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Synthesis, Spectral Characterization and Biological Applications of Tri- and Diorganotin(IV) Derivatives of 2-[N-(2,6-Dichloro-3-methylphenyl)amino]benzoic acid

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A series of tri- and diorganotin(IV) compounds with the general formulae R_3SnL and R_2SnL_2 (where R = Me, n-Bu, Ph and L = 2-[N-(2,6-dichloro-3-methylphenyl)-amino]benzoate) were synthesized. These compounds were characterized by different instrumental methods such as infrared, multinuclear NMR (^1H, ^{13}C, ^{119}Sn) and mass spectrometry. The spectroscopic investigation illustrates that the carboxylate group acts as a bidentate in solid state and as a monodentate in solution. Biological screening tests reveal that the investigated compounds have potential as antibacterial agents.

Introduction

There have been several reports dealing with the impact of organotin chemistry in the biosphere[1,2]. Organotin compounds show a large spectrum of biological activity but mainly are used commercially as industrial and agricultural biocides because of their antifungal properties[3]. Some organotins are currently being investigated for antitumur activity[4]. Some R_3SnL derivatives (L = monodentate or bidentate ligand) are highly toxic[5−10], while diorganotin(IV) derivatives like diethyltin(IV) and dibutyltin(IV) carboxylates are known antitumur agents[11−14]. Previously, we synthesized and characterized various organotin(IV) derivatives of donor ligands[15−17]. We have also reported their structural chemistry[18−21] as well as some of their biological applications[22−24]. In this paper we report the synthesis, spectroscopic characterization (multinuclear NMR, IR and mass) and biological activity of organotin(IV) derivatives of 2-[N-(2,6-dichloro-3-methylphenyl)amino]benzoic acid (HL), commonly known as meclofenamic acid (Figure 1), one of the most frequently used analgesic and anti-inflammatory drugs.

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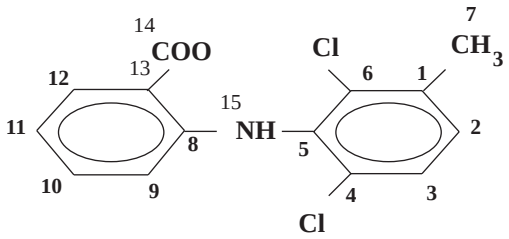


Figure 1. Numbering scheme and structure of 2-[N-(2,6-dichloro-3-methylphenyl)-amino]benzoic acid.

Results and Discussion

Infrared Spectroscopy

The IR spectra of tri- and diorganotin(IV) derivatives were recorded in solid state as KBr disks in the range 4000-250 cm^{-1}. The important absorption bands for the structural assignments are given in Tables 1 and 2. The type of coordination of the carboxylate group is decided on the basis of separation ($\Delta\nu$) of the νCOO_{asym} and νCOO_{sym}, band. If $\Delta\nu$ is > 240, the carboxylate is acting as a monodentate, otherwise it is bidentate[25]. The bands in the range 605 $\pm$ 20 cm^{-1} and 480 $\pm$ 20 cm^{-1} in particular indicate the presence of Sn–C and Sn–O bonds, respectively. The absence of Sn–Cl at ca. 330 cm^{-1} further consolidates the formation of organotin(IV) carboxylates.

Table 1. Physical data of organotin(IV) 2-[N-(2,6-dichloro-3-methylphenyl) amino]benzoate.

