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Equilibria involved in the diorganotin(IV) and triorganotin(IV) phosphomycin interaction in aqueous solution

Girolamo Casella[1], Tiziana Fiore[1], Mahmoud M. A. Mohamed[2], László Nagy[3], Claudia Pellerito[1], Lorenzo Pellerito[1]*, Silvio Sammartano[4] and Michelangelo Scopelliti[1]

[1]Dipartimento di Chimica Inorganica e Analitica 'Stanislao Cannizzaro', Università di Palermo, Viale delle Scienze, Parco d'Orleans, 90128 Palermo, Italy
[2]Department of Chemistry, Faculty of Education, Assuit University, New Valley, Egypt
[3]Department of Inorganic and Analytical Chemistry, University of Szeged, PO Box 440, H-6701 Szeged, Hungary
[4]Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Salita Sperone 31, I-98166 Messina (Villaggio S. Agata), Italy

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The interaction of the dimethyltin(IV) and trimethyltin(IV) cations with the phosphomycin disodium salt, Na_2[(1*R*,2*S*)-1,2-epoxypropylphosphonate], has been investigated using potentiometric and UV–visible techniques at 25 °C and 0.1 M ionic strength ($NaClO_4$) in aqueous solution. The species Me_2SnLH^+, Me_2SnL, $Me_2SnL_2^{2-}$, Me_2SnLOH^- and $Me_2SnL(OH)_2^{2-}$ (L = phosphomycinate^{2-}) for dimethyltin(IV)–phosphomycinate, and the species Me_3SnL^-, and Me_3SnLOH^{2-} for trimethyltin(IV)–phosphomycinate systems were considered. The protonation of the phosphomycinate^{2-} and formation constants of the complexes formed in solution were calculated using different computer programs. The speciation diagrams of the various complex species were evaluated as a function of pH. The involvement of different ligand functional groups in the binding to organotin(IV) is discussed. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: ISE-H^+ potentiometric study; UV–visible study; dimethyltin(IV); trimethyltin(IV); phosphomycin

INTRODUCTION

Polymers deriving from the reaction of organotin(IV) moieties and penem (as amoxicillin,[1,2] ampicillin,[3] methicillin[3] and penicillin[4]), cephem (as cephalexin),[5,6] quinolone (as nalidixic acid)[7] and fluoro-quinolone (ciprofloxacin and norfloxacin)[8–11] antibiotics have been reported along with the implications for their particular geometries. Polymeric trigonal bipyramidal (tbp) configurations were hypothesized for diorganotin(IV)chloro and triorganotin(IV)chloro penem antibiotic derivatives, as for triorganotin(IV) in penem antibiotics. Diorganotin-bis(antibiotics) form monomeric *trans*-R_2 skew trapezoidal configurations in which coordination of the antibiotics to the tin(IV) occurs through monoanionic ester-type carboxylate and β-lactamic carbonyl. As far as diorganotin(IV)–ciprofloxicinate is concerned, two major arrangements are found, with one having the geometry about the tin four-coordinated and the second being octahedral.[10] The four-coordinated geometry corresponds to an N–Sn–N arrangement around the tin atom, while the six-coordinated geometry corresponds to an O–Sn–O arrangement with each carboxylate unit chelating with both oxygen atoms to the tin atom. Infrared spectral results are consistent with the interpretation of the Mössbauer spectroscopy results. Solid-state and *in vivo* investigations of some diorganotin(IV) derivatives with the

