Equilibrium and spectroscopic studies of diethyltin(IV) complexes formed with carbohydrate derivatives of thiazolidine-4-carboxylic acid

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Abstract

Coordination of six 2-substituted thiazolidine-4-carboxylic acid derivatives by the diethyltin(IV) cation was studied in aqueous solutions. The formation constants of the complexes MLH, ML and MLOH and of the hydrolysis products of diethyltin(IV) ion were determined by potentiometric equilibrium measurements. The ligands are effective complexing agents with amino acid type coordination in the pH > 5 range, where the mixed hydroxo species MLOH predominates. The polyhydroxyalkyl substituents on the ligand do not show direct coordination to tin(IV), they exert only sterical effects on the process. The solid compounds with composition MLOH show, according to Mossbauer investigations based on the partial quadrupole splitting concept and according to IR spectroscopic studies, trigonal bipyramidal arrangement of the donor atoms around the tin(IV) ion with hydroxide, carboxylate and amine coordination.

Key words: Equilibrium studies; Formation constants; Tin complexes; Carbohydrate derivative complexes

Introduction

It is known that organotin(IV) compounds have a strong biological activity. The moieties $R_nSn^{(4-n)+}$ ($n = 2$ or 3) may be bound to proteins and glycoproteins of cell membranes, as well as to cellular proteins; e.g. Et_2Sn^{2+} to ATPase and hexokinase [1], But_2Sn^{2+} or But_3Sn^+ to ATPase and acetylcholine esterase of human erythrocyte membrane [2], But_2Sn^{2+} may be bound to skeletal muscle membranes, too [2]. Some organotin(IV) compounds have shown antitumor activity [3].

The presence of carbohydrates in organotin(IV) complexes modifies the biological properties of the system [4]. This is the reason for the increasing interest in interactions between organotin(IV) compounds and carbohydrate derivatives [5, 6].

Recently we studied diethyltin(IV) and dibutyltin(IV) complexes formed with carbohydrate type ligands. The symmetry and local structures of the complexes were determined by Mössbauer spectroscopy [7, 8] and by EXAFS [9], respectively.

As a part of our research program dealing with the coordination behaviour of carbohydrate derivatives the coordination ability of biologically important adducts of L-cysteine and monosaccharides, i.e. 2-(polyhydroxyalkyl)thiazolidine-4-carboxylic acid derivatives (PHTAc), toward transition metal ions, has been studied both in aqueous solution [10] and in solid state [11]. The present paper reports the formation equilibrium study and structural investigation of diethyltin(IV) complexes formed with these ligands.

Experimental

Materials

All reagents were Reanal products of analytical purity. Diethyltin(IV) dichloride and oxide were prepared according to basic descriptions presented in ref. 7. The ligands were obtained using the method of Weitzel *et al.* [12].

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Preparation of the solid diethyltin(IV) complexes were performed as follows. Equimolar amounts (25 mmol) of Et_2SnO and the PHTAc ligand were suspended in 50 cm^3 dry methanol, and the mixture was refluxed for 2 h. The products were obtained after removal of the methanol by rotary evaporation. The compounds were washed with a small amount of diethyl ether and dried *in vacuo*. The composition of the compounds was determined by standard analytical procedures. These measurements have shown that the complexes contain the carbohydrate and the dialkyltin(IV) moieties in a 1:1 molar ratio.

pH-metric measurements

Both hydrolysis and coordination equilibria of diethyltin(IV) dichloride were investigated by potentiometric titrations in aqueous solution. The ionic strength was adjusted to 0.1 mol dm^{-3} with $NaClO_4$, and the cell was thermostated to 298 ± 0.1 K. The electrode system (Radelkis OP-0718P glass electrode and Radelkis OP-0831P silver–silver chloride reference electrode) was calibrated before each measurement by titrating a mixture of TRIS (tris(hydroxymethyl)methylamine) and $HClO_4$ of known composition with standard sodium hydroxide solution. The electrode potential was recorded with a Radelkis OP-208/1 precision digital pH-meter in a full automatic titration set. The measured e.m.f. values (E) were converted into hydrogen ion concentrations using the modified Nernst eqn. (1):

$$E = E_0 + K \log[H^+] + J_H[H^+] + J_{OH}[H^+]^{-1} K_w \quad (1)$$

where J_H and J_{OH} are fitting parameters in acidic and alkaline media for the correction of experimental errors, mainly due to liquid junction and to the alkaline and acidic errors of the glass electrode; K_w is the autoprotolysis constant of water: $10^{-13.75}$. Calculation of the parameters was performed by a non-linear least-squares method.

