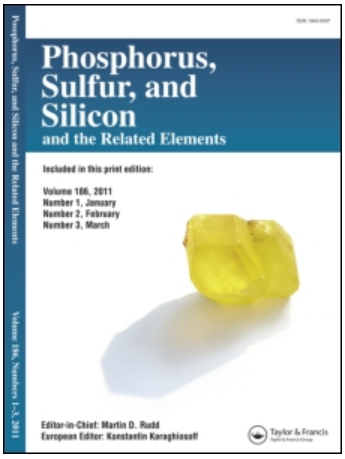

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TRIMETHYLTIN CHLORIDE AND PSEUDOHALIDE COMPLEXES OF TRYPTOPHAN

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Organotin chloride and pseudohalide complexes of tryptophan of the type $Me_3SnX.Tryp$ (Me = methyl, X = Cl, SCN, N_3, CN and NCO; Tryp = tryptophan) were prepared by the addition reactions of tryptophan with trimethyltin chloride and the appropriate pseudohalide prepared *in situ*. The complexes were characterized by elemental analyses, spectroscopic (IR, NMR) studies, melting point and conductance measurements. Melting point and conductance measurements show them to be stable and non-electrolytes in DMSO. The spectroscopic data indicate that tryptophan coordinates with tin covalently through its carboxylate group as an asymmetric bidentate ligand. It is suggested that the complexes have an octahedral geometry.

Key words: Trimethyltin chloride, trimethyltin pseudohalide, conductivity, NMR, IR.

INTRODUCTION

The capacity of amino acids to form metal complexes is both of theoretical and practical significance. The complexing behavior of amino acids towards transition metal ions yielding several types of coordination complexes has been investigated.[1–3] Our studies on the interactions of potentially multidentate amino acids, namely, glycine, leucine and cystine with some Group IV metal halides and organotins have shown that amino acid coordination occurs through the amino nitrogen as a unidentate ligand in titanium and zirconium complexes, and as a bidentate ligand involving both amino nitrogen and carboxylate oxygen in tin complexes.[4] Tryptophan, $C_{11}H_{12}N_2O_2$, is a potentially multidentate ligand having indolyl nitrogen, amino nitrogen and carboxylate oxygens.

The ability of organotin halides to behave as Lewis acids is well known compared to tin pseudohalides. The complexes of some amino acids with triphenyltin showed antifungal activity on Aspergillus niger and Helminthosporium tanlosum.[5–8] The organotin fungicides are claimed to be better fungicides than the fungicides of the other metal ions because on degradation they do not leave any toxic residue.

In view of the multidentate behavior of tryptophan, coordination of tin(IV) moieties with biologically important ligands is of particular interest in medicine and agriculture.[8,9] In continuation of our work in the field of Group IV metal halides and organotin(IV) complexes of a variety of ligands,[10] we decided to investigate the coordinating behavior of tryptophan towards trimethyltin chloride and pseudohalides to explore the possibility of formation of a monomeric, polymeric or chelate complex so as to allow comparisons between the chloride and pseudohalide complexes.

This paper reports the synthesis and characterization based on spectroscopic stud-

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ies, elemental analyses and molar conductance measurements of the complexes of tryptophan with trimethyltin chloride, thiocyanate, azide, cyanide and isocyanate.

RESULTS AND DISCUSSION

All the complexes formed are in 1:1, metal:ligand molar ratio. The direct reaction of trimethyltin chloride with a stoichiometric amount of tryptophan in non-aqueous medium (acetone and methanol) produced the $Me_3SnCl.Tryp$ complex. The pseudohalide complexes of trimethyltin with tryptophan were prepared by synthesizing the pseudohalide in situ and then adding a stoichiometric amount of tryptophan to the reaction mixture. The methods used for the preparation, isolation and purification of the complexes gave complexes of high purity and high yield. Table I lists the analytical data of the complexes. The molar conductance values (Table I) of the complexes in DMSO of 10^{-3} M concentration show they do not ionize, although the slight conductivity may be either to some dissociation or to slight hydrolysis.