*Correspondence to: Lorenzo Pellerito, Dipartimento di Chimica Inorganica e Analitica "Stanislao Cannizzaro", Università di Palermo, Viale delle Scienze, Parco d'Orleans II, 90128 Palermo, Italy.
E-mail: bioinorg@unipa.it
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antibiotics chloramphenicol and cycloserine have also been carried out,[12] while the 9*R*,12*S*-[^{t}Bu$_2$Sn]$_2$O derivative of erythromycin A (a macrolide antibiotic) was the target of modeling in organotin(IV) chemistry using NMR restraints,[13] and new organotin(IV) derivatives of 9-substituted tetracycline antibiotics were synthesized and biologically evaluated.[14] Finally, to the best of our knowledge, only the co-ordination of [dimethyltin(IV)]$^{2+}$ cation to penicillin derivatives (penicillin G, ampicillin, amoxicillin and methicillin) as ligands has been investigated in aqueous solution by means of potentiometric titrations. The results showed that, if there is no electron-withdrawing group on the R substituent of the penicillin derivative (as in penicillin G and methicillin), the fast opening of the β-lactamic ring and the time-consuming method hinder the investigation of the interaction.[15] Following our research on the interaction between antibiotics and organotin(IV) moieties, we chose to investigate the interaction of dimethyltin(IV) and trimethyltin(IV) cations with phosphomycin disodium salt, which is one of the most representative of the phosphonic antibiotic class.

EXPERIMENTAL

Materials and methods

The Me_2SnCl_2 and Me_3SnCl used in the investigation were Fluka Riedel-de Haën (Sigma Aldrich Co., St Louis, MO, USA) products, and were recrystallized from benzene, while the free phosphomycin disodium salt antibiotic ligand (Fig. 1) was a Sigma-Aldrich Co. (St Louis, MO, USA) product, with a purity > 99%. Perchloric acid (Sigma-Aldrich Co.) and potassium hydroxide (Merck & Co., Inc., NJ, USA) were prepared by diluting concentrated solutions and were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. All of the solutions were prepared using CO_2-free freshly prepared distilled water (resistance = 18 MΩ) and 'A'-grade glassware.

Titration data

Spectrophotometric titrations were performed using a DU640 spectrophotometer (Beckman Coulter Inc., Fullerton, CA, USA), with 4 ml quartz cells, 1 cm optical path length, thermostated at 25.0 ± 0.1 °C. The spectra were collected in the 230–200 nm wavelength range using a scan speed of 600 nm/min. Absorbance measurements were carried out in the same range by using a polystyrene film as reference. The calculated error was lower than 1.0×10^{-2} a.u. The titrant was added to the cell using a 100 µl (±0.01 µl) micropipette.

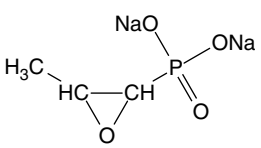

Figure 1. Phosphomycin disodium salt.

Potentiometric measurements were carried out using an E654 potentiometer (Metrohm AG, Hereisau, Switzerland) with an automatic titration set including a Dosimat 665 autoburette (Metrohm AG) and an Orion 81-02 ROSS combination pH electrode (Thermo Electron Corporation, MA, USA). The estimated accuracy of this system was ±0.2 mV and ±0.003 ml for e.m.f. and titrant volume readings, respectively. Pure nitrogen was bubbled through the solutions to avoid O_2 and CO_2 in titration cell, and the solution was constantly stirred.

A volume of solution (2 ml for UV–vis titration and 40 ml for potentiometric titration), containing the phosphomycinate^{2-} and organotin(IV) in different concentration ratios, in the presence of an appropriate amount of $NaClO_4$ to adjust the ionic strength to 0.1 M was titrated with standard potassium hydroxide solution at 25.0 °C (±0.1). For each potentiometric experiment, independent titrations of perchloric acid solutions with standard potassium hydroxide solutions were performed, in the same conditions of ionic strength and temperature as for the systems under study to determine the formal electrode potential (E° and ionic product of water). The same titration of perchloric acid was performed at strong acidic medium, at pH ranging from 1.3 to 2.0, to calculate the acid junction potential J_H, for the correction of experimental errors mainly due to the liquid junction and the acidic errors of the glass electrode. Moreover, phosphomycinate titrations were performed in the same strong acidic medium to refine the protonation constant of acidic phosphate group of phosphomycinate ligand. Tables 1 and 2 show the experimental details for potentiometric and spectrophotometric titrations, respectively.

