Organotin Esters of *N*-Phthaloylamino Acids: Synthesis, Spectroscopic Characterization, and Biological Activities

Muhammad Ashfaq,* Abdul Majeed,† Abdul Rauf,†† Abdul Wahab Khan Khanzada,††† Wali Ullah Shah,††† and Muhammad Iqbal Ansari†††

Department of Chemistry, Gomal University, D. I. Khan, Pakistan

†Department of Chemistry, Islamia University, Bahawal Pur, Pakistan

††Department of Chemistry, B. Z. University, Multan, Pakistan

†††National Center of Excellence in Analytical Chemistry, Sindh University, Jamshoro, Pakistan

(Received October 26, 1998)

The synthesis, physical nature and spectroscopic characterization, i.e. CHN analyses as well as the IR, ^{1}H-, ^{13}C-, ^{119}Sn NMR and ^{119m}Sn Mössbauer spectrometries, of a series of new organotin complexes of *N*-phthaloylamino acids are described. The monomeric diorganotin complexes possess a trans octahedral geometry. The dimeric tetraorganotin complexes have a penta-coordinate environment. The triphenyltin with *N*-phthaloylamino acids are assigned a polymeric trigonal bipyramidal geometry in the solid form and a tetrahedral structure in an inert solvent, while tricyclohexyltin with *N*-phthaloylamino acids complexes possess a tetrahedral geometry. ED_{50} and biological activities tests were also carried out, which indicated powerful biocidal effects.

Organotin compounds cover a wide spectrum of uses, such as fungicides, pesticides, antifouling coating materials, PVC stabilizers, catalysts in polymer chemistry, precursors for forming SnO_2 films on glass, wood preservatives, and anti-tumours substances.[1—8] It was reported that diorganotin complexes with the derivatives of carboxylic acids, amino acids, fluorocarbons, purines, pyrimidines, and peptides show maximum antitumour activity, low mammalian toxicity, and less nephro-toxicity, unlike *cis*-platin.[4—7,9—11] As an extension of these studies, based on carboxylates and amino acid-containing compounds, we prepared and characterized a series of new organotin carboxylates. Bactericidal and fungicidal activity testes were carried out, revealing that they are powerful biocides. An ED_{50} (effective dose) test against brine shrimp larvae was also performed. The compounds prepared were: A-type monomeric diorganotin *N*-phthaloylamino acid, B-type dimeric tetraorganotin di-*N*-phthaloylamino acids, and C-type triorganotin *N*-phthaloylamino acid complexes.

Experimental

Materials: Phthalic anhydride, glycine, β-alanine, dibutyltin(IV) oxide, triphenyltin(IV) chloride, and tricyclohexyltin(IV) chloride were commercially available from Merck Chemicals Co., Ltd. and were used without further purification. The ligands were prepared according to a reported general procedure.[12] The A-, B-, and C-type complexes were prepared according to reported procedures.[4,7] They were soluble in chloroform and ethanol (on heating) and were insoluble in methanol and water.

Physical Measurements: The melting points were accurately measured on a Reichert thermometer of F. G. Bode Co. Austria, by taking a crystal of the compound. The results related to all of the physical data are given in Table 1. IR spectra were obtained in KBr pellets using a Perkin–Elmer FT IR-1605 spectrophotometer. Elemental analyses were performed on a Yanaco MT-3 high-speed CHN analyzer with an antipyrene as the reference compound. The ^{1}H-, ^{13}C-, and ^{119}Sn NMR spectra were recorded on a multinuclear FT NMR 90 MHz of JEOL EX-90 instrument using TMS as an internal standard. Some of the ^{13}C spectra were measured on a Bruker AM 270 instrument at 67.93 MHz and some of ^{119}Sn spec-