No.	Compound	Molecular formula and weight	M.p. (°C) (% Yield)	% C Found (calcd.)	% H Found (calcd.)	% N Found (calcd.)
	LNa	$C_{14}H_{11}Cl_2O_2NNa$-H_2O 319	289-91 (–)	–	–	–
I	Me_3SnL	$C_{17}H_{19}Cl_2O_2NSn$ 459	138-40 (78)	44.62 (44.44)	4.22 (4.14)	3.21 (3.05)
II	Ph_3SnL	$C_{32}H_{25}Cl_2O_2NSn$ 645	148-50 (80)	59.80 (59.53)	3.91 (3.88)	2.31 (2.17)
III	Me_2SnL_2	$C_{30}H_{26}Cl_4O_4N_2Sn$ 739	156-8 (78)	48.89 (48.71)	3.70 (3.52)	3.72 (3.79)
IV	Et_2SnL_2	$C_{32}H_{30}Cl_4O_4N_2Sn$ 767	141-2 (74)	49.97 (50.06)	4.02 (3.91)	3.49 (3.65)
V	Bu_2SnL_2	$C_{36}H_{38}Cl_4O_4N_2Sn$ 823	81-3 (77)	52.55 (52.49)	4.70 (4.62)	3.32 (3.40)
VI	Ph_2SnL_2	$C_{40}H_{30}Cl_4O_4N_2Sn$ 863	117-9 (75)	55.77 (55.62)	3.56 (3.48)	3.33 (3.24)

Mass Spectrometry

The mass spectral data for tri- and diorganotin(IV) derivatives are given in Tables 3 and 4. In organotin compounds, the molecular ion peaks are usually not observed or are sometimes present with very low intensities[26]. In the present series similar results are observed for molecular ion peaks. The fragmentation pattern of triorganotin(IV) 2-[N-(2,6-dichloro-3-methylphenyl)amino]benzoate (Scheme 1) appeared due to the loss of ligand and the subsequent stepwise removal of alkyl groups. As an alternate route, alkyl groups

are gradually eliminated in the primary fragmentation pattern, which is followed by the removal of the CO_2 molecule from the ligand attached to the tin atom. On further fragmentation the remaining ligand group is evolved to give Sn^+/SnH^+.

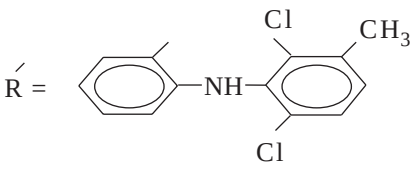
The fragmentation of diorganotin(IV) derivatives passes through different routes (Scheme 2). The primary fragmentation is proposed as the removal of CO_2 from 1 of the ligands and 2 alkyl/aryl (R) groups and then ligands to give Sn^+/SnH^+. Another route is the loss of an alkyl/aryl group first and then of 2 CO_2 molecules in successive steps from the 2 ligands, which is followed by the removal of the remaining ligand to give Sn^+/SnH^+ as the end product. There is also a third route of fragmentation, in which CO_2 is removed in a first step, followed by the removal of a ligand and lastly the elimination of 2 alkyl/aryl groups to give Sn^+/SnH^+.

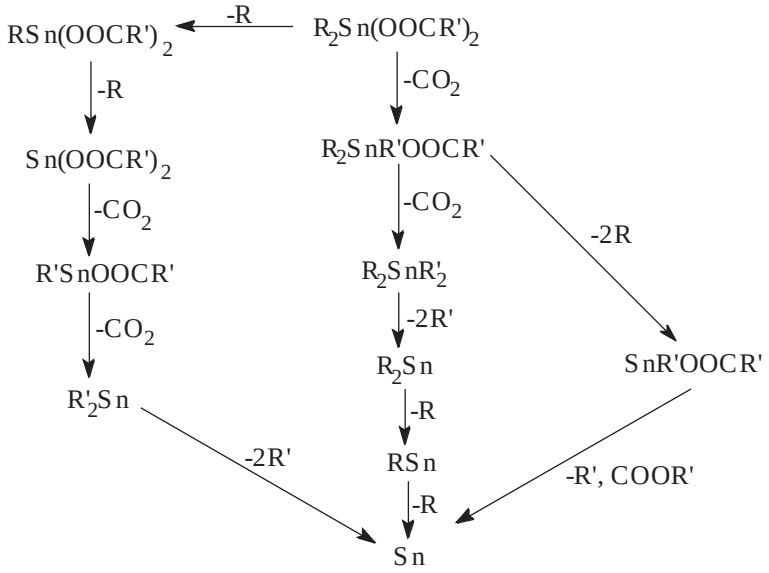
Table 2. Infrared data (cm^{-1}) of organotin(IV) 2-[N-(2,6-dichloro-3-methyl-phenyl)amino]benzoate.

