The Stability and Structure of Complex Species Formed in Equilibrium Reactions of Diethyltin(IV) with N-D-Gluconylamino Acids in Aqueous Solution

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\textit{Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday}

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Diethyltin(IV), N-D-Gluconylamino Acid Complexes, Potentiometry, Mössbauer Spectra, NMR Spectra

Complex formation equilibria of diethyltin(IV) with five N-D-gluconylamino acids in aqueous solution (I = 0.1 M, NaClO\textsubscript{4}) were studied and the stabilities of the species were determined by potentiometric titrations. Diethyltin(IV) complexes of \(\alpha\)-amino acid derivatives are water-soluble in the physiological pH range, while in the presence of N-D-glucosyl-\(\beta\)-alanine a precipitate is formed, which dissolves with increasing pH. \(\textsuperscript{13}C\) NMR measurements showed that in the N-D-glucosyl-\(\alpha\)-amino acid complexes the ligand is coordinated through its deprotonated carboxylate oxygen, amide nitrogen and C(2)-hydroxy group, while for the soluble N-D-glucosyl-\(\beta\)-alanine complex the ligand is coordinated via the deprotonated carboxylate and C(3)-, C(4)-, C(5)-hydroxy groups. Mössbauer measurements reflected the geometry of the complexes formed.

Introduction

Organotin(IV) compounds are known to exert therapeutic effects to different tumor cells [1], but little is known concerning their mode of interaction. Simple relationships between the solid state structure of organotin(IV) compounds and their biological activity cannot be expected, because the structure of the solid compound may dramatically change on dissolution. In order to obtain more information about the molecular basis of interactions between organotin(IV) species and biologically important molecules the structure of dissolved species should be determined and pH-dependent equilibria in solution should be characterized.

Barbieri and Silvestri monitored the species distribution in aqueous solution during the hydrolysis of Me\textsubscript{2}Sn\textsuperscript{2+} and Me\textsubscript{3}Sn\textsuperscript{+} cations by Mössbauer spectroscopy [2]. The same authors made plausible suggestions on the structures of different organotin(IV) complexes formed with amino acids or peptides in solution. These complexes have promising antitumor activity [3–7]. They also studied by means of Mössbauer spectroscopy the binding mode of alkyltin(IV) cations to rat hemoglobin and to its model system in aqueous solution [8].

In our previous papers we discussed the coordination chemistry of diethyltin(IV) and dibutyltin(IV) cations with non-protected carbohydrates [9, 10] and 2-polyhydroxyalkyl-thiazolidine-4-carboxylic acids [11]. The symmetry and local structure of the complexes have been determined by Mössbauer and FTIR spectroscopy [9–11] and by EXAFS [12]. Continuing these investigations the formation equilibria and structure of diethyltin(IV) complexes of N-D-gluconylamino acids in aqueous solution are reported in the following. These compounds are pseudopeptide derivatives of D-glucono-\(\delta\)-lactone and amino acids. The methods used in this work reveal information necessary to further studies on the biological activity of the metal complexes. The pH-metric titrations are suitable to determine the number of deprotonated coordinating groups, while NMR helps in the assignment of the coordinated donor atoms. The geometry of the species formed at different pH can be determined by Mössbauer spectroscopic measurements.

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Experimental

Materials

All reagents except for D-glucono-δ-lactone (Fluka) were Reanal products of analytical purity. Diethyltin(IV) dichloride was prepared according to published procedures [9]. The ligands were obtained as described previously [13, 17]. The purities of the ligands were checked by elemental analysis, 1H and 13C NMR spectroscopy and by potentiometric titrations. The structure of the ligands studied are depicted in Fig. 1.