Infrared Spectra

The IR spectra of the complexes were recorded as KBr mulls. One of the most important features of the IR spectra (Table II) is found in the 3700–2200 cm^{-1} region, in which there appear N—H stretching vibrations of the indole at 3387vs and 3335m cm^{-1} and of the amino N—H groups at 3200m cm^{-1}. The assignment of these bands is confirmed by the fact that, although the ligand does not appear in the zwitterionic form, the NH of the amino group is involved in intermolecular hydrogen bonding with the carboxylate oxygens of the other ligand molecules, while the NH of the indole group is not involved with hydrogen bonds, as is shown in the crystal structure of the N-acetyl-L-tryptophan.[11] As the hydrogen bonding of the amino group is absent in the sodium salt, the ν(N—H) of the amino group is shifted to higher wave numbers (3280sh, b cm^{-1}), while the $\nu(N—H)_{indole}$ is unchanged with respect to the ligand. Since on complexation these bands do not change significantly in shape and position with respect to those of the sodium salt, we may exclude

TABLE I

Analytical data and some physical properties of the complexes

Complex	Color	m.p. °C	% C Found (Calc.)	% H Found (Calc.)	% N Found (Calc.)	% M Found (Calc.)	% X Found (Calc.)	Molar Conductivity (Ohm^{-1} cm^{-1} mol^{-1})
$Me_3SnCl.Tryp$ $Sn(C_{14}H_{21}O_2N_2)Cl$	Pale-white	300	41.60 (41.67)	4.99 (5.21)	6.91 (6.94)	29.40 (29.44)	8.75 (8.80)	25
$Me_3SnSCN.Tryp$ $Sn(C_{15}H_{21}O_2N_3S)$	Light-yellow	63	42.25 (42.28)	4.90 (4.93)	9.85 (9.87)	27.83 (27.88)	7.50 (7.52)	20
$Me_3SnN_3.Tryp$ $Sn(C_{14}H_{21}O_2N_5)$	Light-yellow	250	41.00 (41.01)	5.12 (5.13)	17.00 (17.09)	28.90 (28.97)	—	18
$Me_3SnCN.Tryp$ $Sn(C_{15}H_{21}O_2N_3)$	Yellow	275	45.70 (45.72)	5.29 (5.33)	10.60 (10.67)	30.00 (30.15)	—	17
$Me_3SnNCO.Tryp$ $Sn(C_{15}H_{21}O_3N_3)$	Yellow	58	43.92 (43.94)	5.12 (5.13)	10.21 (10.25)	28.90 (28.97)	—	19

TABLE II

Some characteristic IR bands of tryptophan and the complexes (cm^{-1})

Compound/Complex	$\nu(NH)_i$	$\nu(NH)_a$	$\nu(OCO)$	$\Delta\nu(CO_2)$	$\nu(Sn—CH_3)$	$\nu(Sn—O)$
Tryp	3387vs, 3335m	3200m	1710vs, 1235vs	475	—	—
Na.Tryp	3387vs, 3335m	3280sh, b	1588s, 1398s	190	—	—
Me_3SnCl.Tryp	3387s, 3335m	3275m	1630vs, 1403s	227	790s	450m
Me_3SnSCN.Tryp	3390s, 3337m	3280m	1610vs, 1388vs	222	770s	442m
Me_3SnN_3.Tryp	3390s, 3337s	3280m	1615vs, 1404vs	211	780s	440m
Me_3SnCN.Tryp	3386s, 3336m	3278m	1615vs, 1405vs	210	780s	445m
Me_3SnNCO.Tryp	3387s, 3336m	3280m	1620vs, 1404vs	216	775s	445m

vs = very strong, s = strong, m = medium, sh = shoulder, b = broad; i = indolyl and a = amino.

