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Thiolate anchor in organotin(IV) induced amide deprotonation: equilibrium and NMR spectroscopic studies on dimethyltin(IV) complexes formed with *N*-(2-mercaptopropionyl)glycine and L-alanyl-glycine

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The coordination properties of the simple dipeptide L-alanyl-glycine (Ala-Gly) towards dimethyltin(IV) cation have been compared with its mercapto analogue *N*-(2-mercaptopropionyl)glycine (MPGly), using potentiometric, ^{1}H and ^{13}C NMR spectroscopic methods. The replacement of the terminal amino group of Ala-Gly by a thiol group (MPGly) induces fundamental changes in the coordination processes and in the speciation of metal complexes, though the composition of the species formed is identical. The considerably higher stability of the MPGly complexes is due to the outstanding affinity of dimethyltin(IV) cation toward sulfur donor atoms. In the MLH and ML complexes, formed in the acidic pH range, monodentate carboxylate and thiolate coordination has been observed for Ala-Gly and MPGly, respectively. Therefore, different donor groups in the case of the two ligands assist the metal promoted deprotonation of amide nitrogen. Our data provide the first example, that thiolate can act as an anchoring group in the diorganotin(IV) induced amide deprotonation.

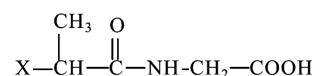
Introduction

In the past 40–50 years organotin compounds have been accumulated in nature due to their various industrial and agricultural applications.[1] The discovery of their dangerous impacts on living organisms has led to a significant decrease of usage from the late 1980s, however due to their high toxicity[2,3] they still signify notable risk for nature. On the other hand, organotin(IV) compounds may have potential future pharmaceutical applications, for example as antitumour agents, since they have been found to possess anticancer effects on different tumour cells *in vitro*.[4–7] Peptides or proteins are well-known and efficient biological metal ion binders, therefore their interaction with organotin cations may play an important role in the mechanism of the above mentioned toxic/antitumour effect. Model studies using small peptides as low molecular weight protein mimics may furnish essential details on the metal ion–protein interaction. A recent review[8] summarises the achievements that have been made on organotin(IV)–peptide interaction, but also points out the lack of solution equilibrium studies that could provide essential information on the biospeciation of organotin and thus on its bioavailability. Several reports have discussed the coordination chemical behaviour of different di- or tri-alkyltin(IV) ions towards amino acids,[8–13] and di-[13–17] and tripeptides[18,19] in the solid state or in organic solvents and a few works focused on the spectroscopic properties of the complexes formed in aqueous solutions.[13,15,19] Recently, we reported that dialkyltin(IV) cations are able to promote amide nitrogen deprotonation in aqueous solution at a surprisingly low pH.[20–22] The dimethyltin(IV)-induced deprotonation of amide nitrogen in these cases is facilitated by the anchoring coordination of the carboxylate group. The presence of side-chain donor groups (in His- and Asp-peptides) or the replacement of the terminal amino group by a phenolic-OH in salicyl-glicine has only a minor effect on the formation and stability of the trigonal-bipyramidal amide-bound species. In proteins, one of the main binding site for organotin compounds is the thiol group(s) of cysteine residue(s). Therefore, in the present paper we report equilibrium and solution structural investigations on the dimethyltin(IV) complexes of L-alanyl-glycine (Ala-Gly) and of its mercapto analogue *N*-(2-mercaptopropionyl)glycine (MPGly), a ligand structurally related to glutathione. Our former studies[12,25,26] and other reports[13,19,23,24] pointed out the great affinity of sulfur donors towards organotin(IV) cations. Indeed, the presence of the terminal thiol group in MPGly induces fundamental changes in the complex formation processes and speciation as compared with the simple dipeptides.

Experimental

Materials

N-(2-Mercaptopropionyl)-glycine (Sigma), L-alanyl-glycine (Sigma) (Scheme 1.) and dimethyltin(IV) dichloride (Fluka) were used without further purification. A fresh dimethyltin(IV) dichloride solution was prepared and standardized by acid–base titration every 2 days. The pH-metric titrations were performed using NaOH (Fluka) standard solutions.