The species formed in the systems studied were characterized by the general equilibrium processes (2) while the formation constants for these generalized species are given by eqn. (3).

$$pM + qL \overset{\beta_{M_pL_qH_{-r}}}{\rightleftharpoons} M_pL_qH_{-r} + rH$$

or

$$pM + qL + rH_2O \overset{\beta_{M_pL_qOH_r}}{\rightleftharpoons} M_pL_q(OH)_r + rH \quad (2)$$

$$\beta_{M_pL_qH_{-r}} = \beta_{M_pL_qOH_r} = \frac{[M_pL_qH_{-r}][H]^r}{[M]^p[L]^q}$$

$$= \frac{[M_pL_q(OH)_r]K_w^r}{[M]^p[L]^q[OH]^r} \quad (3)$$

(Charges are omitted for simplicity; M denotes Et_2Sn^{2+}.)

The equilibrium constants were determined from five independent titrations in each system, the organotin(IV) cation to ligand ratios varying from 1:2 to 1:5 and the organotin(IV) concentration ranging from 2×10^{-3} to 1×10^{-2} mol dm^{-3}. The experimental data were evaluated by the computer program PSEQUAD [13].

Spectroscopic methods

The ^{119}Sn Mössbauer spectra were recorded at liquid nitrogen temperature, as described earlier [14]. Computer evaluation was used to determine isomer shift (*IS*) and quadrupole splitting (*QS*) values. The reproducibility of the Mössbauer parameters was found to be ± 0.02 mm s^{-1} in each measurement. The *IS* values are referred to that of SnO_2. The linewidth of a 25 mg cm^{-2} white tin foil was 0.97 mm s^{-1} in our measurements.

IR spectra in the region 4000–400 cm^{-1} were recorded on samples in KBr pellets with a Specord spectrometer.

Results and discussion

Equilibrium studies

Hydrolysis of diethyltin(IV)

The hydrolysis of alkyltin(IV) ions was investigated extensively by Tobias *et al.* [15] in perchlorate, by Asso and Carpeni [16] in chloride and by Arena *et al.* [17] in nitrate medium. Stability constants of the hydroxo species determined under the experimental conditions (0.1 mol dm^{-3} $NaClO_4$) we used have not yet been reported. We performed, therefore, potentiometric titrations to obtain the latter data. The concentration of the organotin(IV) ion ranged from 1×10^{-3} to 4×10^{-2} mol dm^{-3}, but above 1×10^{-2} mol dm^{-3} precipitation prevented the titrations at pH > 6.

In our calculations MOH, $M(OH)_2$ and $M(OH)_3$ were considered as dominant complexes (where $M = Et_2Sn^{2+}$ ion). Comparison of the formation functions for the systems with different total metal ion concentrations provide further information about the compositions of the hydrolysis products. The curves show small but significant differences and an intersection point at about $\overline{OH}^* = 1.5$ and pH = 5.5 indicating the formation of polynuclear species with the composition of $M_2(OH)_3$ or its polymers. Similar results were obtained in the case of the dimethyltin(IV) cation [15] and the formation constants of several polynuclear species were reported under different conditions. We have found that the involvement of the $M_2(OH)_2$ and $M_2(OH)_3$ species in the model improves the fit of the calculated curve to the experimental points but caused only small changes

*$\overline{OH}$ is the average number of hydroxide ions bound by one metal ion.