Calculations

The nonlinear least-squares fitting computer program BSTAC4[16] was used to calculate all of the parameters of an acid–base titration (analytical concentration of the reagents, electrode potential, junction potential coefficient, ionic product of water and formation constants). The following additional computer programs were also used: HYPERQUAD[17] for the calculation of protonation and formation constants, and HYSS2003[18] to draw speciation diagrams. In all the calculations, both the hydrolysis constants of the organotin(IV) cation and the protonation constants of phosphomycinate in $NaClO_4$ aqueous medium were taken into account. The formation constants (β_{lpq}) are expressed according to the equation:

$$l(\mathrm{M}) + p(\mathrm{L}) + q(\mathrm{H}) \rightleftharpoons (\mathrm{M})_l(\mathrm{L})_p(\mathrm{H})_q$$

$$\beta_{lpq} = \frac{\left[(M)_l(L)_p(H)_q\right]}{[M]^l[L]^p[H]^q}$$

where *M*, *L* and *H* are the organotin(IV) cation, phosphomycinate and proton, respectively (charge omitted for simplicity). The species (*111*), (*110*), (*120*), (*11-1*) and (*11-2*) for dimethyltin(IV), and the species (*110*) and (*11-1*) for

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Table 1. Experimental details for the potentiometric measurements

System	C_{Sn}^0, mmol dm^{-3}	C_L^0, mmol dm^{-3}	C_H^0, mmol dm^{-3}	C_{KOH}^0, mol dm^{-3}	pH range	No. of data points
Phosphomycin		12.50	37.50	1.022	1.52–1.96	32
		25.00	50.00	1.022	1.41–1.99	47
		37.50	75.00	1.022	1.36–1.98	56
		1.25	2.50	0.1022	2.67–10.44	50
		2.50	5.00	0.1022	2.56–10.62	50
		3.75	7.50	0.1022	2.50–10.50	75
Dimethyltin(IV)	1.25			0.1022	3.03–10.50	60
	2.50			0.1022	3.00–10.60	75
	3.75			0.1022	2.95–10.60	90
Trimethyltin(IV)	1.25			0.1022	5.26–10.91	40
	2.50			0.1022	4.93–10.91	50
	3.75			0.1022	4.90–11.00	75
Dimethyltin(IV)-phosphomycin	1.25	1.25	2.50	0.1022	2.82–10.70	50
	1.25	2.50	5.00	0.1022	2.72–10.69	60
	1.25	3.75	7.50	0.1022	2.68–10.69	75
	1.25	5.00	10.00	0.1022	2.63–10.68	100
Trimethyltin(IV)-phosphomycin	1.25	1.25	2.50	0.1022	2.96–9.26	50
	1.25	2.50	5.00	0.1022	3.03–9.50	70
	2.50	1.25	2.50	0.1022	2.90–9.50	60

C_{Sn}^0, C_L^0, C_H^0 and C_{KOH}^0 are the initial concentrations of organotin(IV), phosphomycin, $HClO_4$ and KOH as titrant, respectively.

Table 2. Experimental details for UV–vis measurements

System	C_{Sn}^0, mmol dm^{-3}	C_L^0, mmol dm^{-3}	C_H^0, mmol dm^{-3}	C_{KOH}^0, mmol dm^{-3}	Wavelength range, nm	No. of data points
Phosphomycin		5.00	10.00	0.0511	200–230	20
		7.50	15.00	0.0511	200–230	20
		8.75	17.50	0.0511	200–230	20
Dimethyltin(IV)	2.50			0.0511	200–230	25
	5.00			0.0511	200–230	25
	7.50			0.0511	200–230	25
Trimethyltin(IV)	2.50			0.0511	200–230	20
	5.00			0.0511	200–230	20
	7.50			0.0511	200–230	20
Dimethyltin(IV)-phosphomycin	5.00	5.00	10.00	0.0511	200–230	19
	2.50	5.00	10.00	0.0511	200–230	19
	2.00	6.00	12.00	0.0511	200–230	19
Trimethyltin(IV)-phosphomycin	5.00	5.00	10.00	0.0511	200–230	19
	2.50	5.00	10.00	0.0511	200–230	19
	5.00	2.50	5.00	0.0511	200–230	19