Table 1. Physical Data of Organotin Complexes

	Name of compounds	Physical state	Yield (%)	Melting point (°C)
A-1	$[SnBu_2\{C_6H_4(CO)_2NCH_2COO\}_2]$	Crystalline	91	208—210
A-2	$[SnBu_2\{C_6H_4(CO)_2NC_2H_4COO\}_2]$	Crystalline	89	122—125
B-1	$[\{C_6H_4(CO)_2NCH_2COOSnBu_2\}_2O]_2$	Crystalline	87	212—215
C-1	$[(C_6H_5)_3SnOCOCH_2N(CO)_2C_6H_4]$	Amorphous	81	85—90
C-2	$[(C_6H_5)_3SnOCOC_2H_4N(CO)_2C_6H_4]$	Amorphous	82	103—105
C-3	$[(C_6H_{11})_3SnOCOCH_2N(CO)_2C_6H_4]$	Amorphous	89	175—180
C-4	$[(C_6H_{11})_3SnOCOC_2H_4N(CO)_2C_6H_4]$	Amorphous	82	190—195

tra were recorded on a Bruker WM 500 instrument at 186.5 MHz. The ^{119m}Sn Mössbauer spectra were recorded on a V. G. Micromass 7070 F instrument at a temperature of 200 °C. ED_{50} of the complexes was determined against a brine shrimp hatching method[13] while bactericidal and fungicidal bioassays were performed by agar-well diffusion and agar-tube dilution methods.[14]

Results and Discussion

Spectral Studies of A-Type Monomeric Complexes: Elemental analyses verified the monomeric behavior of the complexes and showed linearity between the theoretical and experimental percentages of CHN. The results are given in Table 2. The important IR bands for both the ligands and complexes are given in Table 3. The OH broad band of the ligands disappeared in the complexes. Both asymmetric and symmetric stretching of the phthalimide group (C_2O_2N) were found at 1779—1774 cm^{-1} and 1728—1718 cm^{-1}. The ν_{asym} and ν_{sym} vibrations of the carbonyl (CO) group are stretched at 1671—1638 cm^{-1} and 1399—1270 cm^{-1}, respectively.[15] The ν_{asym} values were raised and the ν_{sym} values were lowered upon comparing using the values of the ligands, indicating unidentate asymmetrical bonding or weak bridging bidentate bonding of the carboxylic group with Sn(IV).[10,16,17] The Sn–O and Sn–C absorption bands are also displayed according to the literature.[18] All protons of A-type complexes were shifted, as reported in the literature.[19] The ^{1}H NMR data are given in Table 4. The butyl protons substituted on tin were resolved on their position which indicates one tin site, as reported.[4] Sharp ^{119}Sn NMR spectral signals were observed in the range −144 to −152 ppm, suggesting a five coordinate tin center.[20] The tin spectral data are summarized in Table 6. The ^{13}C NMR signals were properly resolved, and showed a signal for each butyl carbon around the tin atom. This confirmed the octahedral geometry of the complexes (Table 5). At the same time, the ^{119m}Sn Mössbauer spectra display quadrupole splitting values over the range of 3.38—3.53 mm s^{-1} (Table 6), which is greater than the 2.1 mm s^{-1} value recently reported by Sandhu and Kaur[21] for a *trans* octahedral geometry around tin atom monomeric diorganotin dicarboxylate complexes. Similarly, Gielen et al.[7] and Tiekink[22] reported on the geometry of A- type complexes that possess *trans* octahedral structure given in Chart 1.

Spectral Characterization of B-Type Complexes: The IR asymmetric and symmetric stretching of phthalimide (C_2O_2N) and carbonyl functional groups (CO) were found at the same position as that reported in the literature.[15] The assignment of Sn–C and Sn–O showed consistency with the reported values.[18] The ν_{asym} and ν_{sym} vibrations of the complex and the ligand were compared. B-1 exhibits bidentate symmetric bonding, since the ν_{asym} value is decreased and ν_{sym} is increased, while $\Delta\nu$ is also higher than the ligand's values.[18] The ^{1}H NMR spectra of a B-type complex also displayed resolution of protons at the proper position, which can be seen in Table 4. Their positions were verified according to the literature.[7,23,24] However, the butyl-substituted protons with Sn metal were shifted at 1.57—0.85 ppm. These protons remained in two unresolved sets of signals: One for butyl groups linked to *endo*-cyclic tin, and the other one for the *exo*-cyclic tin, respectively. This may be due to the fluxional behavior of carboxylate groups in the dimeric type of complexes.[4] The ^{13}C NMR spectra show pairs of signals deriving from two different butyl environments around the tin atoms. The ^{119}Sn NMR spectra give two signals at −198.51 and −207.45 ppm for the B-1 compound because of two unequal pentacoordinate tin sites.[7,25] They adopt a tetra dicarboxylato distannoxane structure.[4,26] Each tin atom from the two pairs of *exo*- and *endo*-cyclic tins is linked by a bidentate bridging *N*-phthaloyl carbox-