in the stability constants of the mononuclear hydroxo complexes. Thus, the extent of polynuclear complexes may not exceed 10% of the total metal ion concentration even in the presence of 0.01 mol dm^{-3} diethyltin(IV). Other polynuclear species, such as $M_3(OH)_4$ or $M_4(OH)_6$, may also be involved, but they have no significant effect on the fit and therefore there is no reason to take them into account. The overall formation constants of the hydroxo complexes are listed in Table 1, together with some literature data. It can be seen that our constants are near to those published by Arena *et al.* [17] in nitrate medium (0.1 mol dm^{-3} KNO_3). Thus, chloro complex formation may be omitted in the chloride concentration range $<2\times10^{-2}$ mol dm^{-3}, but according to the result from ref. 6 it may be significant in 1.0 mol dm^{-3} solutions (see Table 1).

Complex formation of PHTAc ligands

Six PHTAc ligands were selected (see Fig. 1) to study the effect of substituents on the C(1′) carbon atom on the coordination. These ligands form with zinc(II) [10], nickel(II) and manganese(II) [18] ions ML and ML_2 parent complexes with high stabilities in those cases when the alcoholic hydroxy group on the C(1′) carbon is situated in a sterically favourable position for coordination to the metal ion (as in case of GLUCYS and GALCYS). The stability of these complexes will be somewhat smaller when (2′) or (3′) hydroxy groups hinder sterically the coordination of the latter (1′) hydroxy group (RAMCYS). Complexes with the lowest stabilities in the series of ligands investigated were formed when the position of the (1′) alcoholic hydroxy group is sterically unfavourable for coordination, or the ligand has no hydroxy group on the C(1′) carbon (MANCYS and PROCYS). (PHECYS ligand may also be of interest, but its poor solubility does not allow the investigations in aqueous medium.) The pH-metric measurements were performed up to pH = 6 in order to avoid the complications arising from the equilibrium between the cyclic and open chain forms of the PHTAc ligands.

TABLE 1. Overall formation constants for the hydroxo complexes of diethyltin(IV) ion

Species	log β[a]	log β[b]	log β[c]
MOH	-3.02 ± 0.02	-3.10	-2.65
$M(OH)_2$	-8.45 ± 0.02	-8.56	-7.49
$M(OH)_3$	-19.70 ± 0.05		
$M_2(OH)_2$	-5.09 ± 0.09	-5.07	-4.00
$M_2(OH)_3$	-9.69 ± 0.04	-10.26	-7.60

[a]This work. [b]From ref. 17 (I = 0.1 mol dm^{-3}, KNO_3). [c]From ref. 16 (I = 1 mol dm^{-3}, KCl).

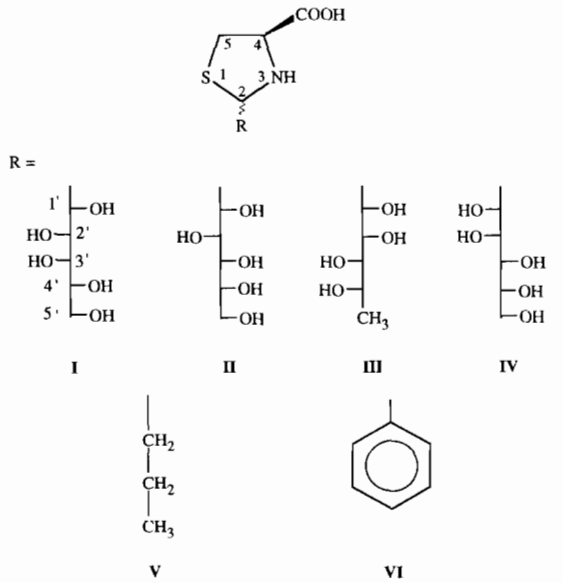


Fig. 1. Structures of the PHTAc ligands studied: I, GALCYS; II, GLUCYS; III, RAMCYS; IV, MANCYS; V, PROCYS; VI, PHECYS.