Ala-Gly : X = NH_2
MPGly : X = SH

Scheme 1 Schematic structures of the studied ligands.

pH-Metric measurements

The protonation and coordination equilibria were investigated by potentiometric titration in aqueous solution (I = 0.1 M, $NaClO_4$, and T = 298 ± 0.1 K) using an automatic titration set including a Dosimat 665 (Metrohm) autoburette, an Orion 710A precision digital pH-meter and an IBM-compatible PC.

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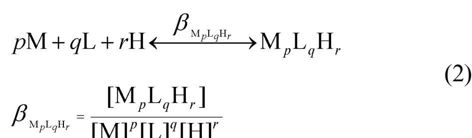
The Orion 8103BN semimicro pH glass electrode was calibrated[27] using the modified Nernst equation (1):

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

where J_H and J_{OH} are fitting parameters in acidic and alkaline media for the correction of experimental errors, mainly due to the liquid junction and to the alkaline and acidic errors of the glass electrode; $K_w = 10^{-13.75}$ M^2 is the autoprotolysis constant of water.[28] The parameters were calculated by a non-linear least squares method. The species formed in the systems were characterised by the following general equilibrium process (2):



$$p\mathrm{M} + q\mathrm{L} + r\mathrm{H} \xleftrightarrow{\beta_{\mathrm{M}_p\mathrm{L}_q\mathrm{H}_r}} \mathrm{M}_p\mathrm{L}_q\mathrm{H}_r$$

$$\beta_{\mathrm{M}_p\mathrm{L}_q\mathrm{H}_r} = \frac{[\mathrm{M}_p\mathrm{L}_q\mathrm{H}_r]}{[\mathrm{M}]^p[\mathrm{L}]^q[\mathrm{H}]^r} \quad (2)$$

where M denotes the dimethyltin(IV)$^{2+}$ cation and L the non-protonated ligand molecule. Charges are omitted for simplicity, but can be easily calculated, since the composition of the fully protonated dipeptides is described as LH_2 (MPGly) and LH_2^+ (Ala-Gly). The formation constants were calculated by means of the computer program PSEQUAD.[29]

The protonation and complex formation constants were determined from 4 and 7 independent titrations (60–90 data points per titration), respectively. The metal-to-ligand ratios varied between 1 : 1 and 1 : 3, and the metal ion concentration ranged from 1.0×10^{-3} to 4.0×10^{-3} mol dm^{-3}.

NMR Measurements

^{1}H and ^{13}C NMR measurements were performed on Bruker DRX400 and Varian VXR 300 spectrometers. The chemical shifts δ were measured with respect to 1,4-dioxane as an internal reference and converted relatively to TMS, using $\delta_{\mathbf{dioxane}} = 3.70$ ppm for ^{1}H and 67.4 ppm for ^{13}C NMR. The individual chemical shifts and ^{1}H–^{117,119}Sn coupling constants of the different hydrolysed species of the dimethyltin cation, as well as the geometry of the complexes were reported in detail earlier.[20,30] The individual $^2J(^{119}\mathrm{Sn}–^1\mathrm{H})$ heteronuclear couplings can be converted to C–Sn–C angles by using the published equation.[31]

For ^{1}H NMR measurements, the ligand concentration was 0.01 mol dm^{-3} for both ligands with 0.005 mol dm^{-3} metal concentration (in some cases, spectra were also performed with [L] = [M] = 0.01 mol dm^{-3}). In the case of ^{13}C NMR, the concentrations used for the ligand and for the metal were 0.07 and 0.035 mol dm^{-3}, respectively. Measurements were generally made in a 9 : 1 H_2O : D_2O mixture. In a few cases they were performed in pure D_2O.

Results and discussion

The protonation constants of Ala-Gly and MPGly determined in this study (Table 1) agree well with the earlier reports.[32–34] The hydrolysis constants[20] of dimethyltin(IV) cation were taken into consideration during the evaluation of the pH-metric data.