Table 2. Elemental Analyses of Organotin Complexes

Compounds	Analyses[a)]		
	C (%)	H (%)	N (%)
A-1	52.10 (52.40)	4.82 (4.68)	4.32 (4.37)
A-2	53.79 (53.82)	5.10 (5.08)	4.22 (4.21)
B-1	48.23 (48.56)	5.50 (5.43)	3.20 (3.16)
C-1	60.66 (60.67)	3.87 (3.81)	2.53 (2.54)
C-2	61.01 (61.05)	4.58 (4.56)	2.44 (2.45)
C-3	58.66 (58.76)	6.92 (6.82)	2.45 (2.46)
C-4	59.41 (59.49)	5.65 (5.64)	2.35 (2.39)

a) Calculated values are in parenthesis.

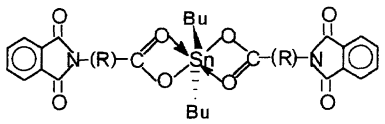


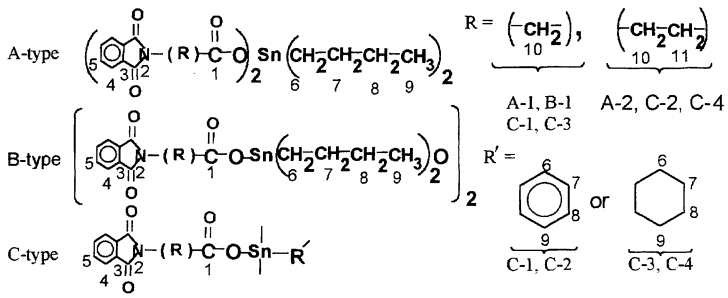
Chart 1. A-type complexes.

Table 3. IR Data (cm^{-1}) of Organotin Complexes

Compounds	Phthalamide (C_2O_2N)		Carbonyl (CO)		$\Delta\nu$	Sn–C	Sn–O
	(asym)	(sym)	(asym)	(sym)			
A-1	1774(s)	1726(s.sp)	1670(s.sp)	1270(m.sp)	400	532(w.sp)	504(s.sp)
A-2	1775(sp)	1728(s)	1671(s.sp)	1351(m.sp)	320	528(sp)	478(s.sp)
B-1	1778(s.sp)	1724(s.b)	1615(s.b)	1368(s.b)	217	528(sp)	479(s.sp)
C-1	1774(s)	1526(s.sp)	1592(s.sp)	1372(sp)	220	560(w)	534(w)
C-2	1774(s.sp)	1708(v.s)	1648(sp)	1396(v.s.sp)	252	542(sp)	503(w)
C-3	1772(sp)	1708(s.sp)	1661.9(s.sp)	1343.9(s.sp)	218	537(w)	504(s.sp)
C-4	1784(v.s.p)	1729(v.s.b)	1640(v.s.b)	1316(v.s.b)	324	548(sp)	527(sp)

where; s = strong, sp = sharp, b = broad, v = very, m = medium, w = weak.