Compound	ν $(COO)_{asym}$	ν $(COO)_{sym}$	$\Delta\nu$	ν (Sn-C)	ν (Sn-O)
LNa	1680	1330	350	–	–
I	1605	1397	208	604	498
II	1600	1404	196	582	482
III	1615	1407	208	586	487
IV	1597	1391	206	591	562
V	1603	1408	195	608	469
VI	1610	1406	204	602	508

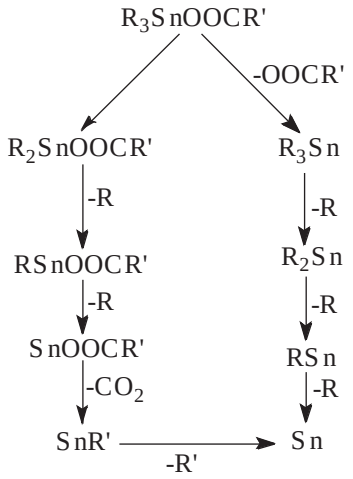
Table 3. Fragmentation pattern of triorganotin(IV) 2-[N-(2,6-dichloro-3-methylphenyl)amino]benzoate.

Fragment	I Me_3SnL (m/z)	Intensity (%)	II Ph_3SnL(m/z)	Intensity (%)
$[R_3SnOCOR']^+$	459	(n.o.)	645	3
$[R_2SnOCOR']^+$	444	10	568	10
$[SnOCOR']^+$	414	5	414	(n.o.)
$[R_2SnR']^+$	400	10	524	20
$[RSnR']^+$	385	(n.o.)	447	20
$[R_3Sn]^+$	165	10	351	55
$[R_2Sn]^+$	150	4	274	5
$[RSn]^+$	135	2	197	25
$[Sn/SnH]^+$	121	6	121	9
LH	294	20	294	18
$[SnOCOC_6H_5\ ]^+$	241	100	241	100
$[R]^+$	15	(n.o.)	77	11





Scheme 1. General fragmentation pattern for $R_2Sn(OOCR')_2$.



Scheme 2. General fragmentation pattern for $R_3SnOOCR'$.

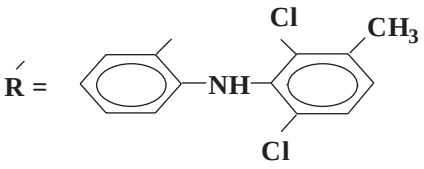
^{1}H NMR Spectroscopy

The ^{1}H NMR spectral data of tri- and diorganotin(IV) 2-[N-(2,6-dichloro-3-methyl-phenyl)amino]benzoate are given in Table 5. These data provide information on the nuclear spin multiplicity, chemical shifts and chemical equivalence of protons in the structures.

The protons of the benzoic ring are assigned as downfield due to the presence of the carbonyl (C=O) group. Protons 2 and 3 give doublets, whereas protons 7 appear as a singlet. Protons 9-12 show certain multiplets due to their complex coupling pattern. Proton 15 is the pecularity of the N–H position in the ligand. The assigned values were invariably present in the organotin(IV) derivatives of 2-[N-(2,6-dichloro-3-methylphenyl)amino] benzoic acid. The prediction of geometry can be proposed by the $^2J[^{119}Sn, ^1H]$ coupling. Such couplings are not observed in *n*-Bu derivatives due to the overlap of the signals. However, in Me and Ph derivatives $^nJ[^{119}Sn, ^1H]$ were observed. The results are given in Table 5.

Table 4. Fragmentation pattern of diorganotin(IV) 2-[N-(2,6-dichloro-3-methylphenyl)amino]benzoate.