Dimethyltin(IV)–Ala-Gly system

The formation constants of the complexes formed, together with some calculated data are listed in Table 1. The composition and solution speciation of these species is very close to that reported earlier for the dimethyltin(IV)–Gly-Gly system.[20] The collected ^{1}H NMR data (Table 2) also suggest identical behaviour with the Gly–Gly complexes. These data indicate a hydrolytic process during the deprotonation of the carboxylate coordinated MLH complex, forming the {COO$^-$,OH$^-$} coordinated M(LH)(OH) species. The next deprotonation could be assigned to several processes. However, the formation of the MLH_{-1} species, having slow ligand exchange on the NMR timescale, results in a well separated set of signals of the bound ligand, which allowed the structural characterisation of the species formed around pH 5. The significant shift of the bound ligand signals (Tables 2 and 3), especially those of the amide carbon atom, and the inequivalence of the metal bound methyl groups suggest the formation of the already described[20,21] {NH_2,N$^-$,COO$^-$} coordinated MLH_{-1} complex. The angle between the two methyl groups of dimethyltin(IV), determined[31] from the $^2J_{^{119}\mathrm{Sn}–^1\mathrm{H}}$ coupling (81 Hz, C–Sn–C ~130°), indicates trigonal-bipyramidal structure, with equatorial position of the two methyl groups.

Table 1 Formation constants and derived data of the dimetyltin(IV) complexes of Ala-Gly and MPGly (as their logarithms) at T = 298 K, I = 0.1 mol dm^{-3} $NaClO_4$; $\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$ with estimated errors in parentheses (last digit). The formation constants of the hydrolytic species are as follows:[20] $\beta_{10-1} = -3.175(5)$, $\beta_{10-2} = -8.415(4)$, $\beta_{10-3} = -19.459(4)$, $\beta_{20-2} = -4.95(4)$, $\beta_{20-3} = -9.96(3)$

pqr [a]	L-Ala-Gly	MPGly
011	8.11(1)	8.39(1)
012	11.28(1)	11.86(1)
111	10.22(6)	12.45(2)
110	6.80(6)	9.52(1)
11–1	1.81(3)	4.93(1)
pK (ML)	3.42	2.93
pK (MLH_{-1})	4.99	4.59
F.P.	0.005	0.006
N.P.	527	557

[a] F.P. fitting parameter (cm^3); N.P. number of experimental points (cm^3).

Dimethyltin(IV)–MPGly system

Although the composition of the complexes formed in this system are identical with the former system, their formation constants (Table 1) are 2–3 orders of magnitude higher than for Ala-Gly. This results in a considerably different solution speciation (Fig. 1). Such important differences between the formation constants can not be explained assuming identical carboxylate coordination in the MLH and ML complexes of the two ligands. ^{1}H and ^{13}C NMR measurements have been performed in order to elucidate the nature of the above mentioned different behaviors. Two sets of peaks appear in the ^{1}H NMR spectra of the dimethyltin(IV)–MPGly system already at pH 2.2 (Fig. 2). Since a single carboxylate coordination does not result in slow ligand exchange, this indicates different binding modes in the MLH complexes of the two ligands, in agreement with the pH-metric data. Several earlier solution equilibrium studies have reported strong binding ability of the thiol group to organotin(IV) cations, even at rather acidic pH.[11,12,26] Moreover, the mondentate thiolate coordination resulted in the formation of slow ligand exchanging species in the case of mercaptocarboxylic acids.[26] The observed significant, *ca.* 0.5 ppm, downfield shift of the CH proton in the MLH complex (Fig. 2. and Table 2), as compared to the free ligand, indicates thiolate coordination in the present case, too. The other proton signals also undergo downfield shift upon the formation of MLH (Table 2). The most significant is the *ca.* 1.1 ppm shift of the amide proton signal. This very important displacement raises the question about the possibility of the amide oxygen coordination. If this happened, a five-membered {S$^-$,C=O} chelate ring would form. The presence of the chiral carbon atom in this chelate would result in inequivalent tin-bound methyl groups (two Sn–CH_3 proton signals should be present in the spectra) in this slow exchanging complex. However, only