Table 4. ^{1}H NMR of Organotin Complexes



Proton	A-1	A-2	B-1	C-1	C-2	C-3	C-4
3,4	7.8—7.73 (m)	7.89—7.62 (m)	7.85—7.60 (m)				
4,5				7.74—7.71 (m)	7.9—7.67 (m)	7.86—7.83 (m)	7.86—7.91 (m)
6,7[a)]	1.5—1.45 (b.m)	1.7—1.26 (b.m)	1.54—1.29 (b.m)				
6-9[a)]						1.71—1.42 (b.m)	1.61—1.31 (b.m)
7-9				7.43 (s)	7.41 (s)		
8,9	1.06—0.74 (m)	1.16—0.85 (b.m)	1.04—0.84 (m)				
10	4.22 (s)	2.68 (t.7,7)	4.19 (s)	5.01 (s)	4.02 (t.9,6)	3.67 (s)	3.9 (t.8,7)
11		4.01 (t.8,8)			2.87 (t.7,8)		2.77 (t.7,7)

where = m = multiplet, b = broad, s = singlet, t = triplet.
a) Protons are not resoluted due to the low resonance power of NMR (90 MHz).

Table 5. ^{13}C NMR Spectra of Organotin Complexes

Carbon[a)]	A-1	A-2	B-1	C-1	C-2	C-3	C-4
1	174.0	176.0	175.8	183.35	177.0	182.6	176.0
2	167.4	167.9	167.4	167.0	167.0	169.5	169.2
3	133.5	131.6	132.5	133.8	135.0	127.6	130.1
4	123.4	123.3	123.3	126.6	123.8	123.1	121.9
5	133.9	133.9	133.8	136.9	136.9	133.3	133.7
6	28.2	28.3	27.6	139.1	138.0	31.3	31.1
7	30.3	28.6	29.9	129.1	127.4	34.0	34.4
8	27.6	27.1	27.1	130.0	128.8		
9	13.6	13.7	13.4	136.3	133.6		
8,9						26.9/28.9	26.9/27.8
10	40.4	34.9	40.4	40.2	34.6	40.1	34.2
11		41.9			32.9		31.5

a) See structures in Table 4 for the numbering of carbon.

Table 6. ^{119}Sn Spectral Data of Organotin Complexes

Compounds	^{119}Sn NMR	^{119m}Sn Mössbauer				
		QS (mm s^{-1})	IS (mm s^{-1})	G_1 (mm s^{-1})	G_2 (mm s^{-1})	δ = QS/IS
A-1	−152					
A-2	−152.1	3.38	1.31	1.11	1.04	2.58
B-1	−198.51/−207.45	3.53	1.37	1.06	1.00	2.57
C-1	−115.1	3.41	1.59	0.82	0.81	2.1
C-2	−115.01	3.43	1.61	0.84	0.83	2.1
C-3	73.1	2.71	1.43	0.93	0.96	1.88
C-4	73	2.68	1.42	0.96	0.97	1.88

ylate ligand, while the remaining *N*-phthaloyl carboxylate groups behave as monodentate ligands with *exo*-cyclic tin atoms, as shown in Chart 2. On the basis of the ^{119m}Sn Mössbauer parameters, the large quadrupole splitting values

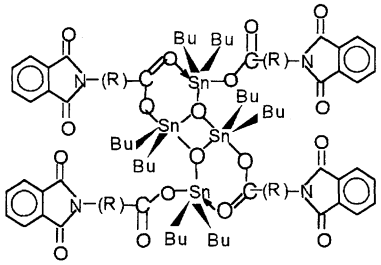


Chart 2. B-type complexes.

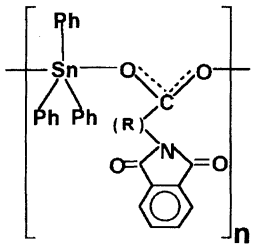


Chart 3. Polymeric trigonal bipyramidal geometry.

