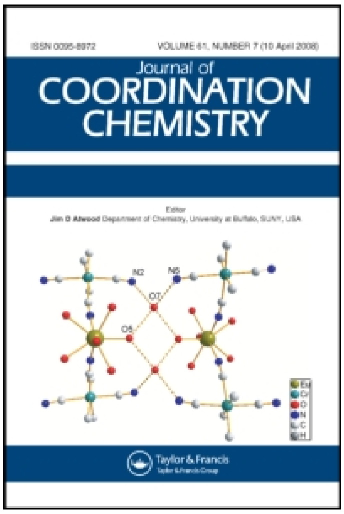

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Complex Formation Reactions of Dimethyltin(IV) with Some Zwitterionic Buffers

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COMPLEX FORMATION REACTIONS OF DIMETHYLTIN(IV) WITH SOME ZWITTERIONIC BUFFERS

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Equilibrium studies in aqueous solution are reported for dimethyltin(IV) complexes of zwitterionic buffers, such as bicine and tricine (L). Stoichiometry and stability constants for the complexes formed were determined at 25°C and ionic strength 0.1 M $NaNO_3$. The results showed the best fit of the titration curves were obtained for complexes MLH, ML, ML_2, MLH_{-1}, and MLH_{-2} with the hydrolysis products of the dimethyltin(IV) cation. The bonding sites of the dimethyltin(IV) complexes with bicine and tricine at different pH were characterized in the solid state by elemental analyses, FTIR, and TG analysis. The molecular formula of the complexes synthesized at $pH = 3.0$ is $[(CH_3)_2Sn(L)(H_2O)]Cl$ while in neutral and alkaline media the hydrolytic species are formed.

Keywords: Equilibrium studies; Dimethyltin(IV) complexes; Bicine; Tricine

INTRODUCTION

Organotin(IV) compounds R_nSnX_{4-n} exhibit a variety of biological effects depending on the number n, on the type of organic groups R bound to tin and on the ligand X^-. The antitumor activity of platinum complexes [1], indicated organotin compounds as possible candidates for antitumor agents, especially compounds containing active antitumor organotin moieties $R_nSn^{(4-n)+}$ (with respect to n and R) by antileukemia screening test. Diorganotin(IV) derivatives appear to be the most active [2–6]. Correlation between antitumor activity and structure suggested that coordination of organic ligands would facilitate transport across membranes, where the antitumor activity would be exerted by the organotin(IV) moieties [2,7] dissociated from the complexes, which could interact with nucleic acids.

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Some studies were recently published on interactions between organotin(IV) compounds and amino acid derivatives, e.g., salicylglycine and 2-hydroxyhippuric acid [8], revealed that the coordination polyhedron around the tin atom is a distorted trigonal bipyramid, with a tridentate [O^-, N^-, COO^-] ligand. ^{13}C-NMR measurements showed that *N*-gluconyl-α-amino acid complexes are coordinated through deprotonated carboxylate oxygen, amide nitrogen and C(2)-hydroxy group [9]. Furthermore, dialkyltin(IV) cations are able to promote the deprotonation of the peptide-nitrogen in aqeous solutions [COO^-, N^-, NH_2] [10,11]. On the other hand, it is known that *N*,*N*-bis(2-hydroxyethyl)glycine (bicine) and *N*-(2-hydroxy-1,1-bis(hydroxymethyl)-ethyl)glycine (tricine) are important hydrogen ion buffers for biological media. Investigation of the different complex species of the two biologically important compounds (dimethyltin(IV), M and zwitterionic buffers, L) are important. Therefore, a systematic study for this complex system has been carried out. This includes synthesis and characterization of the isolated solid complexes in different pH's. Stoichiometry and stability of the various complex species in the complex system at different pH's have been examined by pH-metric techniques.

EXPERIMENTAL

Materials and Reagents

Dimethyltin(IV) dichloride was received from Aldrich Chemical Co. The ligands (L), bicine and tricine, were supplied from Fluka Chem. Co. Carbonate-free sodium hydroxide stock solutions were prepared by diluting the contents of BDH concentrated volumetric solution vials. These solutions were systematically checked by titration against potassium hydrogen phthalate. All solutions were prepared in deionized water.