The $\bar{H}_{-1}$* versus pH curves in the PHTAc system differ significantly from those referring to the hydrolysis of Et_2Sn^{2+} (Fig. 2(a)) indicating competition between PHTAc and hydroxide ion. The best fit between experimental and calculated data was achieved using the model with species MOH, $M(OH)_2$, MLH, ML and MLH_{-1} (or MLOH). Formation constants are listed in Table 2.

MLH protonated complexes are formed in acidic medium (pH 2–3). The stability constants of species MLH, formed with different PHTAc derivatives, are very close to each other and to the formation constant of the acetate complex of dimethyltin(IV) ($\log K \sim 2.8$) [19], which may suggest that PHTAc is coordinated by its carboxylate group but not by the amine nitrogen to tin(IV) in these species.

On increase of the pH two further deprotonation processes (eqns. (4) and (5)) occur: (i) due to the deprotonation of the amino nitrogen of the organic

$$MLH \overset{K_4}{\rightleftharpoons} ML + H \quad (4)$$

$$ML \overset{K_5}{\rightleftharpoons} MLH_{-1} + H \quad (5)$$

ligand and (ii) to that of a coordinated water molecule. Their pK values are shown in Table 2. On the basis of only potentiometric equilibrium studies one cannot determine which data refer to process (i), which to process (ii). It can be seen that in the case of both processes the differences between the protonation constants of the ligands in the presence and absence of

*$\bar{H}_{-1}$ refers to the average number of released protons by the ligand per metal ions in the coordination process.

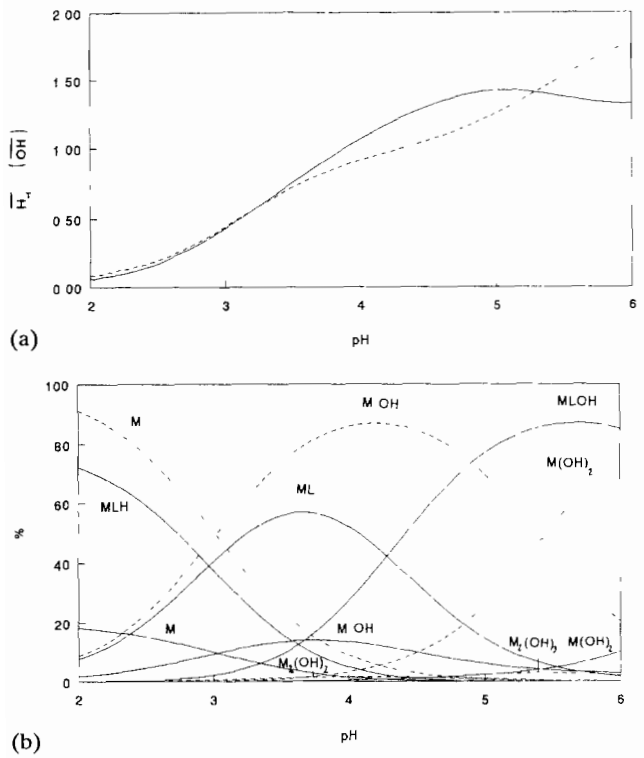


Fig. 2. (a) $\bar{H}_{-1}$ (and $\overline{OH}$) vs. pH curve and (b) species distribution diagram for the diethyltin(IV) GLUCYS (1:3) system (dotted line = the same for the hydrolysis of the diethyltin(IV) dichloride in organic ligand free system), at 0.004 mol dm^{-3} Et_2Sn^{2+} ion concentration in both cases.

Et_2Sn^{2+} ion are very similar, with the exception of PROCYS, which does not carry alcoholic hydroxy groups. These results reveal that the sterical position of the alcoholic hydroxy groups does not affect the coordination mode of PHTAc. The bulky carbohydrate residue has only a non-specific steric effect on the complexation process. This may indicate that the trigonal bipyramidal structure typical for the monohydroxo mixed complexes of dialkyltin(IV) [20] is also characteristic for our system, two coordination sites of diethyltin(IV) occupied by carboxyl oxygen and amino nitrogen donor atoms of PHTAc in amino acid type coordination (see also the solid state investigations).

