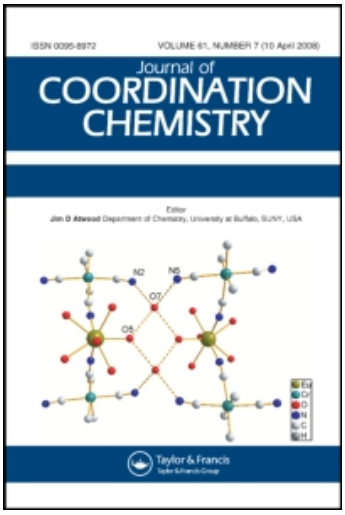

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COORDINATION COMPOUNDS OF TRIMETHYLTIN(IV)

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Complex formation equilibria of trimethyltin(IV) with ligands having a variety of model functional groups (carboxylate, phosphate, amine and thiol) have been investigated. Stoichiometries and stability constants for the complexes formed were determined by glass electrode potentiometry. Results show the formation of 1:1 complexes. The following order of coordination potentiality prevails: thiol ≃ amine > phosphate > carboxylate. Penicillamine is expected to be the most effective antidote for $(CH_3)_3Sn(IV)$ poisoning. The concentration distribution of appropriate complexes formed in solution has been evaluated.

Keywords: Trimethyltin, organotin, stability constants

INTRODUCTION

The use of triorganotin(IV) compounds, R_3SnX, as selective biocides and pesticides has increased rapidly in recent years. All trimethyltin(IV) derivatives have high mammalian toxicity.[1,2] The biological activity of toxic triorganotin(IV) compounds is believed to be due to their ability to bind to certain proteins[3,4] and, although the exact nature of the binding sites is unknown, it has been demonstrated that in cat haemoglobin, cysteine and histidine residues are associated with the trialkyltin group.[4,5]

Although complexes of triorganotin(IV) species have been extensively investigated in the solid state,[6,7] relatively little is known about their solution chemistry.[8,9] A study of the aqueous coordination chemistry of organotin(IV) will evidently be helpful in elucidating the behaviour of such compounds in biological systems. As a continuation of our research on metal complexes of biological interest,[10–13] we report an investigation which traces the establishment of the stoichiometries and stability constants of trimethyltin(IV) complexes with certain ligands. The ligands investigated have a variety of model functional groups (carboxylate, phosphate, amino and thiol), all of which provide potentional coordination sites for binding metal ions in proteins, peptides, and so on.

EXPERIMENTAL

Materials and reagents

Trimethyltin(IV) chloride (TMT) was received from Merck. The ligands used were ethylamine.HCl, propylamine, butylamine, pentylamine, ethylenediamine (en), diethyl-

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enetriamine (dien), formic acid, potassium hydrogen phthalate, sodium dihydrogen phosphate, mercaptoethanol, penicillamine, cysteine and glutathione, as supplied by Fluka. Stock solutions of each of the free amines, except en and dien, were standardized by titration with nitric acid and prepared in equimolar HNO_3 solution. Mercaptoethanol was standardized with iodoacetamide, followed by titration (with strong base) of protons displaced from the thiol group.[14] TMT was determined by estimating chloride content. Dien and en were converted into hydrochlorides (dien.3HCl, en.2HCl), by adding an excess of concentrated hydrochloric acid solution to the amine, and precipitating the hydrochloride using ethanol. The products were thrice recrystallized from an H_2O–EtOH mixture. The concentrations of dien.3HCl and en.2HCl stock solutions were checked potentiometrically. 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.

Procedure

The pH values were measured with a Metrohm 632 pH meter calibrated with standard buffer solutions prepared according to NBS specifications.[15] Titrations were carried out with a Metrohm 655 autotitrator. The following mixtures (A–C) were prepared and titrated potentiometrically with standardized NaOH solution ($\simeq$0.28 M); A: 10 cm^3 of 0.02 M ligand + 30 cm^3 of 0.13 M $NaNO_3$; B: 10 cm^3 of 0.02 M $(CH_3)_3Sn(IV)$ + 30 cm^3 of 0.13 M $NaNO_3$; C: 10 cm^3 of 0.02 M $(CH_3)_3Sn(IV)$ + 10 cm^3 of 0.02 M ligand + 20 cm^3 of 0.20 M $NaNO_3$. Acid dissociation constants of the ligands were determined by titrating mixture (A) in each case. The stability constant of the hydroxo-complex, $[(CH_3)_3Sn(OH)]$, was determined by titrating mixture (B). The stability constants of the organotin(IV) complexes were determined by titrating mixture (C).