Synthesis

Reaction of dimethyltin(IV) dichloride with bicine and tricine was examined by dissolving bicine or tricine (163 or 179 mg, 1 mmol) in few mLs of water. The solution was added dropwise to few mLs of a stirred solution of dimethyltin(IV) dichloride (220 mg, 1 mmol). The pH was adjusted to 3.0, 7.5 and 10.5 for bicine and pH = 3.0, 8.0 and 11.0 for tricine. This mixture was slowly evaporated to obtain a volume of 10 mL. A white precipitate formed, and the mixture was stirred for a further 4 h at 25°C. Then the precipitate was filtered off and washed sequentially with water, ethanol and diethylether. Yield (60–80%) of white powder.

Anal. calcd. for $[(CH_3)_2Sn(Bic)(H_2O)_2]Cl$ at pH = 3.0; m.p. = 134–136°C. C: 25.1; H: 4.7; N: 3.7; Cl: 9.3; SnO: 35.4. Found C: 24.9; H: 4.9; N: 3.7; Cl: 8.8; SnO: 18.4.

Anal. calcd. for $[(CH_3)_2Sn(Tric)(H_2O)_3]Cl$ at pH = 3.0; m.p. = 195°C. C: 23.1; H: 4.3; N: 3.4; Cl: 8.5; SnO: 32.4. Found C: 23.0; H: 4.4; N: 3.2; Cl: 8.2; SnO: 19.27.

Anal. calcd. for $[(CH_3)_2Sn(OH)_2] \cdot 1/2H_2O$ at pH = 7.5 for bicine and 8.0 for tricine; m.p. > 350°C. C: 12.5; H: 4.2; SnO: 70.3. Found C: 13.0; H: 3.9; SnO: 70.1.

Anal. calc. for $[(CH_3)_2Sn(OH)_2]$ at pH = 10.5 for bicine and 11.0 for tricine; m.p. > 350°C. C: 13.1; H: 4.4; SnO: 73.7. Found C: 13.7; H: 3.9; SnO: 73.7.

Apparatus

The pH titrations were performed on a Metrohm 751 GPD titrino. The titroprocessor was calibrated with standard buffer solutions prepared according to NBS specification [12].

The pH meter readings were converted into hydrogen ion concentration by titrating a standard acid solution (0.01), and the ionic strength was adjusted to 0.1 M $NaNO_3$ titrated with standard base (0.1 M) at 25°C. The p(H) is plotted against p[H]. The relationship p(H)–p[H] = 0.05 was observed. The pK_w was calculated as described previously [13].

FTIR spectra were measured on an 80486-PC FTIR Shimadzu spectrophotometer using KBr pellets. Thermal analysis (TGA) was performed in a nitrogen atmosphere with TGA-50 Shimadzu thermogravimetric analyzer.

Procedure and Measuring Techniques

Protonation constants of the ligands were determined by titrating 40 mL of ligand solution (1.25 mM). The hydrolysis constants of dimethyltin(IV) were determined by titrating 40 mL of dimethyltin(IV) solution of concentration 1.25 mM. The formation constants of dimethyltin(IV) complexes were determined by titrating 40 mL of solution containing the ligand (1.25 mM) and dimethyltin(IV) of concentrations 1.25 and 6.25×10^{-1} mM. The ionic strength was adjusted to 0.1 M by $NaNO_3$. The titrations were carried out at 25°C by circulating thermostated water into the appropriate reaction cell under a slow stream of N_2.

The formed species were characterized by the general equilibrium processes (1), while the formation constants for these generalized species are given by Eq. (2).

$$pM + qL + rH \rightleftharpoons [M_pL_qH_r] \tag{1}$$

$$\beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r} \tag{2}$$

Calculations were performed using the computer program [14] MINIQUAD-75 loaded on a Pentium II-233 computer. The stoichiometries and stability constants of the complexes were determined by fitting various possible composition models. The model selected gave the best statistical fit and was chemically consistent with the titration data without systematic drifts in the magnitudes of various residuals, as described elsewhere [14]. The concentration distribution diagrams were obtained using the program SPECIES [15].

RESULTS AND DISCUSSION

Solution-phase Investigations

Dimethyltin(IV) cation is known [16–20] to form stable, water-soluble mono- and polynuclear hydroxo species (see Table I) in the whole pH-range studied. Since the hydroxide ion and ligands are in competition for the metal ion, these species were taken into consideration in the equilibrium systems.