Table 2 ^{1}H NMR chemical shifts (δ) in ppm and coupling constants (J) in Hz (in parentheses) for complexes with dimetyltin(IV) in aqueous solution at different pH; [M] = 0.01 mol dm^{-3}

Species (pH)	$\delta_{NH,amide}$	δ_{CH}	δ_{CH_2}	δ_{CH_3}	$\delta_{SnMe_2}(^{2}J_{Sn-H})$
$Me_2Sn(IV)^{2+}$/Ala-Gly					
MLH 5% + ML 28% + L (4.31)	8.37	4.06	3.87/3.66[a]	1.49	0.80 (90 Hz)
Free L or M (4.31)	8.36	4.06	3.88/3.66[a]	1.48	0.81 (90 Hz)
MLH_{-1} (6.71)	–	–[b]	3.88/3.65[a]	1.36	0.82 (81 Hz) 0.76 (81 Hz)
Free L or M (6.71)	–	4.04	3.86/3.63[a]	1.48	0.65 (80 Hz)
$Me_2Sn(IV)^{2+}$/MPGly					
MLH 66% + ML 17% (2.24)	9.52	4.11	4.02	1.54	0.89 (81 Hz)
Free L or M (2.24)	8.42	3.61	3.95	1.43	0.88 (103 Hz)
MLH 12% + ML 76% (3.74)	–	4.06	~3.80	1.53	0.87 (77 Hz)
Free L or M (3.74)	8.26	3.61	3.82	1.43	0.84 (92 Hz)
MLH_{-1} (7.71)	–	~3.72	~3.72	1.44	0.74 (74 Hz) 0.67 (75 Hz)
Free L or M (7.71)	–	3.58	3.71	1.42	0.64 (81 Hz)

[a] AB quartet. [b] No shift compared to the free L signals, or it is overlapped with the CH_2 signals.

Table 3 ^{13}C NMR chemical shifts (δ) in ppm and coupling constants (J) in Hz (in parentheses) for MLH_{-1} complexes with dimetyltin(IV) in aqueous solution; [M] = 0.075 mol dm^{-3}

Species (pH)	δ_{CO-NH} ($^{2}J_{Sn-C}$)	δ_{COO^-} ($^{2}J_{Sn-C}$)	δ_{CH}	δ_{CH_2} ($^{2}J_{Sn-C}$)	δ_{CH_3}	δ_{SnMe_2}
$Me_2Sn(IV)^{2+}$/Ala-Gly						
MLH_{-1} (6.75)	178.59 (~ 27 Hz)	177.95	51.63	46.39 (21 Hz)	19.64	1.84/ 1.01
free L or M (6.75)	171.79	177.11	50.26	44.25	17.38	3.41
$Me_2Sn(IV)^{2+}$/MPGly						
MLH_{-1} (7.74)	181.97 (52 Hz)	178.40 (8 Hz)	42.08	47.88 (18 Hz)	26.39	4.89/ 3.92
free L or M (7.74)	176.68	178.04	40.37	44.88	24.10	3.54

[a] AB quartet. [b] Broad signal.