![Fig. 1. Structures of the N-D-gluconylamino acid ligands studied: Abbreviations: GLUGLY, N-D-gluconylglycine; GLU-α-ALA, N-D-gluconyl-α-alanine; GLU-β-ALA, N-D-gluconyl-β-alanine; GLUSER, N-D-gluconylserine, and GLUMET, N-D-gluconylmethionine.](image)

pH-metric measurements

The coordination equilibria were investigated by potentiometric titrations in aqueous solution. The ionic strength was adjusted to 0.1 mol dm−3 with NaClO4, 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 as described earlier [11] using the modified Nernst equation (1):

\[
E = E_0 + K \cdot \log [H^+] + J_{\text{H}} \cdot [H^+] + \frac{J_{\text{OH}} \cdot K_w}{[H^+]},
\]

where \( J_{\text{H}} \) and \( J_{\text{OH}} \) 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 eq. (3).

\[
pM + qL \quad \underset{\beta_{\text{MPLqH}_r}}{\longleftrightarrow} \quad M_pL_qH_{r-r} + rH
\]

or

\[
pM + qL + rH_2O \quad \underset{\beta_{\text{MPLq(OH),q}}}{\longleftrightarrow} \quad M_pL_q(OH)_r + rH
\]

\[
\beta_{\text{MPLqH}_r} = \beta_{\text{MPLq(OH)q}} = \frac{[M_pL_qH_{r-r}][H]^r}{[M^p][L]^q} = \frac{[M_pL_q(OH)_r][K_w]}{[M^p][L]^q[OH]^r}
\]

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

The equilibrium constants were determined from five independent titrations in each system, the organotin(IV) cation to ligand ratios varying from 1:3 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 [14].

NMR spectroscopy

The 1H and 13C NMR spectra were recorded on a Bruker AM 400 spectrometer at 400.13 and 100.62 MHz, respectively. All chemical shifts are given relative to TMS (0). The internal reference used was 1,4-dioxane (\( \delta = 3.7 \) ppm for 1H and 67.4 ppm for 13C). The concentrations of diethyltin(IV) ion and N-D-gluconylamino acids were 0.1 mol dm⁻³ and 0.3 mol dm⁻³, respectively, for all NMR measurements. As solvent D₂O was used and the pH-meter reading was uncorrected for the isotope effect. In the SPT (Selective Polarization Transfer) experiments [24] a soft 1H 180° pulse (γH/2π = 20 Hz) selectively inverts proton resonances of either the low-field (C(2)) or the high-field (C(3)) 13C satellite.
Mössbauer spectroscopy

The $^{119}$Sn Mössbauer spectra of quick frozen solutions were recorded on a conventional Ranger spectrometer in constant accelerating mode with an activity of 0.1 GBq. Computer evaluation was used to determine isomer shift (IS) and quadrupole splitting (QS) values. The reproducibility of the Mössbauer parameters was found to be $\pm 0.02$ mm s$^{-1}$ (IS) and $\pm 0.04$ mm s$^{-1}$ (QS), respectively, in each measurement. The IS values are referred to that of CaSnO$_3$.

Results and Discussion

pH-metric and NMR spectroscopic measurements

The hydrolysis of the diethyltin(IV) cation in aqueous solution was studied by several researchers [11, 15, 16]. The present work used hydrolysis constants for the diethyltin(IV) published in [11] and for the protonation constants of the ligands those in [17]. The titration curves show that complexes with one to one ligand to metal ratio were formed irrespectively of the ligand excess applied. There was no evidence of the presence of polynuclear species in significant amount in solutions. The best fit of the titration curves were obtained when complexes ML, MLH$^{-1}$, MLH$^{-2}$ and MLH$^{-3}$ were suggested beside the hydrolysis products of the diethyltin(IV) cation. The results of the calculations are shown in Table I.