The acid dissociation constants of bicine and tricine were determined under the same experimental conditions of ionic strength and temperature (see Table I). These constants should be taken into consideration during the evaluation of the pH-metric data. It was found that $\log\beta_{011} = 8.30$ and 8.10 for bicine and tricine, respectively.

The titration curves for the complex solutions with (1 : 1 and 2 : 1) ligand to metal ratio clearly indicate formation of different complexes (c.f. Fig. 1). The best fits of the titration curves were obtained when complexes MLH, ML, ML_2, MLH_{-1} and MLH_{-2} included with the hydrolysis products of the dimethyltin(IV) cation. The calculations are shown in Table I.

TABLE I Formation constants of $M_pL_qH_r$ species

Log β_{pqr}[a]	*Bicine*	*Tricine*
011	8.30(0.01)[c]	8.10(0.01)
012	10.68(0.02)	10.52(0.02)
110	8.86(0.03)	8.45(0.04)
120	15.29(0.05)	14.87(0.04)
111	12.09(0.03)	11.71(0.04)
11-1	3.44(0.04)	3.23(0.03)
11-2	−4.87(0.02)	−5.06(0.01)
$\log K$[b]	3.79	3.61
pK^1	3.23	3.26
pK^2	5.42	5.22
pK^3	8.31	8.29

Experimental points ~400. [a]The hydrolysis constants of the dimethyltin(IV) ion are the following, $\log\beta_{10\text{-}1} = -3.13(0.01)$, $\log\beta_{10\text{-}2} = -8.35(0.01)$, $\log\beta_{10\text{-}3} = -18.84\ (0.02)$, $\log\beta_{10\text{-}4} = -30.17(0.01)$, $\log\beta_{20\text{-}2} = -3.46(0.01)$, $\log\beta_{20\text{-}3} = -8.98$ (0.06); [b]$\log K$ = refers to the stability constant of the carboxylate complexes ($\log K = \log\beta_{111} - \log\beta_{011}$); [c]Standard deviations are given in parentheses.

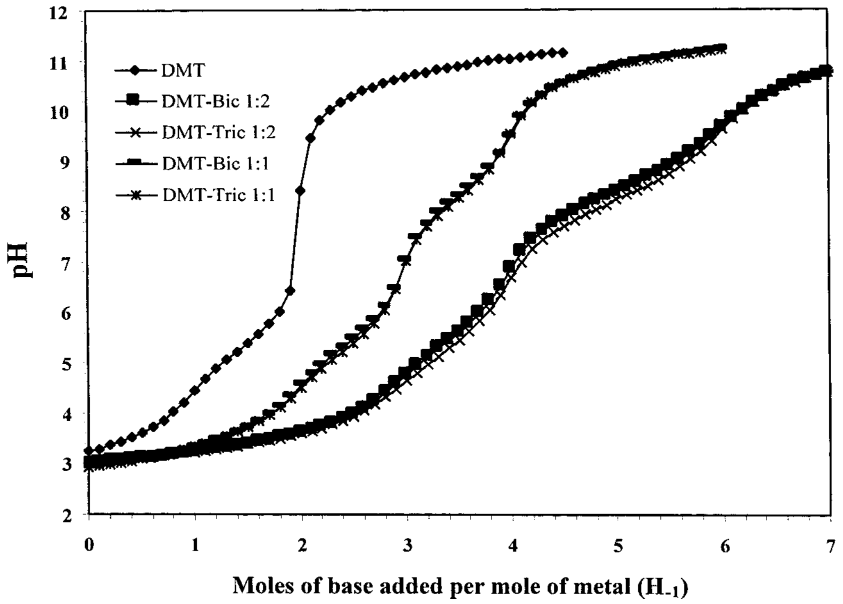

FIGURE 1 pH *vs* H_{-1} curves for the dimethyltin(IV) complexes formed with glycine derivatives (bicine and tricine) and the pH *vs* H_{-1} curve for the hydrolysis of the dimethyltin(IV) cation.

