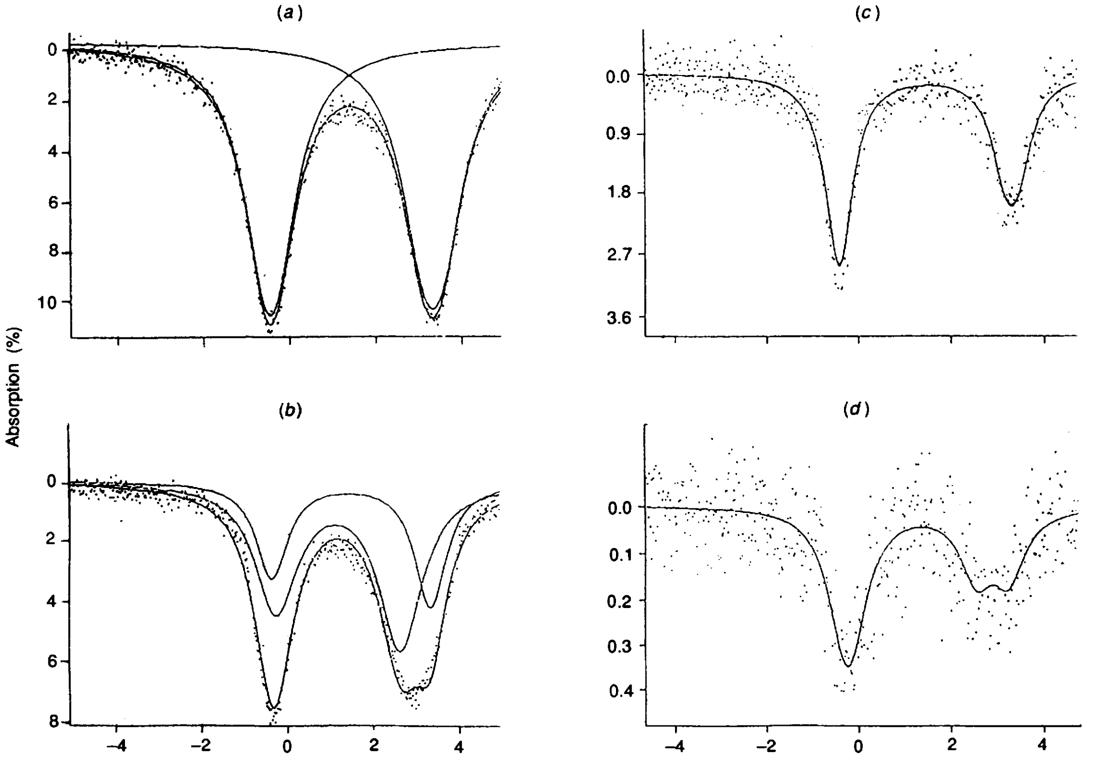

Fig. 2 Mössbauer spectra of the carbohydrate dibutyltin(IV) complexes **5** [(*a*), (*c*)] and **7** [(*b*), (*d*)] at liquid-nitrogen [(*a*), (*b*)] and at room temperature [(*c*), (*d*)]

of the molecule and f_K depends on the vibration of the tin within the molecule.[13]

Intermolecular interactions leading to oligomerization or even polymer formation may increase the value of f_M, and the strength of the intramolecular bonding is proportional to f_K.