coordination of these groups to the metal atom. Therefore, the carboxylate group remains the only group of the ligand available for metal binding. Trends in the positions of and separation between antisymmetric and symmetric carboxylate stretching bands provide the most useful observation for assigning its coordination type.[12-14] The carboxylate group exhibits two frequencies at 1710 and 1235 cm^{-1} in tryptophan and in the sodium salt of tryptophan at 1588 and 1398 cm^{-1}.[11] The reported $\Delta\nu(\nu(OCO)_{as} - \nu(OCO)_{sym})$ of 190 cm^{-1} for the sodium salt shows the symmetric nature typical of the carboxylate ion. It may be assumed to typify the tryptophanate ion. In our adducts, $\Delta\nu$ of 210–227 cm^{-1}, which are significantly greater than those of the ionic ligand, may be attributed to the presence of inequivalent C—O bonds. This suggests that the carboxylate acts as an asymmetric bidentate or monodentate group coordinating covalently to tin.[15,16] The cyano complex exhibits a sharp C≡N stretching band at 2240 cm^{-1}. Two bands at 2250 and 2180 cm^{-1} in the spectrum of isocyanato complex are assigned to the ν antisymmetric stretch due to NCO group. The thiocyanato complex shows a ν_{as} (CN) stretch at 2119 cm^{-1}. The band due to C—S at 700 cm^{-1} is obscured by the ring vibrations of the ligand. A strong band at 2080 cm^{-1} assigned to the N=N=N asymmetric vibrations is observed in the azido complex. This band is close to that observed in covalent organic azides[17] but shifted to a higher frequency compared to ionic azides.[18,19] The symmetrical stretching of the N=N=N bond at 1286 cm^{-1}[20,21] could not be identified with certainty due to masking by other bands in this region.

The ν Sn—Me and ν Sn—O stretches are observed in the 770–790 cm^{-1} and 450–440 cm^{-1} region, respectively, in all the complexes. A strong band at 330 cm^{-1} is observed in the chloro-complex due to a Sn—Cl bond stretch. Presence of ν Sn—O stretch in the spectra of all the complexes further supports the coordination through carboxylate oxygens.

NMR Spectra

The NMR spectra of the complexes and the ligand are reported in Table III. Variations in the signals were observed for free and bound amino acid and organotin

TABLE III

Some α proton chemical shifts of tryptophan and the complexes

Compound/Complex	Proton Chemical Shift (ppm)		
	α CHCOO	Amino Proton	Sn—CH_3 Proton
Tryp	4.75s	6.21s	—
$Me_3SnCl.Tryp$	4.68s	6.33s	1.15s
$Me_3SnSCN.Tryp$	4.65s	6.45s	0.98s
$Me_3SnN_3.Tryp$	4.60s	6.41s	1.00s
$Me_3SnCN.Tryp$	4.65s	6.40s	0.99s
$Me_3SnNCO.Tryp$	4.67s	6.42s	0.99s

moieties. The chemical shift of the proton attached to carbon α to metal-bound carboxylate group shifts to a lower frequency in all these complexes compared to tryptophan. There is upfield movement of the resonance of protons attached to tin and amino nitrogen with respect to free organotin and amino acid. The other amino acid resonances are also affected by complexation. It was not possible to obtain accurate values for the chemical shifts of all the bound amino acid protons as their resonances give complex low intensity signals. Downfield movement of chemical shift for the α CHCOO proton on complexation suggests coordination through the carboxylate group[22] of the tryptophan. The upfield shift of the resonance of amino proton cannot be explained in terms of the difference in electronegativity because the drift of electrons would be towards oxygen resulting in the deshielding of the amino proton. It could be best explained by taking into consideration the electric field and the magnetic anisotropic effect due to carboxylate group. Most likely it is the magnetic anisotropy due to the carboxylate group that plays the dominant role. The upfield shift of protons closest to the coordinating ligand atom, with magnetic anisotropic effect is clearly stronger than those of the other protons. Therefore, the upfield shift of the amino protons shows that the carboxylate groups are directly involved in bonding to tin. The upfield movement of amino hydrogen resonances also rules out the participation of the indolyl ring nitrogen in coordination, in addition to the amino nitrogen. Bonding through indolyl nitrogen would have caused amino proton resonance shifts to downfield. Interaction with the amino acid also causes small but real shifts of δ of methyl protons attached to tin to upfields in all the complexes.

An octahedral structure is proposed for all the complexes where carboxylate group of the tryptophan binds covalently to tin as an asymmetric bidentate ligand. Figures 1 and 2 show the ligand and the proposed structures for the complexes.