The species distribution diagram (Fig. 2(b)) shows that the complex MLH_{-1}, which is considered on the basis of above discussion to have MLOH composition, predominates in the system at about pH = 6 in spite of the strong tendency of diethyltin(IV) to form dihydroxo species in this region. Similar results were found for complexation with citrate, tripolyphosphate and nitrilotriacetate [21] but not with acetate, malonate and succinate [19]. Consequently in order to avoid the hydrolysis of diethyltin(IV) in the pH > 5 range ligands with donor groups other than only carboxylate, are needed.

Solid state investigations

Previous solid state studies have shown that coordination of the polyhydroxy chain of carbohydrates to R_2SnO led to the release of equimolar amount of water [5, 6]. On the other hand several results [22–25] confirm that peptides and amino acids coordinate with their amino nitrogen and carboxyl oxygen and/or by the sulfur of their thiol group to organotin(IV).

Since our thiazolidine derivatives are the reaction products of a sulfur containing amino acid and monosaccharides (see Fig. 1), two coordination possibilities of these ligands to Et_2Sn^{2+} may be suggested:

(a) with oxygen, nitrogen and/or sulfur donor atoms of the thiazolidine ring,

(b) with deprotonated oxygen atoms of the polyhydroxy chain participating in the (a) type coordination.

Both type of reactions may be complemented by the coordination of non-deprotonated hydroxy groups of the polyhydroxy chain.

To find out which process leads to the solid complex, the mother liquids after reactions between Et_2SnO and PHTAc derivatives were titrated by Karl-Fischer solution for determining the water eventually released by the system. The results did not show the release of water indicating that the latter reaction is not the condensation process between Et_2SnO and PHTAc ligands.

GALCYS and GLUCYS were chosen for the preparation of solid complexes since they are the strongest complex forming agents in this series of ligands [10]. For comparison PROCYS and PHECYS carrying in place of the carbohydrate moiety an alkyl chain and

TABLE 2. Equilibrium constants for the complex formation processes in the diethyltin(IV) PHTAc systems

Species	log β_{HL}[a]	log β_{MLH}	log β_{ML}	log β_{MLOH}	pK_4[b]	pK_5[b]
GALCYS	5.53	8.24 ± 0.05	5.33 ± 0 04	1.01 ± 0.03	2.91	4 32
GLUCYS	5.31	8 14 ± 0 06	5.19 ± 0.04	0.91 ± 0 02	2 97	4.28
RAMCYS	5.51	8.03 ± 0.07	5.01 ± 0.03	0 82 ± 0.02	3 02	4.19
MANCYS	5.14	7 89 ± 0.05	4.91 ± 0.05	0.79 ± 0.03	2 98	4.17
PROCYS	6.25	7.96 ± 0.08	4.96 ± 0 05	0 63 ± 0.03	3.00	4.33

[a]Protonation constants of the amino group of the ligands from ref 10. [b]K_4 and K_5 refer to the equilibria (4) and (5), respectively

a phenyl group, respectively, were also synthesized and studied.

IR spectra

The characteristic IR absorption bands of the complexes and the corresponding free ligands in the region 4000–400 cm^{-1} are given in Table 3.

The NH_2^+ stretching vibrations of all ligands appeared between 3070 and 3170 cm^{-1} in the IR spectra, the asymmetric ($\nu_a(COO^-)$) and symmetric ($\nu_s(COO^-)$) stretching vibrations of the carboxylate groups at 1600–1660 and 1400 cm^{-1}, respectively, indicating that all of the ligands studied here have a zwitterion structure.

The OH region in the IR spectra of the free ligands reflect the presence of different hydrogen bonds. Three types of H bonds may occur in thiazolidine-4-carboxylic acid derivatives: O–H...O, O–H...N and N–H...O bonds with the participation of alcoholic hydroxy, carboxylate and amine groups. The first type of H bond may be much shorter than the other two. Correlations have been found [26] between the OH stretching frequencies (ν(OH)) and the O...O distances in H bonds. Lower ν(OH) corresponds to stronger H bonds. Increase of bandwidth and intensity enhancement occur at the same time. H bonds of the O–H...O type are expected to have ν(OH) values between 3500 and 2600 cm^{-1} for O...O distances of 2.90–2.60 Å. The ν(OH) values of GALCYS and GLUCYS are in the range 3460–3290 cm^{-1}, implying the presence of hydrogen bonds with O...O distances in the range 2.88–2.83 Å [26].