Table 4 Total absorptions (A) and percentages of areas of right wings (M_π) and left wings (M_σ) of the Mössbauer spectra of dibutyltin(IV) carbohydrate complexes at room and at liquid-nitrogen temperature

		Room temperature				77 K			
Compound	Carbohydrate	A (%)	M_σ	M_π	M_π/M_σ	A (%)	M_σ	M_π	M_π/M_σ
1	Mannitol	0.10	92.8	7.2	0.077*	6.0	47.5	52.5	1.11
2	Maltose	1.50	53.7	46.3	0.863	7.8	44.9	55.1	1.23
3	Raffinose	2.90	59.0	41.0	0.695	8.7	44.9	55.1	1.23
4	Lactobionic acid	4.30	54.3	45.7	0.841	12.0	46.1	53.9	1.17
5	D-Galacturonic acid	3.60	56.1	43.9	0.782	11.2	48.6	51.4	1.06
6	D-Gluconic acid γ-lactone	2.00	57.5	42.5	0.740	10.7	46.6	53.4	1.20
7	D-Glucose	0.40	57.8	42.2	0.729	9.7	41.4	58.6	1.41
8	D-Ribose	0.95	54.4	45.6	0.837	9.6	45.6	54.4	1.19
9	D-Arabinose	0.55	59.3	40.7	0.685	10.1	40.2	59.8	1.48
10	L-Arabinose	0.45	60.1	39.9	0.664	6.2	46.0	54.0	1.17
11	D-Xylose	0.60	56.5	43.5	0.771	9.8	45.8	54.2	1.18
12	D-Galactose	0.45	63.1	36.9	0.586	10.4	46.5	53.5	1.15
13	D-Mannose	0.55	52.4	47.6	0.910	8.5	45.7	54.3	1.19
14	L-Rhamnose	0.45	59.6	40.4	0.677	11.4	45.3	54.7	1.21
15	D-Fructose	0.32	54.6	45.4	0.832	10.2	40.0	60.0	1.50
16	L-Sorbose	0.85	56.6	43.4	0.765	12.0	45.8	54.2	1.18
17	Sorbitol	0.80	61.6	38.4	0.623	7.1	44.2	55.8	1.26
18	Maltitol	0.90	58.0	42.0	0.725	9.6	45.0	55.0	1.22
19	D-Gluconic acid δ-lactone	0.85	56.9	43.1	0.759	9.0	46.9	53.1	1.13

* Due to the extremely low room-temperature Debye–Waller factor of compound **1** (A = 0.10%) the experimental line areas are uncertain leading to uncertainty of M_π/M_σ for this compound.

Dialkyltin(IV) complexes with a co-ordination number not higher than four must be considered monomeric. Tin(IV) species with a co-ordination number higher than four may be either oligomeric or monomeric. Five- or six-co-ordination may be due to ligand bridge formation, or the fifth and sixth co-ordination sites of the tin(IV) may be occupied by hydroxy oxygens of the carbohydrate which is bound to the tin *via* its two deprotonated hydroxy groups. The present sugar ligands with their hydroxy oxygen donor atoms are specially suitable for the formation of ligand bridges, resulting in polynuclear tin(IV) complexes as shown by X-ray diffraction[12] and extended X-ray absorption fine structure (EXAFS) measurements.[14] In such chain-like compounds, the species at both ends of the chain are expected to be different from those within the chain. Since in this type of complex at liquid-nitrogen temperature* the Debye–Waller factors of the different tin(IV) centres can be considered, to a good estimation, to be equal, the ratio of the intensities of the Mössbauer lines assigned to the two types of tin(IV) atoms should indicate the composition of the oligomer, and even the degree of oligomerization in the system. Ring-forming oligomers or long-chain polymers may show the presence of only one type (five- or six-co-ordinated) tin(IV).

The above considerations demonstrate with certainty that one complex, the dibutyltin derivative of mannitol **1**, is monomeric. This is supported by the fact that at room temperature this compound had the smallest Debye–Waller factor in this series of compounds (Table 4).

The Mössbauer spectra of the other five complexes containing equivalent tin(IV) atoms (**2**–**6**) had much higher Debye–Waller factors than those of any of the other complexes, indicating a high degree of oligomerization. The cyclic or long-chain oligomeric nature of **2**–**6** may thus be inferred.