C_{Sn}^0, C_L^0, C_H^0 and C_{KOH}^0 are the initial concentrations of organotin(IV), phosphomycin, $HClO_4$ and KOH as titrant, respectively.

trimethyltin(IV)–phosphomicinate systems were considered, with (l, p, q) referring to organotin(IV), phosphomycinate and proton, respectively. The stoichiometric coefficient of the proton can be also negative, indicating the formation of hydroxo species [$H_{-q}{\equiv}(OH)_q$]. The calculations were carried out for different combinations of the species (i.e. different models) by using all the data points for different concentrations (Tables 1 and 2) and it was concluded, on the basis of the best fit,

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Table 3. Stability constants of [organotin(IV)]$^{n+}$ complexes with phosphomycin ligand at 25.0 °C and $I = 0.1$ mol dm^{-3} ($NaClO_4$), with estimated errors in parentheses (last digit)

(l, p, q)	$\log \beta_{lpq}$,[a] BSTAC4[16]	$\log \beta_{lpq}$, HYPERQUAD[17]	$\log \beta_{lpq}$,[b] HYPERQUAD[17]	Accepted value[c]
Dimethyltin(IV)				
pK_1 (in highly acidic medium)	1.32(1)			
011	6.63(1)	6.63(1)	6.60(1)	6.62(2)
012	7.87(2)	7.90(1)		7.88(3)
10-1	−3.18(1)	−3.20(1)	−3.20(3)	−3.20(3)
10-2	−8.50(1)	−8.52(1)	−8.52(1)	−8.52(1)
10-3	−19.88(1)	−19.91(1)	−19.92(1)	−19.90(5)
20-2	−4.95(1)	−5.02(9)	−5.02(9)	−5.0(1)
20-3	−9.95(5)	−10.05(7)	−10.05(8)	−9.95(15)
111	9.56(1)	9.45(4)		9.50(5)
log K(M + HL)				2.9(1)
110	6.64	6.45	6.64	6.55(10)
120	10.42(2)	10.25(9)	10.97(2)	10.5(2)
log K(M + ML)				4.0(2)
11-1	1.58(1)	1.43(5)	0.86(8)	−1.3(2)
log K(MOH + L)				1.9(2)
11-2	−5.91(1)	−6.17(7)	−5.62(4)	−5.8(4)
Trimethyltin(IV)				
10-1	−6.22(1)	−6.21(1)	−6.21(1)	−6.21(1)
10-2	−16.31(3)	−16.45(2)	−16.50(3)	−16.4(1)
20-1	−4.139(5)	−4.29(3)	−4.80(6)	−4.2(2)
110	3.19(1)	3.20(1)	3.20(1)	3.20(1)
11-1	−3.93(2)	−4.09(4)	−4.09(1)	−4.0(1)
log K(MOH + L)				2.2(1)
11-2	−13.81(9)	−14.01(6)	−14.00(4)	−14.0(3)

[a] These data were used to draw distribution diagrams.
[b] Fitted model from potentiometric and UV–vis titrations.
[c] These data were used in the discussion.

that the species listed in Table 3 are formed for each organotin(IV)–phosphomycinate system.

RESULTS AND DISCUSSION

Protonation and hydrolysis constants

In order to analyze the potentiometric and spectrophotometric data obtained for the investigated system, we first studied the acid–base behavior of both phosphomycinate and organotin(IV) ions. The pK_{a1} ($\equiv \log \beta_{012} - \log \beta_{011}$) of the first proton dissociation constant of the acidic phosphate group of the phosphomycin, determined by titrations at low pH (Table 3), was equal to 1.32, while the second proton dissociation constant pK_{a2} ($\equiv \log \beta_{011}$) of the less acidic hydrogen phosphate group was 6.62. This last value is comparable with that of D-glucose-1-phosphate (6.20), D-glucose-6-phosphate (6.18), D-ribose-5-phosphate (6.20) or adenosine-monophosphate (6.20).[19] These differences are probably due to the electron-withdrawing effect of oxygen atoms on the latter ligands.