Fragment	III Me_2SnL_2 (m/z)	Intensity (%)	IV Et_2SnL_2 (m/z)	Intensity (%)	V Bu_2SnL_2 (m/z)	Intensity (%)	VI Ph_2SnL_2 (m/z)	Intensity (%)
$[R_2Sn(OCOR')_2]^+$	738	(n.o.)	766	(n.o.)	822	5	862	10
$[RSn(OCOR')_2]^+$	723	10	737	60	765	10	785	25
$[R_2SnOCOR']^+$	444	90	472	35	528	10	568	18
$[R_2SnR']^+$	400	35	428	5	484	23	524	5
$[RSnR']^+$	385	(n.o.)	399	5	427	(n.o.)	447	23
$[SnR']^+$	370	15	370	13	370	10	370	5
$[R_2Sn]^+$	150	5	178	10	234	5	274	(n.o.)
$[RSn]^+$	135	15	149	10	177	10	197	5
$[Sn/SnH]^+$	121	10	121	5	121	5	121	8
L H	294	40	294	38	294	40	294	50
$[SnOCOC_6H_5\ ]^+$	241	100	241	100	241	100	241	100
$[R]^+$	15	(n.o.)	29	(n.o.)	57	12	77	10



^{13}C NMR Spectroscopy

^{13}C NMR data for the investigated compounds are given in Table 6. In 2-[N-(2,6-dichloro-3-methylphenyl) amino]benzoate there are 2 phenyl rings. Therefore, a certain overlap of the values was observed for ^{13}C NMR signals. In the case of diphenyl and triphenyl species the region became more condensed; however, comparison of the precursors spectra and the incremental method[27] helped us to assign the signals. The carbonyl (C=O) group appeared in a specific low field region. The C–Sn–C angles were calculated with literature methods[28,29] and they suggested that triorganotin(IV) 2-[N-(2,6-dichloro-3-methylphenyl)amino]benzoate had a pseudotetrahedral geometry. However, in the case of diorganotin(IV) 2-[N-(2,6-dichloro-3-methylphenyl)amino]benzoate a C–Sn–C bond angle indicated a the coordination number higher than 4 in non-coordinateling solvents ($CDCl_3$). The^{13}C NMR spectra of organotin(IV) derivatives of 2-[N-(2,6-dichloro-3-methylphenyl)amino] benzoate helped us to obtain the skeletal information of the structures.

^{119}Sn NMR Spectroscopy

The chemical shifts, δ^{119}Sn, of the organotin(IV) derivative were taken in $CDCl_3$, a non-coordinating solvent. The values obtained for the tri- and diorganotin(IV) derivatives are given in Table 7. Trimethyl and triphenyltin(IV) derivatives have δ values of 137 and 113, respectively, which indicated a tetrahedral geometry around tin in these compounds[30−32]. In diorganotin(IV) compounds δ values are -113, -115, -144 and –149, showing the hexa coordinated geometry around the tin atom[26,30,33−35].

Table 5. ^{1}H NMR data of organotin(IV) 2-[N-(2,6-dichloro-3-methyl-phenyl)amino]benzoate^{a,b}.