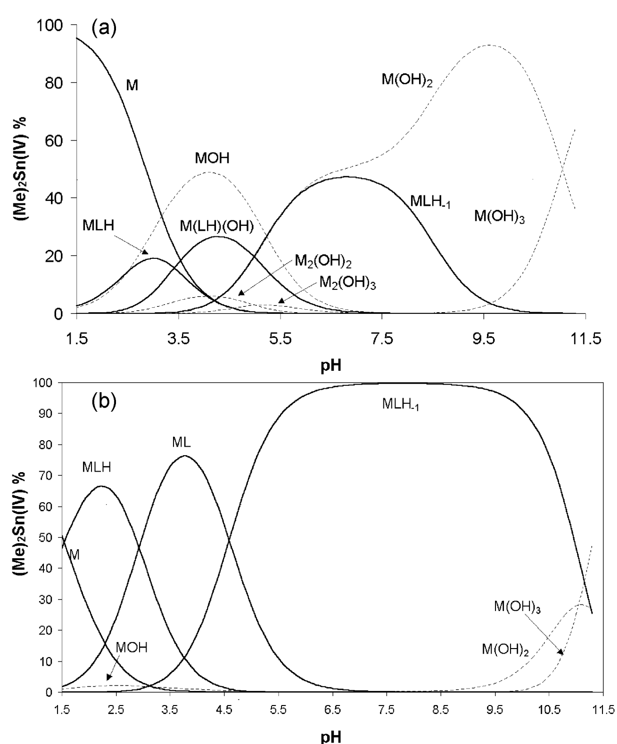


Fig. 1 Species distribution curves of the dimethyltin(IV)–Ala-Gly (A) and –MPGly (B) systems (2[M] = [L] = 0.01 mol dm^{-3}). Hydrolytic species are shown by dashed lines.

one methyl signal can be detected for the MLH complex, strongly overlapped with that of the free dimethyltin(IV), suggesting monodentate thiolate coordination in this species.

The MLH complexes of the two ligands form in nearly the same pH range. Considering the rather different pK values of the two donor groups (COO^- and S^- for Ala-Gly and MPGly, respectively), MPGly provides several orders of magnitude higher stability, in agreement with the high affinity of organotin(IV) cations towards thiolate groups.[11,12,26]

The deprotonation of the complex MLH (pK = 2.93) may concern both a metal-bound water molecule, as in the case of Ala-Gly, and the C-terminal carboxylate group. Between pH 2.2 and 4.6 a continuous shift of the CH_2 signals of the metal-bound ligand was observed in the ^{1}H NMR spectra, indicating that the deprotonation does not alter the coordination sphere of the slow exchanging complex, *i.e.* the proton loss of the C-terminal carboxylate takes place without metal assistance. Although, the tin-bound methyl signals of dimethyltin(IV), MLH and ML are not separated, the *ca.* 80 Hz $^{2}J_{^{119}Sn-^{1}H}$ coupling constants, observed between pH 2 and 5 (Table 2), suggest trigonal-bipyramidal structures for MLH and ML.

Above pH 4 a further deprotonation can be observed leading to species MLH_{-1}, which is again considerably more stable ($\Delta\log\beta_{11-1}$ = 3.1) than the analogous complex of Ala-Gly, and thus becomes the unique species over a wide pH range (Fig. 1). Parallel with the above deprotonation, a new set of peaks appear in the ^{1}H NMR spectra. The methyl groups of the $(CH_3)_2Sn$ unit become inequivalent, indicating the formation of a rather rigid chelate ring involving the chiral CH carbon atom. This suggests the metal promoted deprotonation of the amide

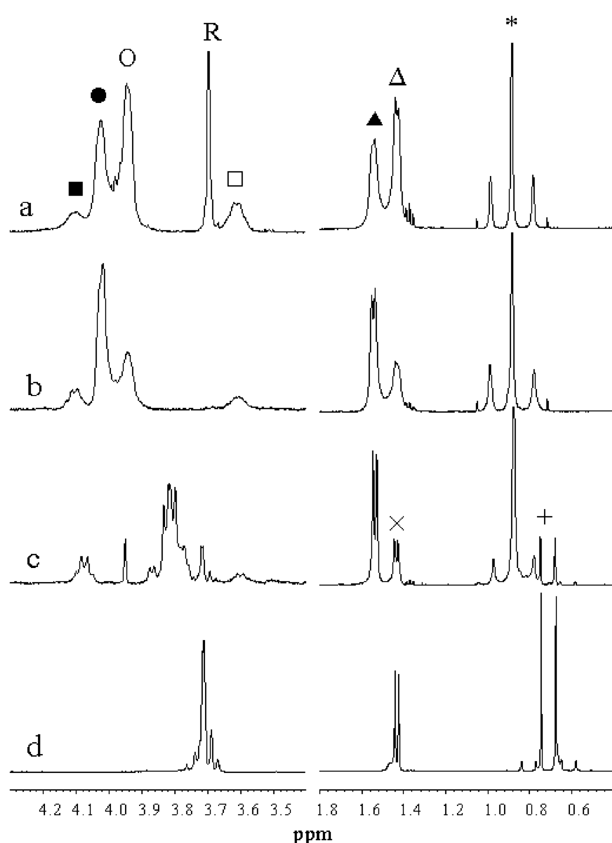
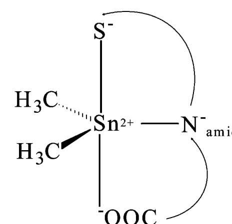