With the assumption of chain-type oligomerization in compounds containing two tin(IV) atoms in different stereochemical environments, the ratio of terminal and within-chain tin(IV) moieties was calculated for each complex from the intensities of the corresponding Mössbauer doublets. The results are presented in the last column of Table 3. It can be seen that in each compound which contains tin(IV) in a *TBPY* 5 arrangement, that this is in a terminal position, *i.e.* the oligomer chain is terminated at both ends by trigonal-bipyramidally co-ordinated tin(IV) centres with the two alkyl groups in apical positions. This indicates that intermolecular interactions between the tin(IV) complexes, leading to oligomerization, proceed through the equatorially situated hydroxy groups of the carbohydrates. Octahedrally co-ordinated tin(IV) moieties are situated in each case within the chains. Their presence favours the formation of longer chains than those containing only five-co-ordinated tin(IV) moieties with different symmetries. The number of in-chain moieties in the complexes varies between two and seven, indicating oligomeric chains built up from four to nine tin-containing moieties. In two compounds (**11** and **12**), the ratio of internal and terminal moieties was 1 : 1. These latter could be either tetra- or di-meric species. The much lower room-temperature Debye–Waller factors of compounds **7**–**19** than those of the complexes containing equivalent tin(IV) atoms (**2**–**6**) seem to suggest a much lower degree of polymerization in **7**–**19** than in **2**–**6**. The data in Table 4 reveal that the intermolecular interaction leading to oligomerization is strongest in the complexes containing carboxylate ligands (**4** and **5**).

A comparison of the data in the last column of Table 3 and those in the first column of Table 4 did not reveal a correlation between the chain length and the Debye–Waller factor of the species belonging in the groups of complexes containing tin(IV) atoms in two different environments. This seems to indicate that f_K has a stronger influence on f than does f_M [equation (11)].

Our aim was to find a correlation between the original conformation of the carbohydrate ligands co-ordinated to the tin(IV) in the complexes and the co-ordination number, the symmetry of the co-ordination sphere and the degree of oligomerization of the complexes. Such a correlation does not seem to exist. The binding of the dialkyltin(IV) moiety by the carbohydrate seems to change the conformation and steric properties of the latter. Elucidation of these changes demands further investigations.

In a similar previous study of a series of carbohydrate complexes of diethyltin(IV),[4] the p.q.s. calculations did not distinguish between deprotonated and non-deprotonated hydroxy groups of the sugar moieties. This treatment permitted

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* Debye–Waller factors even if different at room temperature will become similar at liquid-nitrogen temperature.

Table 5 Mössbauer parameters of diethyltin(IV) carbohydrate complexes,[4] and suggested configurations of tin(IV)

		i.s.$_1$	q.s.$_1$		i.s.$_2$	q.s.$_2$	
Compound	Carbohydrate	mm s^{-1}		Configuration	mm s^{-1}		Configuration
20	Mannitol	1.37	2.19	*TBPY* 4			
21	Dulcitol	1.60	3.12	O_h 4			
22	Raffinose	1.37	2.25	*TBPY* 2			
23	Lactose	1.36	2.14	*TBPY* 4			
24	Galacturonic acid	1.83	3.95	*TBPY* 5			
25	Saccharose	1.27	2.25	*TBPY* 3			
26	Maltose	1.37	2.20	*TBPY* 4	1.56	3.14	O_h 4
27	Lactobionic acid	1.50	3.13	O_h 4	1.68	3.86	*TBPY* 5
28	L-Glucose	1.46	2.89	O_h 4	1.79	3.54	*TBPY* 5
29	Maltitol	1.40	2.72	*TBPY* 1	1.71	3.35	O_h 4
30	L-Arabinose	1.41	2.77	*TBPY* 1	1.72	3.39	O_h 4
31	L-Xylose	1.44	2.87	O_h 4	1.78	3.54	*TBPY* 5
32	L-Galactose	1.35	2.58	*TBPY* 1	1.74	3.37	O_h 4
33	Sorbitol	1.44	2.41	*TBPY* 1	1.61	3.45	*TBPY* 5
34	*meso*-Inositol	1.32	2.48	*TBPY* 1	1.65	3.13	O_h 4
35	L-Mannose	1.51	3.06	O_h 4	1.77	3.59	*TBPY* 5
36	D-Glucosamine	1.65	3.07	O_h 4			

determination of the co-ordination number of the tin(IV), but not the positions of the two types of hydroxy oxygens in the co-ordination sphere of tin(IV) and consequently a direct comparison of the results with those of our present investigations. Using the present model, therefore, we have recalculated the previous data. The results are given in Table 5.