The hydrolysis of trimethyltin(IV) and dimethyltin(IV) cations has been investigated in a variety of media by several authors,[20–24] and the results are summarized in a recent review.[25] The hydrolysis constants of organotin(IV) cation obtained in this study (see Table 3) are consistent with earlier findings.[19–25]

Formation of complex species

The analysis of the potentiometric (Fig. 2) and UV–vis titration (Fig. 3) curves of dimethyltin(IV) and trimethyltin(IV)–phosphomycin systems allows consideration of the following results.

Potentiometric and UV–vis titrations of dimethyltin(IV) showed that, at lower pH (~4), with a metal : ligand ratio of 1 : 1, protonated and deprotonated complexes are predominant. Metal : ligand and hydroxo complex ratios of 1 : 2 appear at higher pH (>6). The hydroxo-complexes

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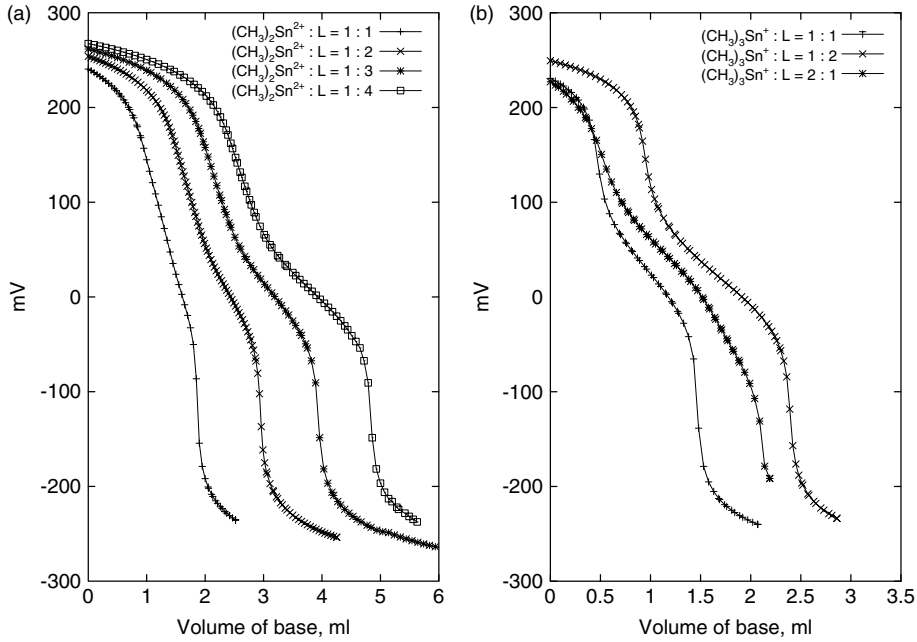

Figure 2. Potentiometric titration curves of: (a) dimethyltin(IV)-L; (b) trimethyltin(IV)-L, at different organotin : L ratios (L = phosphomycinate^{2-}).