Fig. 2 Part of the ^1H NMR spectra of the dimethyltin(IV)–MPGly system at pH = 2.24 (a, b), 3.78 (c) and 7.72 (d). 2[M] = [L] = 0.01 mol dm^{-3} (a), [M] = [L] = 0.01 mol dm^{-3} (b, c, d). Squares, circles and triangles denote the CH, CH_2 and CH_3 signals of the bound (filled symbols) and free ligand (open symbols). Asterisk denotes the tin-bound methyl protons in M, MLH and ML, while × and + denote the ligand and tin-bound methyl protons in MLH_{-1}, respectively. R denotes the dioxan signal.

nitrogen, as in some other $(CH_3)_2Sn$(IV)–dipeptide systems.[20–22] The CH proton signal of the bound ligand is shifted downfield (0.2 ppm), as compared to the free ligand, and is strongly overlapped with the bound CH_2 signals at around 3.7 ppm. Similarly, two sets of peaks appear on the ^{13}C NMR spectra at pH 7.7 and at two-fold ligand excess, which gives further evidences for the coordination mode of MPGly (Fig. 3). All peaks of MLH_{-1} undergo a downfield shift as compared to the free ligand (Table 2). The important displacement (5.3 ppm, Table 3) of the amide carbon atom, as well as its remarkable scalar coupling with the tin nucleus ($^2J_{Sn-C}$ = 52 Hz) further support the metal-promoted deprotonation of amide nitrogen. The carboxylate carbon atom undergoes a relatively small downfield shift (0.37 ppm) upon complex formation, but its metal coordination is indicated by the observed 8 Hz $^2J_{Sn-C}$ coupling. Although the NMR data do not provide direct evidence, several indirect proofs (the *ca.* 3 ppm downfield shift of the CH and CH_3 carbon atoms of the bound ligand, the inequivalence of the tin-bound methyl signals, the notably higher $\log\beta_{11-1}$ value for MPGly as compared to Ala-Gly) are in favour of the metal coordination of the thiolate group in the MLH_{-1} complex.

Accordingly, MPGly provides a tridentate {S^-,N^-,COO^-} coordination for dimethyltin(IV) in MLH_{-1}. The coordination of the amide nitrogen and the carboxylate group takes place in a cooperative manner during the process ML = MLH_{-1} + H^+, and thus the deprotonation of amide nitrogen involves fundamentally different processes in the case of Ala-Gly, or any other dipeptides, and MPGly. The C–Sn–C angle in the complex MLH_{-1} of MPGly, determined[31] from the $^2J_{^{119}Sn-^1H}$ coupling (72.5 Hz) is about 122–124°, suggesting trigonal bipyramidal-geometry around the metal ion (Scheme 2), like in the analogous complex of Ala-Gly or other dipeptides.



Scheme 2 The proposed structure of the MLH_{-1} species in the dimethyltin(IV)–MPGly system.