Comparison of the data in Tables 2 and 4 with those in Table 5 reveals some small differences between the behaviour of the diethyl- and dibutyl-tin(IV) derivatives.

Diethyltin derivatives seem to favour six-co-ordination relative to dibutyltin species. Of 17 diethyltin(IV) compounds, 11 contained octahedrally co-ordinated tin(IV), while of 19 dibutyltin complexes, only seven did so, all 18 of these displaying O_h 4 symmetry, *i.e.* with the alkyl groups in a *trans* arrangement. The reason for this difference may be the smaller space requirement of ethyl relative to butyl groups. The difference in size between the two alkyl groups may also be a reason for the formation of *TBPY* 4 isomers (four species) besides the predominant *TBPY* 5 (seven species) and *TBPY* 1 (five species) in the diethyl derivatives, but not in the dibutyl ones. The R–Sn–R bond angle is ≈180° in *TBPY* 5, and ≈120° in *TBPY* 1, but only ≈90° in *TBPY* 3 and *TBPY* 4 arrangements. The importance of steric factors increases upon a narrowing of the R–Sn–R angle.

All the doublets in the measured spectra exhibit asymmetry, as demonstrated in Table 4. At room temperature $M_\pi/M_\sigma < 1$, but at liquid-nitrogen temperature $M_\pi/M_\sigma > 1$ where the terms M_π and M_σ represent the probability of the transitions $\Delta m = 1$ $(\frac{1}{2} \longrightarrow \frac{3}{2})$ and $\Delta m = 0$ $(\frac{1}{2} \longrightarrow \frac{1}{2})$, respectively, between the ground and excited states of the nucleus of the tin absorber. This experimental finding can be considered a special type of Goldanskii–Karyagin effect, which changes its direction with the temperature. The first compound which was discovered to have this property was $SnMe_2F_2$.[15] The present work reports a further 19 tin compounds showing the same behaviour.

This phenomenon can be explained by the greater temperature expansion coefficient in the direction of the *c* axis than that in the direction of the *a* or the *b* axis. Consequently, a decrease of temperature can result in a stronger reduction of the amplitude of the vibration of the tin atoms in the *c* direction than in the *a* or *b* directions. This mechanism leads to $M_\pi/M_\sigma < 1$ at low temperature.

Conclusion

Comparison of experimental Mössbauer q.s. values with those calculated on the basis of the p.q.s. concept has led to the determination of the co-ordination number and configuration of the central tin(IV) atoms in diorganotin(IV) complexes with carbohydrates. Four types of compounds were demonstrated, in which the central tin(IV) atoms were present (*a*) only in a trigonal-bipyrimidal environment, (*b*) only in an octahedral environment, (*c*) in both types of environment and (*d*) in a tetrahedral environment.

The investigations distinguished between the different structural isomers of both trigonal-bipyramidal and octahedral complexes. The formation of the structural isomers was shown to depend on the size of the alkyl group on the tin(IV) and on the situation (terminal or in-chain) of the tin atoms in question.

The ratios of the integral intensities of the Mössbauer doublets assigned to the two types of tin, and also the room-temperature Debye–Waller factors, indicated the degree of oligomerization in the systems.

No correlation was observed between the original conformation of the carbohydrates and the configuration of the tin(IV) in their diorganotin complexes. Complex formation seems to change the conformation of the carbohydrate ligand.

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