The stabilities of the parent ML complexes are very similar to the stabilities of complexes of organotin(IV) ions with ligands containing carboxylate functional group(s) only [18] and also to those of amino acid complexes coordinated only by their carboxylate group [19]. The log $\beta_{ML}$ values of N-D-gluconylamino acid complexes are between the stabilities of the two types of complexes [18, 19] mentioned above, similarly as the order of the protonation constants of carboxylate groups in the mentioned systems. The only significant difference between $^{13}$C NMR spectra of diethyltin(IV)-GLUGLY 1:3 system and metal-free ligand at pH = 2.6 (Table II) are the chemical shifts of carboxylate carbon, which also demonstrates the coordination of this group.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\log \beta_{HL}$</th>
<th>$\log \beta_{ML}$</th>
<th>$\log \beta_{MLH^{-1}}$</th>
<th>$\log \beta_{MLH^{-2}}$</th>
<th>$\log \beta_{MLH^{-3}}$</th>
<th>pK$_4$</th>
<th>pK$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GLUGLY</td>
<td>3.39</td>
<td>2.36 ± 0.08</td>
<td>-0.96 ± 0.06</td>
<td>-5.42 ± 0.03</td>
<td>-15.87 ± 0.03</td>
<td>3.32</td>
<td>4.46</td>
</tr>
<tr>
<td>GLU-$\alpha$-ALA</td>
<td>3.35</td>
<td>2.85 ± 0.06</td>
<td>-0.67 ± 0.06</td>
<td>-4.92 ± 0.06</td>
<td>-15.74 ± 0.09</td>
<td>3.52</td>
<td>4.25</td>
</tr>
<tr>
<td>GLU-$\beta$-ALA</td>
<td>4.24</td>
<td>2.87 ± 0.07</td>
<td>-0.80 ± 0.03</td>
<td>-5.15 ± 0.03</td>
<td>-15.48 ± 0.03</td>
<td>3.39</td>
<td>4.15</td>
</tr>
<tr>
<td>GLUSER</td>
<td>3.13</td>
<td>2.39 ± 0.05</td>
<td>-1.00 ± 0.05</td>
<td>-5.15 ± 0.05</td>
<td>-16.08 ± 0.07</td>
<td>3.40</td>
<td>4.55</td>
</tr>
<tr>
<td>GLUMET</td>
<td>3.24</td>
<td>2.80 ± 0.09</td>
<td>-0.60 ± 0.08</td>
<td>-5.15 ± 0.05</td>
<td>-16.08 ± 0.07</td>
<td>3.40</td>
<td>4.55</td>
</tr>
</tbody>
</table>

$^a$ K$_4$ and K$_5$ refer to the equilibria (4) and (5), respectively.

Table II. $^{13}$C NMR chemical shifts in diethyltin(IV):GLUGLY = 1:3 (1–3 rows) and in diethyltin(IV):GLU-$\beta$-ALA = 1:3 (4th row) systems at different pH values.

| pH | C(1) | C(2) | C(3) | C(4)$^a$ | C(5)$^a$ | C(6) | C(7) | C(8) | C(9) | C(1)' | C(2)'
|----|------|------|------|----------|----------|------|------|------|------|-------|------|
| 1  | 2.6  | 175.7| 74.2 | 71.4     | 72.8     | 72.1 | 63.6 | 175.8| 42.3 | –     | 25.0 | 9.7
|    | (157.7)$^b$ | (74.1) | (71.2) | (72.7) | (71.9) | (63.5) | (174.2) | (41.8) |       |       |       |
| 2  | 3.9  | 175.4| 74.3 | 71.3     | 72.8     | 72.1 | 63.6 | 177.0| 43.3 | –     | 22.1 | 9.5
|    | (175.2) | (74.1) | (71.2) | (72.7) | (72.0) | (63.5) | (176.3) | (43.2) |       |       |       |
| 3  | 9.1  | 179.3| 79.6 | 70.4     | 74.8     | 71.8 | 63.7 | 179.1| 46.5 | –     | 13.8 | 9.3
|    | (175.0) | (74.2) | (71.2) | (72.8) | (72.1) | (63.6) | (177.3) | (43.9) |       |       | 13.2 |
| 4  | 10.2 | 181.2| 74.2 | 71.6     | 73.3     | 72.6 | 63.6 | 175.8| 37.5$^a$ | 37.2$^a$ | 13.9 | 10.1
|    | (180.9) | (74.2) | (71.2) | (72.9) | (72.0) | (63.5) | (174.9) | (37.2) | (37.1) |       |       |

$^a$ Assignment may not be straightforward; $^b$ the values for free ligands at corresponding pH values are given in parentheses.
According to the $\bar{H}_-\dagger$ vs. pH curves (Fig. 2), above pH = 3, several deprotonation processes occur with increasing pH. The first deprotonation takes place in almost the same pH region as the formation of the monohydroxo species of the diethyltin(IV) cation [11], consequently the pK values for the process (4) is the same within experimental error as the pK of the Et$_2$Sn(OH)$^+$ species (Table I).

$$\text{ML} \xrightarrow{K_4} \text{MLH}_- + \text{H} \quad (4)$$

Fig. 2. $\bar{H}_-\dagger$ vs. pH curves for the diethyltin(IV) complexes formed with N-D-glucouylamino acids and the $\bar{H}_-\dagger$ vs. pH (OH vs. pH) curve for the hydrolysis of the diethyltin(IV) cation.