Proton	LNa	I Me_3SnL	II Ph_3SnL	III Me_2SnL_2	IV Et_2SnL_2	V Bu_2SnL_2	VI Ph_2SnL_2
2	6.21 (d 8.0)	6.31 (d 8.0)	6.37 (d 8.0)	6.35 (d 8.0)	6.33 (d 8.0)	6.39 (d 8.5)	6.34 (d 8.5)
3	7.1 (d 7.5)	7.08 (d 7.5)	7.12 (d 7.5)	7.2 (d 7.5)	7.22 (d 7.5)	7.15 (d 7.5)	7.04 (d 7.6)
7	1.9 (s)	2.39 (s)	2.44 (s)	1.87 (s)	1.87 (s)	1.85 (s)	2.26 (s)
9	6.75 (d 7.56)	6.74 (d 7.56)	6.82 (d 7.56)	6.84 (d 7.5)	6.84 (d 7.5)	6.86 (d 7.5)	6.79 (d 7.5)
10	7.31 (m)	7.25 (m)	7.29 (m)	7.36 (m)	7.36 (m)	7.39 (m)	7.36 (m)
11	7.27 (m)	7.21 (m)	8.17 (m)	7.21 (m)	7.2 (m)	7.32 (m)	7.29 (m)
12	8.15 (d d 7.0,1.7)	8.04 (d d 7.0,1.7)	8.17 (d d 7.0,1.7)	8.25 (d d 7.5,2.4)	8.25 (d d 7.4,2.5)	8.22 (d d 7.5,2.5)	8.16 (d d 7.0,2.2)
15	9.62 (s)	9.53 (s)	9.58 (s)	9.34 (s)	9.31 (s)	9.34 (s)	9.26 (s)
α	-	0.69 (s) ^{2}J[58.5]	-	1.2 (s) ^{2}J[80.0]	1.38 (t) ^{2}J[61.5]	1.87 (m) ^{2}J[63.5]	-
β	-	-	7.96 (m) ^{3}J[59.8]	-	1.38 (d) ^{3}J[13]	1.45 (m) ^{3}J[11]	7.98 (m) ^{3}J[76.3]
γ	-	-	7.49 (m) ^{4}J[6.5]	-	-	-	7.7 (m) ^{4}J[n.o.]
δ	-	-	7.84 (m) ^{5}J[n.o.]	-	-	0.91 (m) ^{5}J[13]	7.5 (m) ^{5}J[n.o.]

a) chemical shift (δ) in ppm $^{n}J[^{117/119}$Sn, H] in Hz, b) multiplicity is given as s = singlet, d = doublet, t = triplet, m = multiplet, n.o. = not observed.

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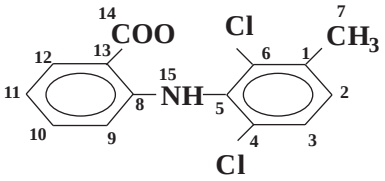

Biological Activity

A number of screening tests [antibacterial (Gram positive and Gram negative) and antifungal] were carried out for the investigated compounds in order to find their potential and applications in biological fields; the results are reported in Tables 8-10.

In general, triorganotin(IV) derivatives (compounds I and II) are more effective against the pathogens of Gram-positive and Gram-negative bacteria (Tables 8 and 9) and various fungi (Table 10). Diorganotin(IV) compounds are comparatively less effective than triorganotin(IV) derivatives, as shown by the results in Tables 8-10.

Table 6. ^{13}C NMR data of organotin(IV) 2-[N-(2,6-dichloro-3-methyl-phenyl)amino]benzoate[a].

Carbon	LNa	I Me_3SnL	II Ph_3SnL	III Me_2SnL_2	IV Et_2SnL_2	V Bu_2SnL_2	VI Ph_2SnL_2
1	135.9	136.2	136.2	135.8	135.9	135.9	136.0
2	128.1	128.0	128.0	128.1	128.1	128.1	128.2
3	128.8	128.5	128.5	128.8	128.8	128.8	128.8
4	131.7	131.5	131.5	131.6	131.7	131.7	131.6
5	136.7	136.7	136.7	136.8	136.7	136.8	136.4
6	134.5	134.5	134.5	134.9	134.5	134.9	134.9
7	21.0	21.0	21.0	21.1	21.0	21.0	20.6
8	148.0	147.5	147.5	148.0	148.0	148.0	148.0
9	114.0	114.1	114.1	114.1	114.0	114.0	114.1
10	134.7	133.6	133.6	134.6	134.7	134.7	134.5
11	117.8	117.6	117.6	117.9	117.8	117.4	117.4
12	133.5	133.0	133.0	133.5	133.5	132.9	134.5
13	112.2	113.9	112.6	112.2	112.2	112.2	110.6
14	177.8	173.7	174.0	177.7	177.8	177.6	176.0
α	-	1.67 ^1J[399, 378]	139.0 ^1J[410.5]	0.61 ^1J[567.4]	18.8 ^1J[531.5]	26.1 ^1J[517.4]	136.9 ^1J[n.o.]
β	-	-	136.8	-	13.4	27.1	135.5
γ	-	-	129.2	-	-	-	129.0
δ	-	-	130.5	-	-	14	130.7
a) chemical shift (δ) in ppm, $^1J[\ ^{117/119}$Sn-^{13}C] in Hz., n.o. = not observed							