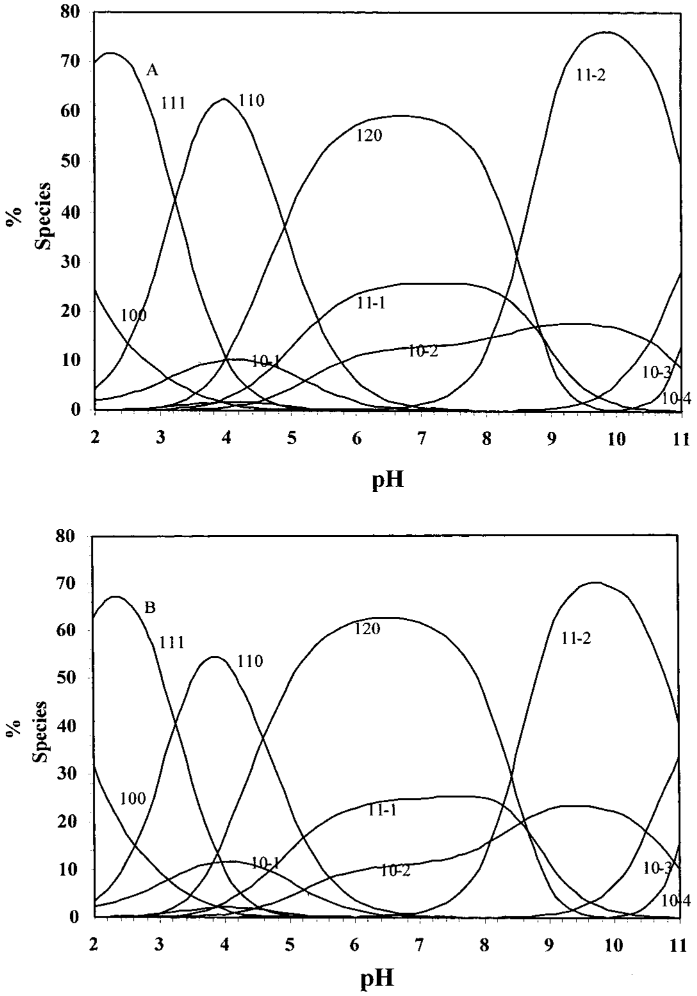

FIGURE 2 Species distribution curves in the dimethyltin(IV)-bicine (A), and tricine (B) systems. $[M] = 6.25 \times 10^{-1}$ mmol, $[L] = 1.25$ mmol. The notation of the different species corresponds to the *pqr* values of the corresponding complex $M_pL_qH_{r(1/2)}$.

The pH *vs* H_{-1} curves of dimethyltin(IV) complexes with both bicine and tricine with stiochiometries (1 : 1 and 1 : 2, metal : ligand) started at lower pH than the analogous curve for hydrolysis of the metal ion (see in Fig. 1). These results suggest that carboxylate ion coordinates in this pH region, forming MLH species. Above $pH = 3.0$ several deprotonation processes occur with increasing pH leading to formation of the complex species Ml, ML_2, MLH_{-1} and MLH_{-2}.

The complex (MLH) is formed in the acidic pH range, as shown in the species distribution curves (Fig. 2). The calculated $\log K$ value of this complex, $M + HL \rightleftharpoons MLH$ (3.79 and 3.61 for bicine and tricine, respectively, c.f. Table I) suggests monodentate coordination of the carboxylate group of the ligand. The MLH complex for bicine is relatively higher than the corresponding one of tricine. This behavior can be ascribed to the relatively high basicity of the carboxylate group of bicine relative to that of tricine. However in the pH range *ca.* 2.5–3.5, the complex MLH undergoes deprotonation leading to the ML species. The pK^1 values corresponding to this process as calculated from $\log\beta_{111} - \log\beta_{110}$ are 3.23 and 3.26 for bicine and tricine, respectively (c.f. Table 1).

Careful examination of Table I reveals that pK^1 values for deprotonation processes ($MLH^+ \rightleftharpoons ML + H^+$) are approximately the same irrespective of the nature of L. Thus the same deprotonation process occurs in both cases, deprotonation of the amide nitrogen as promoted by the metal cation.

The computed formation constants of ML with bicine and tricine ($M + L \rightleftharpoons ML$) are 8.86 and 8.45 respectively. These values are higher than for the corresponding MLH species (3.79 and 3.61, respectively). This behavior can be explained from the expected extra stabilization of the ML species due to chelate behavior of the ligand (COO^- and N) in these complexes.