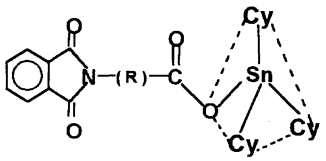


Chart 4. Tetrahedral geometry.

of QS = 3.53 mm s^{-1} for the B-1 complex recommends a penta coordinate environment around the tin atom, which strongly suggests the tetra organo dibutyl bis(*N*-phthaloyl-carboxylato distannoxane) structural mode.[26]

Spectral Studies C-Type Complexes: The percentage of CHN confirms the molar reaction between the ligand's salts and the triorganotin(IV) halides (Table 2). The IR stretching of phthalimide (C_2O_2N), carbonyl (CO), Sn–O, Sn–C is found at the same wavenumbers, as reported.[15,27] The $\Delta\nu$ of the carbonyl group of the C-2 and C-4 complexes are raised by 88—174 cm^{-1} compared to $\Delta\nu$ of the sodium salts of the ligands. At the same time, ν_{asym} is high and ν_{sym} is small compared to the ν_{asym} and ν_{sym} values of carbonyl (CO) of the salts, which indicates asymmetric or unidentate bonding to Sn(IV). However, in the case of the C-1 and C-3 complexes, ν_{asym} and ν_{sym} for carbonyl (CO) is small and large, respectively, at the same time $\Delta\nu$ of complexes other than sodium salts of the ligands is also small, which indicates bidentate bonding to Sn(IV).[28—30] The expected NMR signals were assigned based on their coupling pattern. All protons were properly shifted similarly to that reported in the literature.[31] Similarly, the ^{13}C spectra display the same resolution for each carbon as reported.[27] The ^{119}Sn NMR signals are seen over the range of −115.1 ppm, −115.01 ppm for triphenyl and 73 ppm, 73.1 ppm for the tricyclohexyl moieties bonded to Sn(IV) along with the respective ligands. Based on all these spectral lines and a literature study.[3,4,10,27,31,32] It is suggested that they have a four-coordinate tetrahedral geometry. A ^{119}Sn NMR spectral study strongly recommends a penta coordinate environment around the tin atom, which suggests that the C-1 and C-2 complexes with triphenyl moieties proposed a polymeric trigonal bipyramidal in the solid form and a tetrahedral geometry in a non-coordinating solvent,[33] while compounds with tricyclohexyl moieties i.e. C-3 and C-4 show a tetrahedral geometry in the solid form as well as in solution.[33] Their structures are displayed in Charts 3 and 4, respectively. The ^{119m}Sn Mössbauer spectra of triphenyltin *N*-phthaloylglycinate (C-1) and triphenyltin *N*-phthaloyl-β-alaninate (C-2) exhibit quadrupole splitting values of 3.41 mm s^{-1} and 3.43 mm^{-1}, respectively (Table 6). According to a literature study,[4,34,35] complexes with a QS of 3.59—3.70 mm s^{-1} have a five-coordinate chain structure; at the same time, Danish et al. have reported[4] that complexes with QS 3.39 mm s^{-1} display a trigonal bipyramidal geometry with a bridging carboxylate group in the solid form and a tetrahedral geometry in an inert solvent, where δ = QS/IS also supports the same geometry.[4,33] Also, the QS values of tricyclohexyltin *N*-phthaloylglycinate and tricyclohexyltin *N*-phthaloyl-β-alaninate (C-3,C-4) also advocate the tetrahedral geometry.[4]

Biological Activities: ED_{50} (effective dose) measurements of A-1, A-2, and B-1 complexes were carried out against brine shrimp larvae according to the standard procedure (Table 7).[14] The A-2 complex was found to be more effective to the larvae. The ED_{50} values of the C-1, C-2, C-3, and C-4 compounds fall in a very narrow range of 3.37 to 0.004 $\mu g\,cm^{-3}$, which shows the highest effect against shrimp nauplii. The literature study also indicates that those tin complexes with triphenyl and tricyclohexyl moieties having a partition co-efficient greater than a factor of one, show the highest effect towards toxicity.[6] Both bactericidal and fungicidal bioassays were carried out against a variety of bacteria and fungi using agar-well diffusion and agar-tube dilution methods.[37] The A-1, A-2, B-1, and B-2 complexes totally inhibit the growth of various bacteria and fungi, while the C-type complexes exhibit, themselves, powerful biocides towards bacteria and fungi. The results are described in Tables 8 and 9. It is well established that triorganotin compounds are significantly active biocides compared other classes of complexes.[6] Moreover, any biological activity of organotin compounds is associated with the attached R group to the tin atom, whereas mono organotins have no appreciable activity. In the R_3SnL unit, the function of L plays a key role in transporting the active organotin moiety to an action site, which is released by hydrolysis.[6] Among the organotin compounds, the carboxylates derivatives are used as anticancer and antitumour agents in vivo and in vitro as well as fungicides or bactericides.[36—41] Because the biocidal activity of triorganotin carboxlates is due to the geometry of species produced in solution, the tetrahedral structure in solution is more active.[6] The triorganotin carboxylate may adopt three possible geometric shapes in the solid phase, i.e. tetrahedral, trigonal bipyramidal and the five-coordinate chelate type.[42] The former two kinds are more active than later one, since besides the 4-coordinate monomer, the polymeric 5-coordinate species is rapidly converted into a