This similarity suggests that carboxylate and hydroxide ion coordinated mixed hydroxo species are present in solution, denoted as MLH$_-$. Although on the basis of the potentiometric measurements only, one cannot distinguish between the deprotonation of the bound ligand and that of the coordinated water molecule, $^{13}$C NMR was found suitable for it. The concentration distribution diagram of diethyltin(IV)-GLUGLY system (Fig. 3 a), typical for all systems of $\alpha$-amino acid derivatives, demonstrates that in the pH = 3–5 region MOH, ML, MLH$_-$ complexes are present in solution. However, with increasing total concentrations (Fig. 3 b) the complex MLH$_-$ becomes predominant, which helps to evaluate the results of the spectroscopic measurements.

The signals of the $^{13}$C NMR spectrum obtained in the same pH region were sharp indicating that the system is in the fast exchange regime. Significant change in the spectrum of the complex compared with that of the metal-free ligand have been detected for the carboxylate group only, which is slightly upfield shifted (Table II) similarly to the ML species. However, the ethyl carbon signals changed their positions ($\Delta\delta \approx 3$ ppm) referred to those in the latter complex indicating the changed coordination of diethyltin(IV) cation. This suggests that no other group of the organic ligand than carboxylate is coordinated in the species MLH$_-$. Accordingly, the MLH$_-$ is a mixed hydroxo complex i.e. coordinates a deprotonated water molecule beside the organic ligand.

Further increase of the pH results in significant deviation from the $\bar{H}_-\dagger$ vs. pH curve of the Et$_2$Sn$^{2+}$ hydrolysis. In the case of the $\alpha$-amino acid derivatives the second deprotonation process leading to MLH$_-$ occurs at lower pH than the formation of dihydroxo species of diethyltin(IV), while in the case of GLU-$\beta$-ALA this process is shifted slightly towards higher pH.

$$\text{MLH}_- \xrightarrow{K_5} \text{MLH}_- + \text{H} \quad (5)$$

The pK values for process (5) are listed in Table I. The lower pK values for the complexes of
α-amino acid derivatives clearly demonstrate the deprotonation of one of the ligand’s functional groups. This may be the amide nitrogen or one of the hydroxy groups. The hydroxy groups are relatively far from the first coordinated carboxylate group, we may consider, however, a chelate effect through amide oxygen bringing the alcoholic hydroxy group in a position favourable for coordination. The replacement of the hydroxide ion in $\text{MLH}_2$ by the ligand molecule in the coordination sphere of the diethyltin(IV) cation is also possible. As a result of such a process, the coordination of fused chelate rings through carboxylate, deprotonated amide nitrogen and deprotonated hydroxy group may be formed. Although the organo­­tin(IV) ions show higher affinity toward oxygen than toward nitrogen donor atoms (see the low stabilities of the organotin(IV) neutral amino acid complexes [19, 20]), the deprotonation of the amide group in peptide complexes has been proved in several cases by means of X-ray crys­­tallography [21–23]. The complex denoted by $\text{MLH}_2$ shows high stability and it is the predominant species in the pH 6–10 region.