The IR spectra of the complexes are more simple than those of the ligands. As a consequence of complex formation the $\nu(NH_2^+)$ vibrations disappeared. The appearance of a new shoulder at about 3180 cm^{-1}, assigned to the NH group, and the shifts in the $\nu_a(COO^-)$ and $\nu_s(COO^-)$ bands indicate that the diethyltin(IV) moiety is coordinated to the carboxylate and NH groups of the thiazolidine ring. The differences between $\nu_a(COO^-)$ and $\nu_s(COO^-)$ of the complexes are ~250 cm^{-1}, indicating that the carboxylate groups are coordinated in monodentate mode [27].

Mössbauer spectra

The experimentally determined Mössbauer parameters of the complexes measured at liquid nitrogen temperature are presented in Table 4. All spectra exhibit isomer shift (*IS*) values characteristic for tin(IV) and quadrupole splittings (*QS*) with only one well-developed doublet, which suggests the presence of a single tin environment in these compounds.

Principally, the values of *IS* and *QS* give information about the coordination polyhedron surrounding the tin(IV) atom. Certain ranges of *QS* may be associated with well-defined particular stereochemistries [28]. However most compounds will have structures which deviate to a smaller or larger extent from regular polyhedra. In addition to that, if the complexes studied have nonequivalent coordinating groups (COO^-, O^-, OH^-, NH), the validity of the above-mentioned trends is questionable.

To get information on the steric arrangement of the coordination sphere of tin(IV) in the compounds, *QS* values were calculated according to the partial quadrupole splitting (*PQS*) concept [29] for expected symmetries and compared with the experimental *QS* values.

Based on results of our IR and analytical measurements in the solid state and in agreement with equilibrium studies in solution we concluded on amino acid type coordination (COO^-, NH). In this case the coordination of the ring sulfur atom is sterically hindered and the sugar moiety is not directly bound to diethyltin(IV). The proton of the NH_2^+ group released as a result of coordination is suggested to form with oxygen of Et_2SnO a hydroxy group coordinated to tin(IV). This process is confirmed by the increase in pH of the reaction mixture during the complex formation and by the fact that PROCYS, which does not contain a polyhydroxy chain, forms a complex with diethyltin(IV)

TABLE 3. IR absorption bands of the diethyltin(IV)–PHTAc complexes studied and of the corresponding ligands

Band assignments	PHECYS		PROCYS		GLUCYS		GALCYS	
	Ligand	Complex	Ligand	Complex	Ligand	Complex	Ligand	Complex
ν(OH)					3390–3460	3405	3290–3360	3410
$\nu(NH_2^+)$	3070		3060		3160		3170	
$\delta(NH_2^+)_{sci}$	1580		1595			1565	1570	
$\rho(NH_2^+)_{wag}$	1470		1445			1440	1445	
ν(NH)		3180		3165		3170		3175
$\nu_a(COO^-)$	1650	1665	1640	1660	1630	1665	1650	1660
$\nu_s(COO^-)$	1395	1400	1390	1410	1400	1440	1390	1410
ν(CO)					1020–1100	1090	1020–1100	1085
ν(SnC)		535		535		530		530
ν(CS)	645		643		639		640	

TABLE 4. Experimental ^{119}Sn Mossbauer parameters of diethyltin(IV)–PHTAc complexes and suggested configurations for tin(IV)

Ligand	*IS* (mm s^{-1})	*QS* (mm s^{-1})	Suggested structure
PHECYS	1.36	3.20	tbp4
GALCYS	1.38	2 64	tbp5
GLUCYS	1.36	3.17	tbp4
PROCYS	1.49	2.69	tbp5