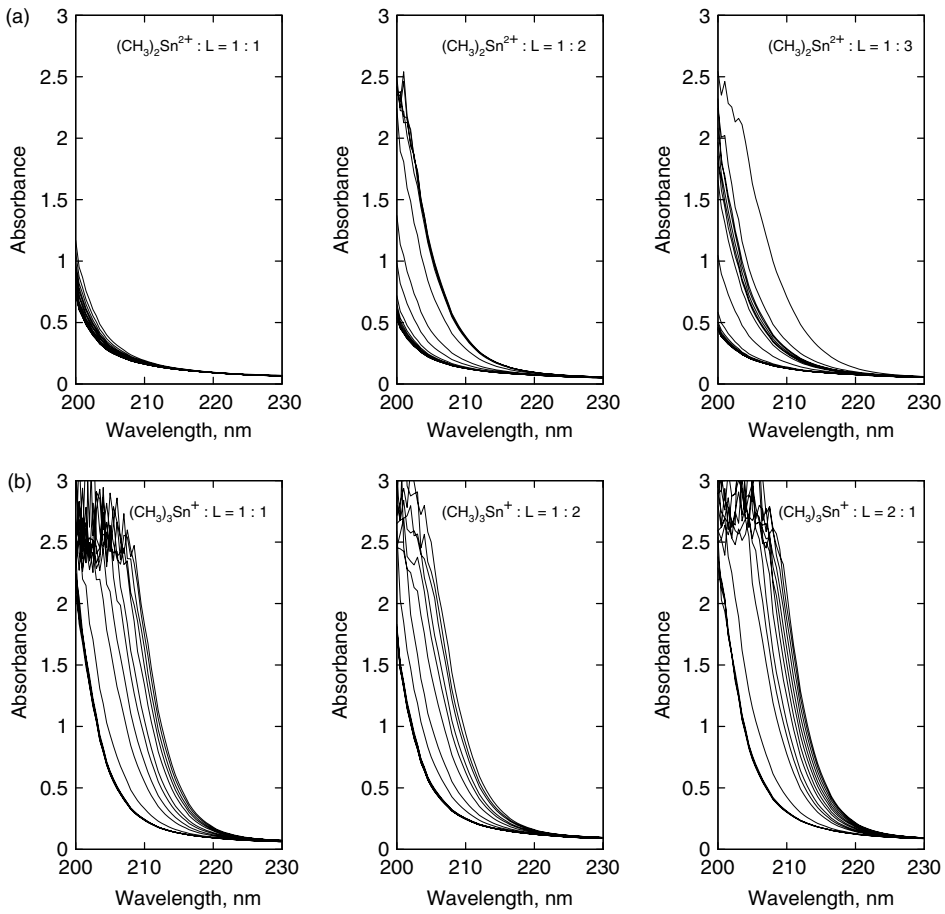

Figure 3. Spectrophotometric titration curves of: (a) dimethyltin(IV)-L; (b) trimethyltin(IV)-L, at different organotin : L ratios (L = phosphomycinate^{2-}).

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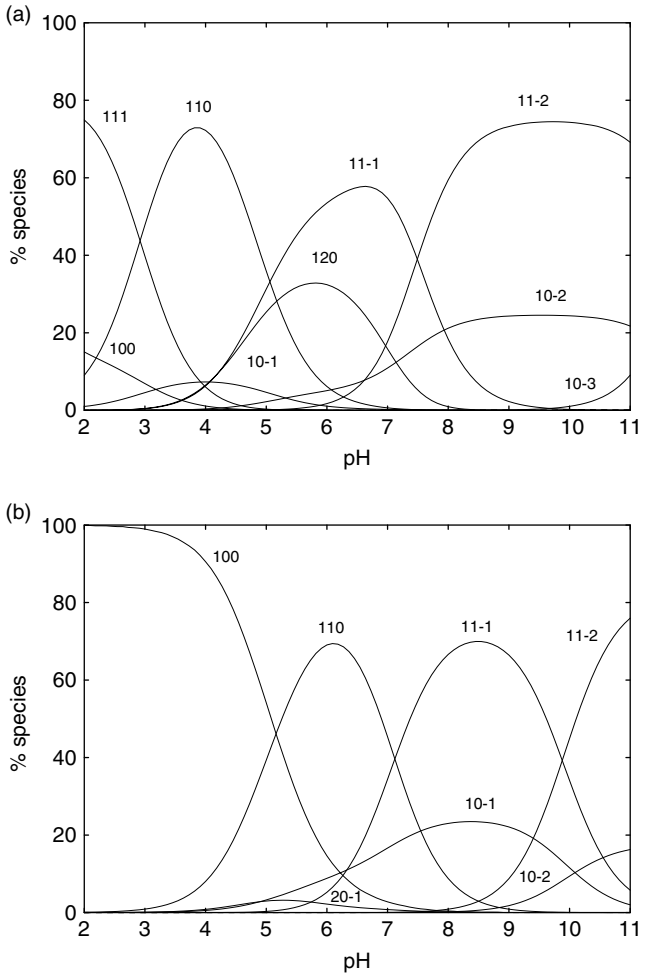