As a result of the very slow ligand exchange in comparison with the NMR time scale, the $^{13}$C signals of the bound and the free ligands can be observed separately in the $^{13}$C NMR spectrum of the $\text{MLH}_2$ complex of the diethyltin(IV) cation and GLUGLY. The significant shifts (Table II, third row) of $-\text{CH}_2-$, $-\text{COO}^-$ and $-\text{CONH}-$ carbon signals of the ligand (the latter two were distinguished by means of proton-coupled $^{13}$C NMR spectra, where the signal of the carboxylate carbon is split into a well resolved triplet, in both free and bound cases) suggested the coordination of the deprotonated peptide nitrogen and of the carboxyl group. The shifts observed in the carbon signals of the polyhydroxyalkyl chain indicate that the alcoholic hydroxy groups are also involved in the coordination. The shift of one of latter signals is significantly larger than that of the others, suggesting stronger interaction of this specific (therefore presumably deprotonated) alcoholic OH group with the metal ion. In order to assign the coordinated OH group, modified selective population transfer $^{13}$C($^1$H) NMR experiments were performed as described by Sarkar et al. [24]. The two doublets at $\delta$ 4.207 and 4.252 ppm in the $^1$H NMR spectrum (Fig. 4a) of the diethyltin(IV)-GLUGLY 1:3 system at pH = 9.1 can be assigned to the C(2) hydro­­gen atom in the free (similarly as in the case of gluconic acid [25]) and bound ligand, respectively. The intensity ratio of the signals of the free and bound ligand protons are 2:1. This observation supports 1:1 ligand to metal ratio in the complex. The selective population transfer due to the selective irradiation of these protons is the reason why in the $^{13}$C NMR spectrum only the signal of the directly coupled carbon appears $i.e.$ of C(2) (Fig. 4b, c). The equilibrium between the bound and free ligands is responsible for the appearance of both carbon signals in Fig. 4b and c. From Fig. 5a one can see that the carbon signal, assigned in the latter measurement has the largest (upfield) shift due to complexation (as well as the doublet of C(2)–H in the proton spectrum in Fig. 4a), consequently the C(2)–OH group is presumably the deprotonated one. On the basis of similar experiments the signal of the C(3) and its com­­plexed counterpart can also be assigned as Fig. 4d shows. The significant difference in the chemical
Fig. 5. Proton decoupled $^{13}$C NMR spectra of diethyltin(IV)-GLUGLY (1:3) system at pH = 9.1 (a) and of diethyltin(IV)-GLU-$\beta$-ALA (1:3) system at pH = 10.2.

shifts of CH$_2$ carbons of ethyl groups at pH = 3.9 and 9.1 ($\Delta$δ ~ 8 ppm) also indicates the drastic change in the coordination sphere of diethyltin(IV) (i.e. coordination of deprotonated functional groups of the ligand at pH 9.1). The signals of the ethylene and methyl carbons are split (approximately 1:1 intensity ratio) due to the dissymmetry in the diethyltin(IV) coordination sphere. From the smallest $^{13}$C shift of the ligand during the complex formation process (3 Hz for C(6) carbon) the estimated ligand exchange rate can be obtained ($1/\tau_M \leq 2\pi\Delta v_M = 20 \text{ s}^{-1}$).

At higher pH values the species MLH$_{-3}$ is formed in solutions. The $^{13}$C NMR spectrum at pH 11 shows beside the pattern of the corresponding spectrum at pH 9.1, several very broad lines, e.g. as the amide carbon signal at δ 175.2 ppm and the C(8) ethylene carbon signal at δ 45.3 ppm. The broad polyhydroxyalkyl carbon signals could not be assigned with certainty. Thus the deprotonation, leading to MLH$_{-3}$ may be either that of the alcoholic hydroxy groups or that of a water molecule, but in both cases the amide group remains coordinated.

The larger distance between the anchoring carboxylate and the other functional groups in GLU-$\beta$-ALA ligand could not prevent the hydrolysis of the diethyltin(IV) cation in the physiological pH region. Consequently, precipitation occurred in the pH 6–8 region, which was dissolved with increasing pH without extra base consumption, indicating the rearrangement of the diethyltin(IV) coordination sphere. The $^{13}$C NMR spectrum of the soluble complex at pH = 10 is depicted in Fig. 5b. The differences in chemical shifts of the ligand carbons in presence and absence of diethyltin(IV) are small, and the signals of the carboxylate and three other carbon atoms (C(3), C(4), C(5)) carrying alcoholic hydroxy groups are broadened, characteristic for the complexes with intermediate ligand exchange rate. The explanation of the above observations may be the coordination of the carboxylate and deprotonation of some of these alcoholic hydroxy groups, due to the presence of the organotin(IV) cation. However, there is neither a noticeable shift nor a line broadening for the amide and methylene carbon signals, excluding the deprotonation and coordination of the amide nitrogen.