Table 7. Brine Shrimp Bioassay of Organotin Complexes

Compounds	% Deaths at doses			ED_{50}	Results
	1000 μg ml^{-1}	100 μg ml^{-1}	10 μg ml^{-1}	μg ml^{-1}	
A-1	60	20	10	616.77	+
A-2	90	50	40	104.22	+++
B-1	40	30	20	6920.9	—
C-1	100	100	70	3.37	++++
C-2	100	100	70	3.37	++++
C-3	100	90	90	0.008	++++
C-4	100	100	90	0.004	++++

where: +++ = significant, ++++ = more significant, — = no activity.

Table 8. Bactericidal Bioassay of Organotin Complexes

Name of bacteria	Activity[a)]						
	A-1	A-2	B-1	C-1	C-2	C-3	C-4
Human pathogens: Bacillus cereus	++++	++++	++++	++++	++++	++++	++++
Cornye bacterium diphtheriae	++	++	++	++++	++++	++++	++++
Escherichia coli ETEC.	++	++	++	++++	++++	++++	++++
Klebsiella pneumoniae	—	—	—	++++	++++	++++	++++
Salmonella typhi	+	+	—	++++	++++	++++	++++
Staphylococcus aureus	++	+++	++	++++	++++	++++	++++
Shigella boydii	—	—	—	—	—	—	—
Pseudomons aeroginosa	—	—	—	—	—	—	—
Proteus mirabillis	—	—	—	—	—	—	—
Streptococcus pyogenes	++++	++++	++++	++++	++++	++++	++++

a) ++++ = highest, +++ = high, ++ = optimum, +, — = no activity.
Incubation period: 8 h., 37 °C, Colony forming unit = 10^4—10^6, Size of well = 5 mm radius.
Reference Drug: Amoxicillin (H_2O), Ampicillin (H_2O), Cepholexin Na.

Table 9. Fungicidal Bioassay of Organotin Complexes

Name of fungi	Activity[a)]						
	A-1	A-2	B-1	C-1	C-2	C-3	C-4
Human pathogens:[b)] Aspergillus flame	—	—	—	++	+++	++++	++++
Trichophyton schoenlem	++++	++++	++++	++++	++++	++++	++++
Pseudallescheria boydii	++	++	++	+++	++++	++++	++++
Candida albicans	+	+	+	—	—	—	—
Aspergillus niger[c)]	+	+	+	++++	++++	++++	++++
Animal pathogens:[b)] Microsporum canis	—	—	—	—	—	—	—
Trichophyton manaegrophytes	—	—	—	—	—	—	—
Trichophyton rubrum	—	—	—	—	—	—	—
Trichophyton	+	+	+	++++	++++	++++	++++
Plant pathogens:[d)]	—	—	—	—	—	+++	+++
Fusanum oxysponumvarlyco Persici							
Fusanum solanivarlycopersici	—	—	—	—	—	+++	+++
Macrophormina phaseolina	—	—	—	—	—	++	++
Rhizoctonia solani	—	—	—	—	—	++	++

a) ++++ = highest, +++ = high, ++ = optimum, +, — = no activity.
Incubation time = 7 h., 27 °C.
Reference Drug : b) Miconazole, Ketoconazole, c) Amphotenicin-B, Flycytosine, d) Benlate, Nabam.

monomeric tetrahedral by intermolcular fragmentation.[23] On the other hand, the chelated monomers retain their 5-coordinate structure in solution, which is evidented by the reported NMR spectral data.[6,24] Davies et al. have reported[43] that the 4-coordinate moiety has a strong tendency to increase the coordination number to more than four by interactions with O, S, or N donor molecules while the 5-coordinate species do not undergo further complexations, which play no long-term role in the vivo chemistry of organotin.[6,44] It has been reported that[4] polymeric arrangements are rapidly converted into monomeric tetrahedral frame. On the other hand, the chelated monomers retain their five-coordinate skeleton even in solution. The C-1 and C-2 compounds display high activity against bacteria and fungi.