At higher pH's further deprotonation was observed leading to MLH_{-1} and MLH_{-2}. MLH_{-1} present in solutions over a wide pH range (3.5–9.5), $\sim$24% in neutral pH. The ML_2 species is present in the same pH range and dominant in the neutral pH range ($\sim$62%). MLH_{-2} is present in solution above pH *ca.* 7.0 and the hydrolytic species of dimethyltin(IV) cation are present above pH *ca.* 9.5 (c.f. Fig. 2).

The pK^2 values for the second deprotonation ($ML \rightleftharpoons MLH_{-1}^- + H^+$) as calculated from the relationship p$K^2 = \log\beta_{110} - \log\beta_{11\text{-}1}$ [16] are 5.42 and 5.22 for bicine and tricine (Table I), respectively. The similar pK^2 values irrespective of the nature of the ligand could be explained from deprotonation of a metal-bound water molecule forming the hydroxo mixed-ligand complex MLH_{-1}, i.e., the same process in both cases. Further examination of Fig. 2 reveals that above pH $\sim$8.0, the complex MLH_{-1} undergoes a third deprotonation process to form the MLH_{-2} species ($MLH_{-1} \rightleftharpoons MLH_{-2} + H^+$). The p$K^3$ values corresponding to this process, as calculated from the relationship ($\log\beta_{11\text{-}2} - \log\beta_{11\text{-}1}$) [16], are 8.31 and 8.22 for bicine and tricine, respectively (Table I). Again, the similar pK^3 values corresponding to this process irrespective of the nature of L may be attributed to the deprotonation of a metal-bound water molecule forming hydroxo mixed-ligand complexes. Convincing evidence of this can be obtained from the observation that pK^3 (8.3) is rather similar to $-\log\beta_{10\text{-}2}$ (8.35), (c.f. Table I).

Solid-phase Investigations

The characteristic IR absorption bands of the complexes and the corresponding free ligands in the region 4000–400 cm^{-1} are given in Table II. The stretching vibrations are at 3094 and 3070 cm^{-1} in the free ligands. The $\nu_{(OH)}$ of the free ligands appears at lower frequencies than expected (3200 and 3310 cm^{-1}, respectively), indicating the participation of these OH groups in stronger H-bonding [21,22]. The asymmetric $\nu_{as}(COO^-)$ and symmetric $\nu_s(COO^-)$ stretching vibrations of the carboxylate groups at (1647 and 1454 cm^{-1}) and (1643 and 1473 cm^{-1}) for bicine and tricine respectively, indicate that the ligands have a zwitterion structure.

In the IR spectra of the isolated solid complexes of bicine and tricine at pH = 3.0, the $\nu_{(NH)}$ and $\nu_{(N)}$ vibrations disappeared while the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands shift to lower frequencies. This indicates that the ligands bicine and tricine are coordinated to dimethyltin(IV) through the carboxylate and N or NH groups of the ligand. The weak shoulder at 3132 cm^{-1} in the IR of the tricine complex could be assigned to $\nu_{(NH)}$ stretching. The differences between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands of the complexes are $\sim$231 cm^{-1} indicating that the carboxylate groups are coordinated in a monodenate mode [23].

TABLE II IR absorption bands of the free ligands and the complexes in KBr (cm^{-1}).

System	*pH*	ν_{OH}	ν_{NH}	ν_{CH}	$\nu_{(COO)asy}$	$\nu_{(COO)sy}$	$\nu_{Sn\text{–}N}$	$\nu_{Sn\text{–}O}$	$\nu_{as(Sn\text{–}C)}$	$\nu_{s(Sn\text{–}C)}$
$(CH_3)_2SnCl_2$				2913, 2777					563	513
Bicine		3200	3094	2974, 2905, 2847	1647	1454				
Tricine		3310	3071	2855	1643	1474				
$[(CH_3)_2Sn(Bic)(H_2O)_2]Cl$	3.0	3433		2993, 2916	1635	1404 br.	432	578	548	530
$[(CH_3)_2Sn(OH)_2]\cdot 1/2H_2O$	7.5	3425 br.		2989, 2920				583	552	528
$[(CH_3)_2Sn(OH)_2]$	10.5	3425 br.		2989, 2920				583	552	528
$[(CH_3)_2Sn(Tric)(H_2O)_3]Cl$	3.0	3433 br.	3132 sh.	2847, 2924	1628	1396 br.	440	578	548	530
$[(CH_3)_2Sn(OH)_2]\cdot 1/2H_2O$	8.0	3425 br.		2989, 2920				583	552	528
$[(CH_3)_2Sn(OH)_2]$	11.0	3425 br.		2989, 2920				583	552	528

All characteristic bands of the ligands completely disappear in the spectra of the complexes isolated at pH = 7.5 and 11.0 in case of bicine and pH = 8.0 and 10.5 for tricine, indicating the existence of only hydrolytic species under such conditions.