All titrations were carried out at 25 $\pm$ 0.1°C in a purified nitrogen atmosphere using a titration vessel described previously.[16] The calculations were performed using the computer program[17] MINIQUAD-75 loaded on an IBM-4331 computer. The model selected was that which gave the best statistical fit and which seemed chemically sensible and consistent with the titration data, without giving any systematic drifts in the magnitudes of residuals, as described elsewhere.[17] The fitted model was tested by comparing the experimental titration data points and the theoretical curve calculated from the values of acid dissociation constants of the ligand and formation constants of the corresponding complexes. The results obtained are listed in Table I.

RESULTS AND DISCUSSION

The acid dissociation constants of the ligands have been reported.[18] We redetermined them under the experimental condition (T = 25°C, μ = 0.1 M $NaNO_3$) used for determining the stability constants of the organotin(IV)complexes. The acid-base chemistry of trimethyltin(IV) has been characterized by fitting the potentiometric data (mixture B), to various acid-base models. The fitted model was found to be consistent with a $[(CH_3)_3Sn(OH)]$ species having $\log \beta_{10-1} = -5.79 \pm 0.01$.

TABLE I
Stability constants of the trimethyltin(IV) complexes.

System	p	q	r[a]	log β[b]	S[c]
$(CH_3)_3Sn(IV)$–OH	1	0	−1	−5.79(0.01)	3.6E-6
Ethylamine	0	1	1	10.43	
	1	1	0	7.35(0.02)	2.1E-6
Propylamine	0	1	1	10.45	
	1	1	0	7.46(0.03)	3.6E-6
Butylamine	0	1	1	10.46	
	1	1	0	7.46(0.03)	3.5E-6
Pentylamine	0	1	1	10.48	
	1	1	0	7.27(0.02)	2.6E-6
Ethylenediamine	0	1	1	9.89	
	0	1	2	16.95	
	1	1	0	7.03(0.01)	1.1E-6
	1	1	1	13.72(0.01)	
Diethylenetriamine	0	1	1	9.84	
	0	1	2	18.92	
	0	1	3	23.15	
	1	1	0	7.53(0.03)	2.2E-6
	1	1	1	16.00(0.03)	
	1	1	2	21.13(0.06)	
Mercaptoethanol	0	1	1	9.70	
	1	1	0	6.98(0.03)	2.8E-6
Formate	0	1	1	3.67	
	1	1	0	2.45(0.02)	1.3E-6
Phthalate	0	1	1	5.08	
	1	1	0	2.85(0.03)	3.6E-6
Phosphate	0	1	1	6.97	
	1	1	0	4.30(0.02)	2.5E-6
Gluthathione	0	1	1	9.47	
	0	1	2	18.13	
	0	1	3	21.61	
	1	1	0	6.99(0.02)	3.2E-6
	1	1	1	15.48(0.02)	
	1	1	2	20.26(0.05)	
Penicillamine	0	1	1	10.41	
	0	1	2	18.27	
	1	1	0	7.59(0.03)	4.1E-6
	1	1	1	15.35(0.03)	
Cysteine	0	1	1	10.15	
	0	1	2	18.31	
	1	1	0	7.22(0.02)	2.9E-6
	1	1	1	15.42(0.02)	

[a] The symbols p, q and r are the stoichiometric coefficients corresponding to organotin(IV), ligand and H^+, respectively. [b] Standard deviations are given in parentheses. [c] Sum of square of residuals.

A solution consisting of equimolar ratio of $(CH_3)_3Sn(IV)$ and ligand is characterized by a potentiometric titration curve having a low buffer region with an inflection at a = 1 (a = number of mols of base added per mol of ligand), corresponding to the formation of a complex species through the release of a hydrogen ion. The results

obtained with all investigated ligands show that the complexes formed are invariably of 1:1 stoichiometry, irrespective of the ligand-to-metal ratio at which titrations are carried out. Ethylenediamine forms with trimethyltin(IV) both mono- and deprotonated complexes. The complexes detected with diethylenetriamine are the di-, mono- and deprotonated species. The acid dissociation constant of a protonated complex is given by (*1*).

$$pK^{H}_{(TMT)(L)(H)} = \log K^{(TMT)}_{(TMT)(L)(H)} - \log K^{(TMT)}_{(TMT)(L)} \qquad (1)$$

The value of pK^{H} is 6.69 for the ethylenediamine complex. This value compares favourably with the pK^{H}_{1} of free ethylenediamine (7.06) if acidification of the NH_3^+ site by the bound organotin(IV) centre is considered. The stability constants for the complexes with ethylenediamine and diethylenetriamine, both deprotonated, are in fair agreement with those obtained for the monodentate amines studied (Table I), if the difference in the basicity of the ligands is considered. This may be explained by assuming binding of ethylenediamine and diethylenetriamine with $(CH_3)_3Sn(IV)$ as monodentates.