References

1 B. Jousseaume, V. Guillou, N. Noiret, M. Pereyre, and J. M. France, *J. Organomet. Chem.*, **450**, 97 (1993); V. L. Narayanan, in "Structure Activity Relationships of Antitumor Agents," ed by D. N. Reinhoudt, T. A. Connors, H. M. Pinedo, and K. W. Van de Poll, Martinus Nijhoff, The Hague (1983).

2 A. Kumari, I. Sing, and J. P. Tandon, *Main Group Met. Chem.*, **17**, 347 (1994).

3 M. Gielen, *Met.-Based Drugs*, **2**, 99 (1995).

4 M. Danish, Alt. G. Helmult, A. Badshah, S. Ali, M. Mazhar, and N. Islam, *J. Organomet. Chem.*, **486**, 51 (1995).

5 K. R. S. Ascher, *Phytoparasitica*, **7**, 17 (1979); N. Isono and M. Mori, *Main Group Met. Chem.*, **19**, 277 (1996).

6 K. C. Molloy, "Bioorganotin Compounds," in "The Chemistry of Metal–Carbon Bond," ed by Fr. Hartley, John Willey and Sons Ltd., New York (1989), Vol. 5, pp. 405—533.

7 M. Gielen, A. E. L. C. Khloufi, M. Biesemans, F. Kayser, and R. Willem, *Appl. Organomet. Chem.*, **7**, 201 (1993).

8 M. Gielen, F. Kayser, O. B. Zhidkova, V. Ts. Kempel, V. I. Bregadze, D. de. Vos, M. Biesemans, B. Mahieu, and R. Willem, *Met.-Based Drugs.*, **2**, 37 (1995).

9 F. Huber, G. Roge, L. Carl, G. Attassi, F. Spreafico, S. Filipeschi, R. Barbieri, A. Silvestri, E. Riverola, G. Ruisi, F. Di. Bianca, and G. Alonzo, *J. Chem. Soc., Dalton Trans.*, **1985**, 523.

10 R. Barbieri, L. Pellerito, G. Ruisi, M. T. Lo Giudice, F. Huber, and G. Attassi, *Inorg. Chim. Acta*, **66**, L39 (1982).

11 G. K. Sandhu, R. Gupta, S. S. Sandhu, R. V. Parish, and K. Brown, *J. Organomet. Chem.*, **279**, 373 (1985).

12 B. Furniss, A. J. Hannaford, P. W. G. Smith, and A. R. Tatchell, "Vogel's Text Book of Practical Organic Chemistry," 5th ed, ELBS Longman Group, U. K. (1989), p. 1281.

13 B. N. Meyer, N. R. Ferrigni, J. E. Putnam, L. B. Jacobsen, D. E. Nicholas, and J. L. Mc. Laughlin, *J. Planta Medica*, **45**, 31 (1982).

14 S. U. Kazmi, S. N. Ali, S. A. Jamal, and Atta-ur-Rehman, *J. Pharm. Sci.*, **4**, 113 (1991).

15 D. L. Pavia, G. M. Loupam, and G. S. Kriz, "Introduction to Spectrscopy," Sander Golden, Sunhurst Series, Saunder College of Philadelphia (1979), p. 100.