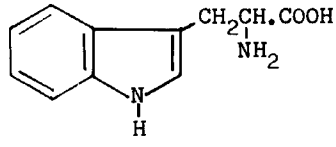
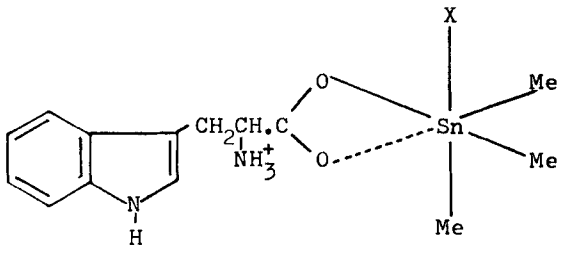


FIGURE 1 Tryptophan.



(X = Cl, SCN, N_3, CN or NCO and Me = CH_3)

FIGURE 2 Proposed structures of complexes.

EXPERIMENTAL

All reactions were carried out under dry oxygen-free nitrogen in a dry-box. All the reagents used were B.D.H. Analar grade and were used as such without further purification, except the pseudohalides which were prepared in the laboratory. The NMR and IR (200–4000 cm^{-1}) spectra were obtained using EM 360 L Varian ^1H NMR spectrometer and Perkin Elmer RB 31000 infrared spectrophotometer, respectively. Melting points were recorded on a Gallenkamp melting point apparatus. Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Coleman analyzer. The determinations of chloride and sulfur were done gravimetrically.[23] The molar conductances of the complexes were determined at 10^{-3} M concentration in DMSO using a Waynekerr universal conductivity bridge type B-221.

Preparations

With Trimethyltin Chloride

Tryptophan (0.510 g, 2.5 mmole) in 100 mL methanol was refluxed for four hours. Trimethyltin chloride (0.2 g, 1 mmole) in 50 mL acetone was added dropwise to the tryptophan solution with stirring. The reaction mixture was refluxed for four hours, then the solvent evaporated to about one third using a rotatory evaporator. After cooling to room temperature a white solid crystallized. The white solid was purified by washing with 20 mL methanol and 20 mL acetone in 10 mL aliquots and later by 10 mL of di-isopropyl ether. After purification it was isolated and dried in an oven at 110°C and then in a vacuum desiccator for 24 hours. The same procedure for purification and isolation was employed for the other complexes.

With Trimethyltin Thiocyanate

Trimethyltin chloride (0.488 g, 2.5 mmole) dissolved in 100 mL acetone was mixed ith potassium thiocyanate (0.238 g, 2.5 mmole) in 50 mL acetone, which resulted in a cloudy mixture. Tryptophan dissolved in 100 mL methanol, was refluxed for four hours and added slowly to the above mixture. The cloudiness disappeared immediately. The clear solution was stirred magnetically for three hours. The colorless solution gradually turned light yellow. A rotatory evaporator was used to remove the solvent under low pressure to nearly dryness when a yellowish solid was obtained which was dissolved in 100 mL acetone leaving a white residue. This white residue was filtered off. The filtrate was concentrated to one third by evaporating using a rotatory evaporator. A yellow sticky solid was obtained after purification and isolation. The procedure for purification and isolation of the complex was the same as employed for the trimethyltin complex. It was dried in an oven at 50°C for six hours and then in a vacuum desiccator for 24 hours.

With Trimethyltin Cyanate

Trimethyltin chloride (0.488 g, 2.5 mmole) in 100 mL acetone was mixed with potassium cyanate (0.199 g, 2.5 mmole) in 50 mL acetone and stirred magnetically for four hours. The mixture was filtered and to the filtrate was added tryptophan (0.5 g, 2.5 mmole) dissolved in 100 mL methanol and then refluxed for four hours. The colorless mixture gradually changed to yellow which deepened with time. The colored mixture was evaporated to one third and kept in a refrigerator for 12 hours after which yellow crystals appeared. After purification and isolation, the crystals were dried in a vacuum desiccator for 24 hours.

With Trimethyltin Azide or Cyanide

Sodium azide or cyanide (0.15 g or 0.12 g, 2.5 mmole) in 50 mL acetone was mixed with 2.5 mmole of trimethyltin chloride (0.488 g) in 50 mL acetone and the mixture stirred. The mixture was filtered and the filtrate mixed with 2.5 mmole of tryptophan (0.5 g) in 100 mL methanol dissolved by refluxing for four hours. This mixture was stirred magnetically for 24 hours at 250 or 275°C for azide or cyanide, respectively. After purification and isolation, the solid was dried in the oven at 110°C then in a vacuum desiccator for 24 hours.

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