The assignment of ν(Sn–C), ν(Sn–O) and ν(Sn–N) are consistent with values reported [21]. However, observation of both ν_{as}(Sn–C), ν_{s}(Sn–C) bands in the infrared spectra rule out a planar arrangement for the Sn–C skeleton.

TG and DrTG analysis

Figure 3 shows the TGA and DrTGA curves of free bicine and the bicine complex isolated at pH = 3.0 (A), free tricine and the tricine complex isolated at pH = 3.0 (B) and the bicine complex isolated at pH = 7.5 and 10.5, (C) at a heating rate of 10°C.

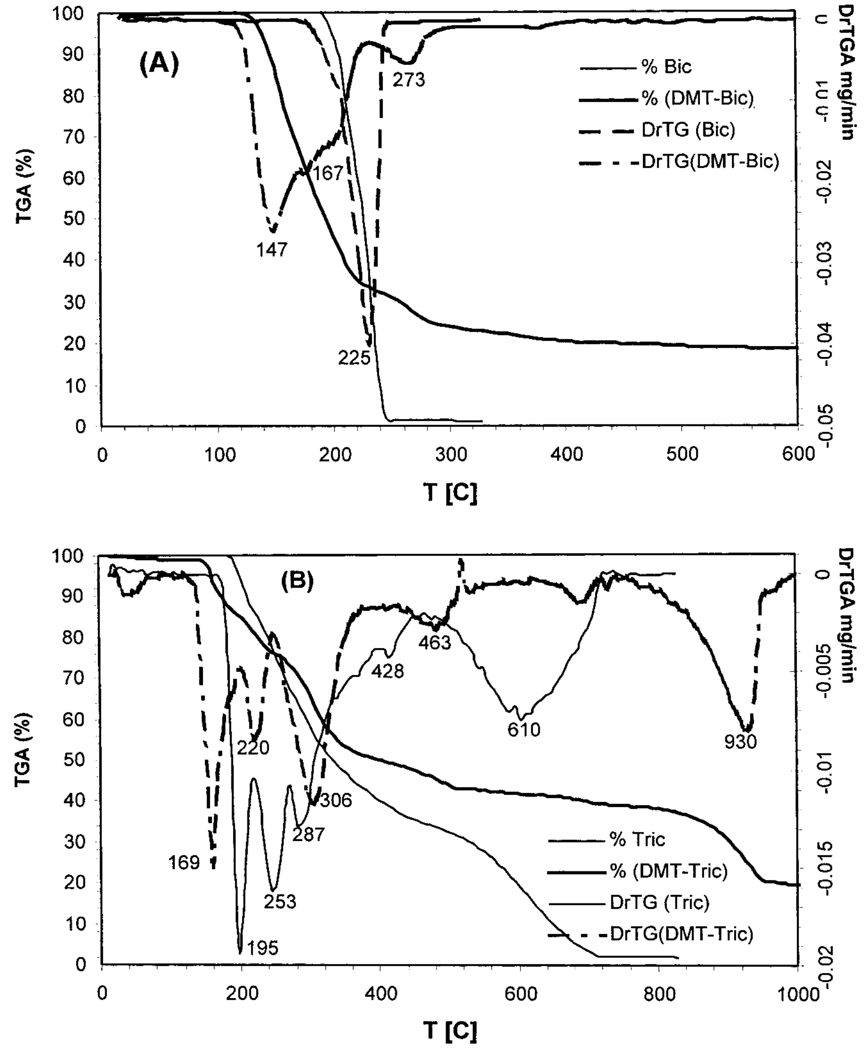

FIGURE 3 TGA and DrTGA curves of the free bicine and DMT–bicine complex at pH = 3.0 (A), free tricine and DMT–tricine at pH = 3.0 (B) and DMT–bicine at pH = 7.5 and 10.5 (C).