16 R. J. Orsler and G. E. Holland, *Int. Biodeterior. Bull.*, **18**, 95 (1982).

17 D. Barug, *Chemosphere*, **10**, 1145 (1981).

18 G. K. Sandhu and S. P. Verma, *Polyhedron*, **6**, 587 (1987).

19 J. D. Thornton and O. Collett, *Mater. Org.*, **14**, 131 (1979).

20 J. Holecek, K. Handlir, M. Nadvornik, and A. Lycka, *J. Organomet. Chem.*, **315**, 299 (1986).

21 G. K. Sandhu and G. Kaur, *Main Group Met. Chem.*, **13**, 149 (1990).

22 E. R. T. Tiekink, *J. Organomet. Chem.*, **408**, 323 (1991).

23 M. Gielen, T. Mancilla, J. Rambarter, and R. Willem, *J. Organomet. Chem.*, **328**, 61 (1987).

24 M. Gielen, A. El. Khloufi, M. Biesemans, M. Mahieu, and R. Willem, *Bull. Soc. Chim. Belg.*, **101**, 243 (1992).

25 H. K. Sharma, S. Lata, K. k. Sharma, K. C. Molloy, and P. C. W. Field, *J. Organomet. Chem.*, **353**, 9 (1988).

26 C. Vatsa, V. K. Jain, T. Kesavadas, and E. R. T. Tiekink, *J. Organomet. Chem.*, **408**, 157 (1991).

27 "Sadtler Standard Spectra," Midgot Edition, Sadtler Research Laboratories Philadelphia 2, Penna, U. S. A., Sp., Nos. 39, 281, 388, 343, 344, 417, 1962.

28 A. Sexena, F. Huber, L. Pellerito, A. Girasolo, and G. C. Stocco, *Inorg. Chim. Acta*, **125**, 197 (1986).

29 G. K. Sandhu, G. Kaur, J. Holecek, and L. Lycka, *J. Organomet. Chem.*, **345**, 51 (1988).

30 W. D. Honnick and J. J. Zukerman, *J. Organomet. Chem.*, **178**, 133 (1979).

31 B. D. P. Hollis, L. F. Johnson, and E. A. Pier, "^{1}H NMR. Spectra Catalog," Copyright Varian Associates, Vol. 2, Sp. Nos. 533, 534, 1963.

32 T. P. Lockhart, W. F. Manders, and J. J. Zukerman, *J. Am. Chem. Soc.*, **107**, 4546 (1985).

33 S. W. Ng and V. G. Kumar Das, *J. Organomet. Chem.*, **409**, 143 (1991).

34 A. Lycka, J. Jirman, A. Kolonicny, and J. Holecek, *J. Organomet. Chem.*, **333**, 305 (1987).

35 P. J. Smith, R. O. Day, V. Chandrasekhar, J. M. Holmes, and R. R. Holmes, *Inorg. Chem.*, **25**, 2495 (1986).

36 N. F. Cardarelli, "Tin as Vital Nutrient," 1st ed, CRC Press Inc., Boca Raton, Florida (1986).

37 I. Omae, *J. Organomet. Chem.*, Elsevier, New York (1986).

38 M. T. Musmeci, G. Madonia, M. T. L. Guidice, A Silvestri, G. Ruisi, and R. Barbieri, *Appl. Organomet. Chem.*, **6**, 127 (1992).

39 M. Baulam, M. Biesemans, J. M. Piret, R. Willem, and M. Gielen, *Appl. Organomet. Chem.*, **6**, 197 (1992).

40 J. M. Hook, B. M. Linahan, R. L. Taylor, E. R. T. Tiekink, L. Van Gorkom, and L. K. Webster, *Main Group Met. Chem.*, **17**, 293 (1994).

41 S. W. Ng, A. J. Kuthbutheen, V. G. K. Das, A. Lindens, and E. R. T. Tiekink, *Appl. Organomet. Chem.*, **8**, 37 (1994).

42 K. C. Molloy, K. Quill, and I. W. Nowell, *J. Chem. Soc., Dalton. Trans.*, **1987**, 101.

43 A. G. Davies, J. P. Goddard, M. B. Hursthouse, and N. P. C. Walker, *J. Chem. Soc., Chem. Commun.*, **1983**, 597.

44 A. G. Davies and P. J. Smith, in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford (1982), p. 608.