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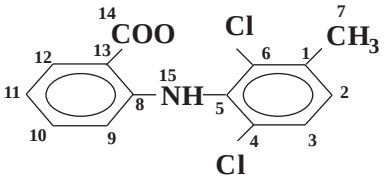

Table 7. ^{119}Sn NMR data of organotin(IV) 2-[N-(2,6-dichloro-3- methylphenyl)amino]benzoate.

No.	Compound	Chemical Shift	No.	Compound	Chemical Shift
I	Me_3SnL	137	IV	Et_2SnL_2	-115
II	Ph_3SnL	113	V	Bu_2SnL_2	-144
III	Me_2SnL_2	-113	VI	Ph_2SnL_2	-149

Table 8. Antibacterial activity (Gram positive) of organotin(IV) 2-[N-(2,6-dichloro-3- methylphenyl)amino] benzoate[a].

Bacterium	Compounds						
	LNa	I	II	III	IV	V	VI
Staphylococcus aureus	-	+++	+++	+	+	+	+
Staphylococcus epidermiedis	-	++	+++	-	+	++	++
Strepotococcus pyogenes	-	++	+++	+	0	+	+
Bacillus anthracis	-	+++	+++	+	+	+	++
Corynebacterium species	-	+++	++	+	++	+	+
Clostridium species	-	+++	++	+	+	+	+
Peptococcus species	-	-	+++	+	++	++	+
Streptococcus pneumonial	-	++	++	+	0	+	+
Streptofaecates	-	+++	+++	+	+	+	+
Listeris monocytogenes	-	++	+++	++	+	+	+
Micrococci	-	+++	+++	+	+	+	+

[a]+++ = High activity, ++ = moderate activity, + = low activity, 0 = not tested, - = no activity, LNa = Sodium 2-[N-(2,6-dichloro-3-methylphenyl)amino]benzoate.

Table 9. Antibacterial activity (Gram negative) of organotin(IV)[a].

Bacterium	Compounds						
	LNa	I	II	III	IV	V	VI
Escherichia coli	-	++	+++	+	0	++	+
Proteus mirablis	-	+++	+++	+	+	+	+
Proteus vulgeris	-	+++	+++	++	0	+	+
Sallmonella typhi	-	+++	++	+	++	++	0
C. diptherial	-	++	++	++	+	+	+
P. aeruginosa	-	+++	+++	+	0	+	++
Aeromans sobrial	-	++	+++	+	+	0	+
Shigella boydie	-	+++	+++	++	0	+	+
Vibrio cholera	-	+++	+++	+	+	++	+
Brucella species	-	+++	++	+	++	+	++

+++ = High activity, ++ = moderate activity, + = low activity, 0 = not tested, - = no activity. LNa = Sodium 2-[N-(2,6-dichloro-3-methylphenyl)amino]benzoate.

Experimental

Hydrated sodium salt of 2-[N-(2,6-dichloro-3-methylphenyl)amino]benzoate was dehydrated by refluxing in toluene using 'Dean and Stark' apparatus. Tri- and diorganotin(IV) chlorides with different stoichiometric ratios (1:1 and 1:2, respectively) were refluxed for 6-8 h with sodium 2-[N-(2,6-dichloro-3-methylphenyl)amino]benzoate to obtain $R_3SnL$and R_2SnL_2 in the same solvent. The reaction mixture was cooled and filtered off to remove NaCl. The solvent from the filtrate was removed in vacuo and recrystallization of the residue was achieved in dichloromethane.

Table 10. Antifungal activity of organotin(IV) 2-[N-(2,6-dichloro-3-methylphenyl)amino]benzoate.