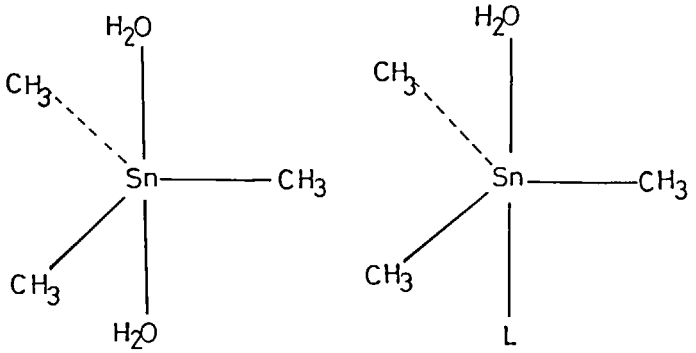
The stability constants for mercaptoethanol and simple amines are nearly equal, *i.e.*, the coordination potentialities of the amino and thiol groups are equivalent. The ligands penicillamine, cysteine and glutathione have various binding sites, *viz*, carboxylic, amino and sulfhydryl groups. Penicillamine and cysteine form mono- and deprotonated complexes. However, glutathione forms the di-, mono- and deprotonated species. The stability constants for the deprotonated complexes with these sulfhydriyl-containing amino acids are of the same order of magnitude as those of mercaptoethanol (S-donor) and amine (N-donor) complexes (Table I). This indicates that they function as monodentates with binding partly at S^- and partly at NH_2 groups, *i.e.*, two isomers exist in equilibrium. Values of first acid dissociation constants of the protonated complexes, calculated using (*1*), are 7.59, 8.20 and 8.49 log units for penicillamine, cysteine and glutathione, respectively. These values compare favourably with the macroscopic acid dissociation constants (pK^{H}_{1} of 7.86, 8.16 and 8.66 (Table I) for penicillamine, cysteine and glutathione, respectively. This further indicates that the proton is located partly on NH_2 and partly on the S^- group.

TABLE II
The maximum proportions of deprotonated complexes.

System	Ethylamine	Propylamine	Butylamine	Pentylamine
pH	6.7	6.8	6.8	6.9
% maximum	79%	80%	82%	80%
	Ethylenediamine	Mercaptoethanol	Diethylenetriamine	Formate
	8.1	6.7	9.3	4.2
	90%	84%	84%	40%
	Phthalate	Phosphate	Glutathione	Penicillamine
	5.3	6.2	9.2	9.0
	49%	73%	79%	84%
	Cysteine			
	9.2			
	88%			

Concentration distributions of various complex species in solution as a function of pH were calculated by the MINIQUAD-75 program. The extent of complex formation is pH-dependent. The extent of formation of the diprotonated complex of glutathione reaches a maximum of 24% at pH 4.2 (16% at pH 4.7 for diethylenetriamine). The maximum degrees of formation of the monoprotonated complexes are 87% at pH 7.6, 75% at pH 6.8, 81% at pH 7.0, 49% at pH 6.3 and 83% at pH 7.4 for glutathione, penicillamine, cysteine, ethylenediamine and diethylenetriamine, respectively. The maximum proportions of the deprotonated complexes are given in Table II, for each ligand.

The coordination geometry of $(CH_3)_3Sn(IV)$ in aqueous solution is believed to be trigonal bipyramidal with three methyl groups equatorial and two water molecules in axial positions (I).[19,20] Complex formation would then involve ligand substitution of one water molecule (II). The location of the two *trans* water molecules prevents the chelation of the ligands as bidentates. Similar behaviour was found for $(CH_3)_3Pb(II)$ complexes with sulfhydryl-containing amino acids.[21]



For the purposes of elucidating the toxicology of $(CH_3)_3Sn(IV)$ however, formation constants are the quantities of interest; values indicate the relative affinities of the various ligands for $(CH_3)_3Sn(IV)$. The results of this study show the formation constant of the penicillamine complex to be larger than those of other ligands. This suggests that, in these terms, penicillamine is the most effective antidote for trimethyltin(IV) poisoning.

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