Mössbauer spectroscopic measurements

From equilibrium studies it was concluded that four different complex species exist in the pH
range studied: ML, ML\(_{-1}\), MLH\(_{-2}\) and MLH\(_{-3}\). The total composition of these complexes differ from each other only by the degree of deprotonation. In order to determine the geometry of these species we have performed \(^{119}\)Sn Mössbauer spectroscopic measurements in frozen solution for the diethyltin(IV)-GLUGLY and -GLU-\(\beta\)-ALA systems. Comparison of the experimental quadrupole splitting values (QS) with those calculated on the basis of the partial quadrupole splitting (PQS) concept [26–28] revealed the steric arrangements of the coordination sphere of tin(IV) in the complexes at the different pH. The PQS values of the different functional groups used in our calculations are given in Table III. The suggested steric arrangements are shown in Fig. 6. The experimental and calculated Mössbauer parameters are listed in Table IV.

The Mössbauer spectra (see Fig. 7) of the diethyltin(IV)-GLUGLY system measured in glassy state in the acidic region (pH = 3.7) indicate the presence of two overlapping doublets. From comparison with the concentration distribution diagram (Fig. 3b) it can be seen that the doublet which has the larger integrated area belongs to the MLH\(_{-1}\) species having higher concentration than the other (ML) which is represented by the doublet having smaller integrated area. The experimental QS for the species ML is in good agreement with that calculated for the five-coordinated trigonal bipyramidal tin(IV) atom in the complex shown in Fig. 6a. A similar structure with equatorial alkyl groups and axial water molecules has been observed for monohydroxo species in the acidic region by Barbieri [2] formed during the hydrolysis of the diethyltin(IV).

Comparison of experimental and calculated QS values indicate that the MLH\(_{-1}\) species contains hexacoordinated tin(IV) with equatorial alkyl groups (Fig. 6b). The Mössbauer data measured for the diethyltin(IV)-GLU-\(\beta\)-ALA system in the acidic region (pH = 3.8) are reflecting the presence of the same species as in the diethyltin(IV)-GLUGLY system (see Table IV).

The Mössbauer spectrum of the diethyltin(IV)-GLUGLY system at physiological pH (pH = 7.0) contains only one doublet. According to its QS value the MLH\(_{-2}\) species dominant in this solution (see Fig. 3b) is a five-coordinated tin(IV) compound, in which the ligand coordinates via three deprotonated groups (carboxylate oxygen, amide nitrogen and alcoholic hydroxy) to the organotin(IV) ion (Fig. 6c), as reflected also by \(^{13}\)C NMR spectroscopy. The same arrangement, two equatorial alkyl groups and an equatorially coordinated peptide nitrogen, was found by Barbieri et al. [22, 23] for dialkyltin(IV) derivatives of dipep-

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**Table III. Partial quadrupole splitting (PQS) values of the functional groups used in calculation of QS values for the tin(IV) coordination spheres.**

<table>
<thead>
<tr>
<th>Group</th>
<th>[R](_{\text{PQS}}) [\text{mm s}^{-1}]</th>
<th>[\text{COO}^{-}] [\text{PQS}] [\text{mm s}^{-1}]</th>
<th>[\text{H}_2\text{O}] [\text{PQS}] [\text{mm s}^{-1}]</th>
<th>[\text{N}_{\text{pept}}] [\text{PQS}] [\text{mm s}^{-1}]</th>
<th>[\text{COO}^{-}] [\text{PQS}] [\text{mm s}^{-1}]</th>
<th>[\text{O}^{-}] [\text{PQS}] [\text{mm s}^{-1}]</th>
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</thead>
<tbody>
<tr>
<td>([R])(_{\text{PQS}})</td>
<td>(-1.13^a)</td>
<td>(-0.10^d)</td>
<td>(+0.18^b)</td>
<td>(-0.30^c)</td>
<td>(-0.135^e)</td>
<td>(-0.21^b)</td>
</tr>
<tr>
<td>[\text{COO}^{-}] [\text{PQS}]</td>
<td>(-1.03^b)</td>
<td>(+0.06^d)</td>
<td>(+0.20^c)</td>
<td>(-0.135^e)</td>
<td>(-0.135^e)</td>
<td>(-0.21^b)</td>
</tr>
<tr>
<td>[\text{H}_2\text{O}] [\text{PQS}]</td>
<td>(+0.18^b)</td>
<td>(+0.20^c)</td>
<td>(-0.30^c)</td>
<td>(-0.135^e)</td>
<td>(-0.135^e)</td>
<td>(-0.21^b)</td>
</tr>
</tbody>
</table>

* From reference [27]; \(^a\) [26]; \(^b\) [6]; \(^c\) [30]; \(^d\) calculated by the relationship between \(t\) et and \(o\) ct \(p.q.s\) values [26], \(R =\) ethyl.