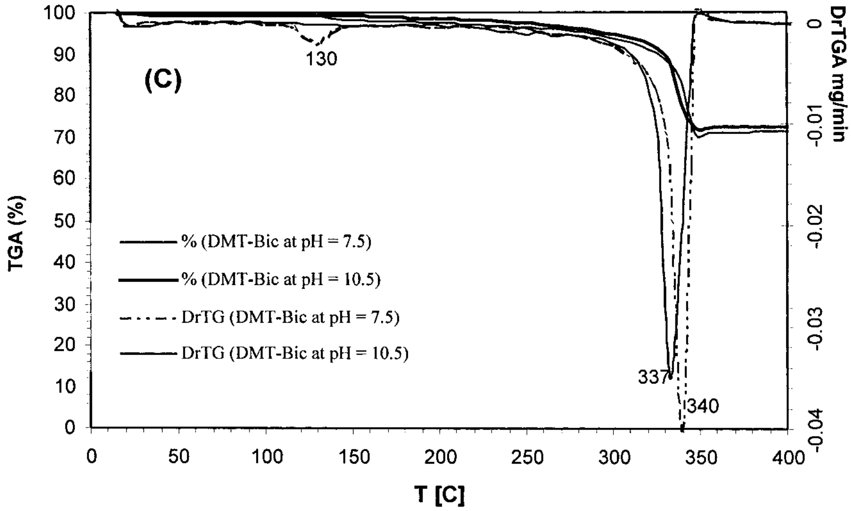

FIGURE 3 Continued

TABLE III Percentage mass loss of dimethyltin(IV) complexes with bicine and tricine at different pH

System	*Stage*	*Temp. range* °C	*Mass loss* (%) *found*
Bicine	I	203–245	99.99
Tricine	I	180–210	17.12
	II	234–263	15.30
	III	280–320	25.60
	IV	392–442	10.00
	V	527–680	30.98
$[(CH_3)_2Sn(Bic)(H_2O)_2]Cl$	I	130–195	67.45
at pH = 3.0	II	239–297	14.35
	M%		18.41
$[(CH_3)_2Sn(Tric)(H_2O)_3]Cl$	I	149–176	15.21
at pH = 3.0	II	209–225	7.47
	III	270–335	26.11
	IV	411–518	8.72
	V	848–952	22.23
	M%		19.27
$[Sn(CH_3)_2(OH)_2]1/2H_2O$	I	122–153	4.67
at pH = 7.5 and 8.0	II	325–348	25.21
	M%		70.12
$[Sn(CH_3)_2(OH)_2]$	I	322–343	26.01
at pH = 10.5 and 11.0	M%		73.70

Details of the steps of thermal decomposition are clear from the DrTGA curve given in the same figure. In Table III, the results of the thermal investigations are summarized. The thermograms of the free bicine (m.p. = 190–192°C) and tricine (m.p. = 182–184°C) indicate sample sublimation immediately after melting. The thermogram of bicine decomposed in one step starting at 203°C and ending at 245°C with a total mass loss 99.99%, while the thermogram of tricine decomposed in five steps starting at 180°C and ending at 680°C (c.f. Table III). This behavior reveals that tricine is thermally stable at a wide temperature range, so that the isolated tricine complex at pH = 3.0 is less affected by heating compared to the bicine complex at pH = 3.0.

Pyrolysis of the bicine complex isolated at pH = 3.0 ends at 297°C with a total weight loss of 81.59%, while tricine analog ends at 952°C with a total weight loss of 80.73%. The observed lower percentage of metal oxide (SnO) residue in both cases compared to that calculated from the suggested molecular formula could be ascribed to the simultaneous sublimation [24]. The thermograms of the solid materials obtained at neutral or alkaline pH's for bicine or tricine reveal that these materials are nearly thermally stable up to high temperature ($\leq 322^\circ$C), where only one main decomposition step is observed (c.f. Fig 3C). This is followed by a constant weight at 350°C. The total weight loss through the observed decomposition step amounts to 29.88 and 26.3 for the solid materials obtained at neutral and alkaline pH. This is consistent with formation of the metal hydrolytic species $[(CH_3)_2Sn(OH)_2]\cdot 1/2H_2O$ and $[(CH_3)_2Sn(OH)_2]$, respectively, as deduced above.

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