Figure 4. Species distribution curves for (a) $Me_2Sn(IV)$-L; (b) $Me_3Sn(IV)$-L systems. $[Me_nSn(IV)^{(4-n)+}] = 12.5$ mmol dm^{-3}; [L] = 25 mmol dm^{-3} ($n = 2, 3$; L = phosphomycinate^{2-}).

reported in Tables 1 and 2 are mononuclear: no evidence was found of di- or polynuclear complexes.

A protonated mononuclear complex with composition MLH^+ is formed in the acidic pH range (pH < 4), as shown in the speciation diagram (Fig. 4). The calculated log *K* value for this complex (= 2.9) suggests the monodentate coordination of one phosphate group, being the proton bound to the other oxygen of the phosphate group. The deprotonation of MLH^+ leads to the species ML ($\log \beta_{110} = 6.55$), while the coordination of a second ligand gives the ML_2^{2-} species with $\log K = (\log \beta_{120} - \log \beta_{110}) = 4.0$. Finally, the deprotonation of a metal-bound water molecule gives $ML(OH)^-$ species with $\log K = (\log \beta_{11-1} - \log \beta_{10-1}) = 1.9$. These results suggest that the ML_2^{2-} species is firstly formed, followed by the $ML(OH)^-$ species. By further increase of pH, the hydroxo complex species $ML(OH)_2^{2-}$ becomes predominant. This last species must be considered with care since a high uncertainty is associated with $\log \beta_{11-2}$ (different calculations give significantly different formation constants with a mean deviation >0.4).

The trimethyltin(IV)–phosphomycin system shows that complexes with 1 : 1 metal : ligand ratio are formed irrespectively of the organotin(IV):ligand ratios used. There is no evidence for the presence of polynuclear species in significant amounts in solution. At pH = 2.9, where the titrations start, there is evidence for the formation of a simple ML^- species. At higher pH (>8) the coordinated water molecules are deprotonated and hydroxo complexes $ML(OH)^{2-}$ and $ML(OH)_2^{3-}$ are predominant, as shown in Fig. 4(b). As for the analogous species of dimethyltin(IV), the complex $ML(OH)_2^{3-}$ must be considered with care since a high uncertainty is associated with $\log \beta_{11-2}$ (different calculations give significantly different formation constants with a mean deviation >0.4). As far as the coordination of dimethyltin(IV) and trimethyltin(IV) to phosphomycin is concerned (1 : 1 species), it is probable that both charged oxygen atoms of phosphate group bind the alkyltin(IV) cation, the difference in stability between dimethyl(IV) and trimethyltin(IV) derivatives being due to both steric hindrance and different charge contributions. Nevertheless, the relatively high stability may suggest the involvement in the coordination of the epoxydic –O– group. This hypothesis is partially confirmed by the differences between formation constants of ML and $ML(OH)^-$ species of phosphomycin and those of AMP, IMP and UMP[26] with diethyltin(IV) and triethyltin(IV) that show a significant trend (AMP, IMP, UMP) > phosphomycin. Moreover, the involvement of the –O– group in the complexation has been observed for oxydiacetic species of methyltin(IV),[27] while, due to the stabilizing effect of additional thioeter coordination, in the case of *S*-methyl-L-cysteine diethyltin(IV), the MLH^{2+} species was also detected.[28]

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