**Table IV. Experimental and calculated \(^{119}\)Sn Mössbauer parameters of different species formed.**

<table>
<thead>
<tr>
<th>Species</th>
<th>IS [\text{mm s}^{-1}]</th>
<th>QS [\text{mm s}^{-1}]</th>
<th>QS(_{\text{calc.}}) [\text{mm s}^{-1}]</th>
<th>pH</th>
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<tr>
<td>(N\text{-D-Gluconylglycine system})</td>
<td></td>
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</tr>
<tr>
<td>ML</td>
<td>1.24</td>
<td>3.69</td>
<td>3.55</td>
<td>3.7</td>
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<tr>
<td>ML(_{-1})</td>
<td>1.78</td>
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<tr>
<td>ML(_{-2})</td>
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<tr>
<td>ML(_{-3})</td>
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<td>(N\text{-D-Gluconyl-}(\beta)-alanine system})</td>
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<tr>
<td>ML</td>
<td>1.36</td>
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<td>ML(_{-1})</td>
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</tr>
<tr>
<td>?</td>
<td>1.10</td>
<td>2.26</td>
<td>-</td>
<td>9.5</td>
</tr>
<tr>
<td>?</td>
<td>1.23</td>
<td>2.88</td>
<td>-</td>
<td>9.5</td>
</tr>
</tbody>
</table>

* Calculated on the basis of the model giving the best agreement with experimental values.
tides studied by single crystal X-ray diffraction and several spectroscopic methods.

Precipitation in the diethyltin(IV)-GLU-β-ALA system in the same pH region prevented its analogous Mössbauer study.

The Mössbauer spectrum of diethyltin(IV)-GLU system in alkaline solution (pH = 11.0) indicates the presence of two overlapping quadrupole doublets, which can be assigned to the species MLH₂ and MLH₃, respectively. The species distribution diagram (Fig. 3b) shows that the MLH₂ species dominant at neutral pH still exists in this pH range. The experimental IS and QS values obtained for this species in systems with different pH are in good agreement. The coordinated groups in the MLH₃ species could not be assigned, because the methods used do not differentiate between the deprotonation of another OH group of the polyhydroxy chain and that of the water, the latter leading to mixed hydroxo complex formation. Since the PQS value of the deprotonated peptide group in octahedral arrangements is unknown, PQS calculations could not confirm structure suggestions for the octahedral species MLH₃. Reasonably good correlations have been found [29], however, between the QS values and the C–Sn–C bond angles (θ) by ignoring the contribution of the non-alkyl ligands. Thus, we could calculate from the experimental QS the θ value for the MLH₃ species (θ ~ 130°) indicating a strongly distorted octahedron.

After dissolving the precipitate formed in the diethyltin(IV)-GLU-β-ALA system the spectrum recorded at pH = 9.5 indicated the presence of two different species. On the basis of the QS values these are suggested to be cis-octahedral tin(IV) isomers (θ = 90–120°).

**Conclusion**

In the course of the study of N-D-gluconyl-amino acid complexes with diethyltin(IV) two significantly different coordination spheres have been observed, with respect of α- and β-amino acid derivatives. The combined application of potentiometric equilibrium measurements with NMR and Mössbauer spectroscopic studies has made possible the structural characterization of the species formed in equilibrium reactions. With the help of these procedures the composition of the species could be determined in solution and the successive deprotonation processes in the system assigned to the corresponding donor atoms. Direct evidence was found for the participation of a deprotonated peptide nitrogen and of a deprotonated hydroxy group in the coordination sphere of MLH₂ complexes of α-amino acid derivatives, while in the case of N-D-gluconyl-β-alanine, for the presence of coordinated oxygen donor atoms only. Suggestions could be made also on the symmetry around the metal ion.

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