Due to the strong competition between the ligand and the hydroxide ion, Ala-Gly and the other dipeptides are not able to suppress completely the formation of the $M(OH)_2$ species, in fact, the dihydroxo complex becomes dominant above pH 8 in all cases (Fig. 1(A) and Fig. 4(b)–(g)). The three orders of magnitude higher stability of the analogous MPGly complex, however, results in the complete formation of the MLH_{-1} complex in the neutral pH range, and the ligand is driven out from the complex only above pH 10 (Fig. 1(B) and Fig. 4(a)).

Conclusion

The replacement of the N-terminal amino group of Ala-Gly by a thiol group, results in a considerably higher organotin(IV)-binding ability for MPGly. This is the consequence of the different primary metal binding sites of the two ligands. In the

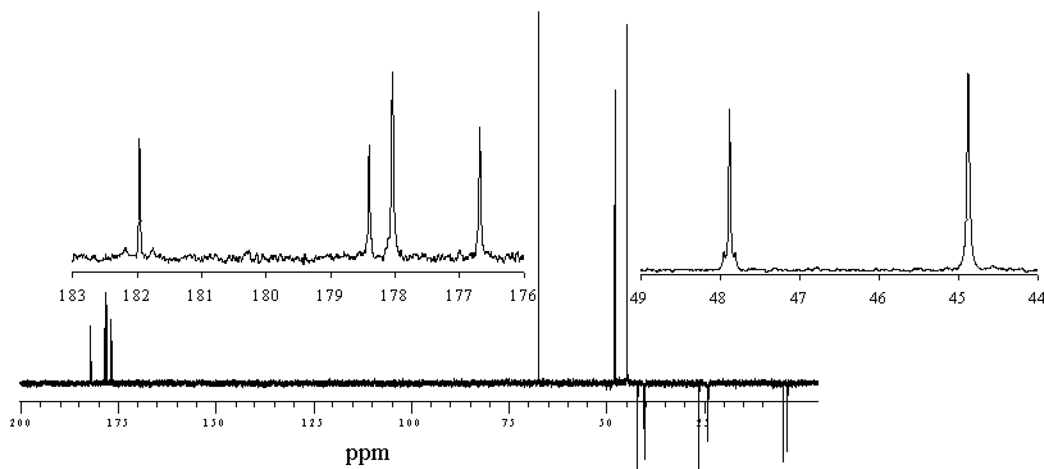


Fig. 3 *J*-Modulated spin–echo ^{13}C NMR spectrum of the dimethyltin(IV)–MPGly (1 : 2) system at pH 7.70. Inserts show the tin–carbon scalar couplings.

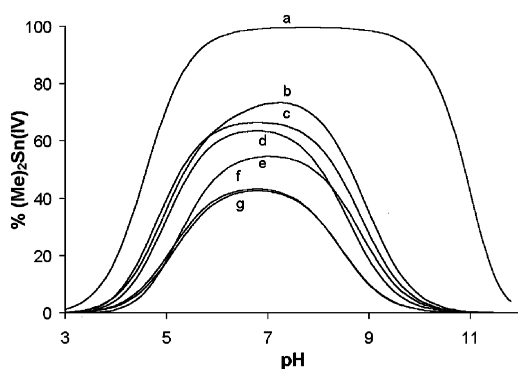


Fig. 4 The speciation of amide-coordinated MLH_{-1} complexes in the different dimethyltin(IV)–dipeptide systems. MPGly (a, this work), glycyl-L-histidine[20] (b), salicyl-glycine[22] (c), L-aspartyl-glycine[21] (d), glycyl-L-asparagin acid[21] (e), glycyl-glycine[20] (f), L-alanyl-glycine (g, this work). [L] = 0.008 M, $[(CH_3)_2Sn(IV)]$ = 0.004 M, I = 0.1 M, T = 298 K.

case of Ala-Gly, and any other dipeptides studied so far, the carboxylate group is bound to the metal ion around pH 2, and acts as an anchoring group for the metal-promoted deprotonation of the amide nitrogen between pH 4 and 7. The primary binding site, and thus the anchoring group for the amide nitrogen deprotonation is the thiolate group in the case of MPGly.

Acknowledgments

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