TABLE 5 Partial quadrupole splitting (*PQS*) values of the functional groups used in calculation of *QS* values for the tin(IV) coordination spheres in trigonal bipyramidal arrangements

$\{R\}^{tba} = -0.94$	$\{COO^-\}^{tba} = 0.04$	$\{OH\}^{tba} = -0.13$	$\{NH\}^{tba} = 0.01$
$\{R\}^{tbe} = -1\ 13$	$\{COO^-\}^{tbe} = 0.25$	$\{OH\}^{tbe} = +0.02$	$\{NH\}^{tbe} = 0.21$

with a *QS* value very close to that of GALCYS. The equilibrium study of the system showed also that the dominant species in solution at pH > 5 is the pentacoordinated mixed hydroxo complex.

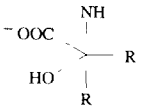
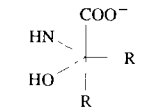
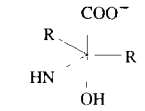
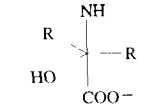
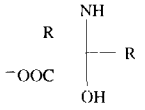
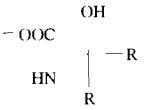
Accordingly we calculated the *QS* values on the basis of the *PQS* concept for the expected trigonal bipyramidal symmetries of $R_2Sn(OH)(NH)(COO)$ compositions. The *PQS* values of the different functional groups used in the calculations are listed in Table 5. Some *PQS* values were taken from refs. 29 and 30. The value of $\{OH\}^{tbe}$ was calculated as in ref. 31. The values of $\{COO^-\}^{tba}$ and $\{COO^-\}^{tbe}$ were taken from Table 4 and formula (41) in ref. 29, respectively.

The formulae corresponding to the structural isomers and the equations belonging to them are given in Table 6, together with the calculated *QS* values for tin(IV) in different stereochemical arrangements.

The structures suggested on the basis of comparison of experimental and calculated *QS* values are presented in the last column of Table 4. The results showed that all compounds contain the central tin(IV) atom in trigonal bipyramidal arrangements, in agreement with our previous assumption.

It can be seen that the experimental *QS* values of PHECYS and GLUCYS complexes are close to the calculated value of tbp4 geometry. The experimental *QS* values of GALCYS and PROCYS complexes are near to those calculated on the basis of tbp1, tbp2, tbp3 and tbp5 geometries. Taking into account that in tbp5 both Et–Sn–COO angles are ~120° and according to the other three symmetries at least one of these angles is ~90° (in tbp3 both), the probability of the formation of tbp5 geometry is higher than that of the others. The conformational effect caused by the difference in the sterical position of the OH group on the C(3′) carbon atom of the polyhydroxyalkyl chain of GALCYS and GLUCYS (see Fig. 1) may be the reason for the different *QS* values and geometries of their complexes.

TABLE 6. The formulae of the structural isomers, the corresponding equations and the calculated *QS* values for tin(IV) in different trigonal bipyramidal arrangements

Structural isomers	Equations	QS_{calc}
tbp1 	$(-2R^{tba} - 5R^{tbe} - 2NH^{tba} + 4COO^{-tbe} + 4OH^{tbe})/\sqrt{13}$	2.38
tbp2 	$(-2R^{tba} - 5R^{tbe} - 2COO^{-tba} + 4NH^{tbe} + 4OH^{tbe})/\sqrt{13}$	2.32
tbp3 	$(-7R^{tbe} + 4OH^{tba} + 4COO^{-tba} + NH^{tbe})/\sqrt{7}$	2 93
tbp4 	$(-7R^{tbe} + 4COO^{-tba} + 4NH^{tba} + OH^{tbe})/\sqrt{7}$	3.07
tbp5 	$(-7R^{tbe} + 4OH^{tba} + 4NH^{tba} + COO^{-tbe})/\sqrt{7}$	2.90
tbp6 	$(-2R^{tba} - 5R^{tbe} - 2OH^{tba} + 4COO^{-tbe} + 4NH^{tbe})/\sqrt{7}$	3.64

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