Fungus	Compounds						
	LNa	I	II	III	IV	V	VI
Candida albican	-	+++	++	+	+	+	+
Pencillium notatum	-	+++	+++	++	+	+	0
Dutarium notatum	-	+++	+++	+	++	0	++
Gurvularia lunata	-	+++	+++	0	+	++	+
Alterneria solani	-	++	+++	+	+	+	+
Fusarium solani	-	+++	+++	+	0	+	0
E. flocosum	-	-++	++	+	+	0	+
Candida tropicalis	-	+++	++	++	0	+	+
Aspergillus nigar	-	+++	+++	+	+	++	0
Ascomycetes	-	+++	+++	+	+	0	++
Microsponum canis	-	+++	+++	+	+	++	+

[A]+++ = High activity, ++ = moderate activity, + = low activity, 0 = not tested, - = no activity. LNa = Sodium 2-[N-(2,6-dichloro-3-methylphenyl)amino]benzoate

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References

1. M. Gielen, **Main Group Met. Chem., 17,** 1 (1994).
2. S.W. Ng, A.J. Kuthubutheen, Z. Arifin, C. Wei, V.G.K. Das, B. Schulze, K.C. Molloy, W.H. Yip and T.C.W. Mak, **J. Organomet. Chem., 403,** 101 (1991).
3. G.J.M. Van der Kerk, **"Organotin Compounds"**, Conf. Tin Consumption, [Pap.] 181 (1972); Chem. Abstr. 83, 10204x (1975).
4. V.L. Narayanan, M. Nasr, and K.D. Paul in **"Tin-Based Antitumor Drugs"** M. Gielen, Ed.; Springer-Verlag, Berlin, pp. 201-17 (1990).
5. R. William, M. Biesemans, M. Boualam, A. Delmotto, A. El Khloufi and M. Gielen, **Appl. Organomet. Chem., 7,** 311 (1993).
6. S.J. Blunden, A.J. Crowe and A.W. Monk, **Appl. Organomet. Chem., 1,** 57 (1987).
7. P.A. Cusak, L.A. Hobbs, P.J. Smith and J.S. Brooks, **J. Text. Inst., 71,** 138 (1980).
8. R. Hill and P.J. Smith, **Int. J. Wood Preserv., 3,** 77 (1983).
9. A.J. Crowe, R. Hill, P.J. Smith and T.R.G. Cox, **Int. J. Wood Preserv., 1,** 119 (1979).
10. X. Qinglan, S. Li-Juan, L. Hua, W. Ru-Ji and W. Hong-Gen, **Appl. Organomet. Chem., 8,** 57 (1994).
11. A. Kumari, I. Singh and J.P. Tandon, **Appl. Organomet. Chem., 9,** 127 (1995).
12. M. Gielen, M. Baulam, B. Mahieu and E.R.T. Tiekink, **Appl. Organomet. Chem., 8,** 19 (1994).
13. Y. Arakawa, **Main Group Met. Chem., 17,** 225 (1994).
14. F. Huber and R. Barbieri, in **"Metal Complexes in Cancer Chemotherapy"**, B.K. Keppler, Ed., VCH Weinheim, Germany, pp. 351-68 (1993).
15. S. Ali, F. Ahmad, M. Mazhar, A. Munir and M.T. Masood, **Synth. React. Inorg. Met-org. Chem., 32,** 357, (2002).
16. F. Ahmad, M. Parvez, S. Ali, M. Mazhar and A. Munir, **Synth. React. Inorg. Met-org. Chem., 32,** 665, (2002).
17. B. Wrackmeyer, G. Kehr, H. Zhou and S. Ali, **Main Group Met. Chem., 15,** 89 (1992).
18. M. Parvez, S. Ali, S. Ahmad, M.H. Bhatti and M. Mazhar, **Acta Cryst., C58,** m334 (2002).
19. M. Parvez, S. Ali, M. Mazhar, M.H. Bhatti and M.A. Choudhary, **Acta Cryst., C55,** 1429 (1999).
20. M. Parvez, S. Ali, M. Mazhar, M.H. Bhatti and M.N. Khokhar **Acta Cryst., C55,** 1280 (1999).
21. M. Parvez, M.H. Bhatti, S. Ali, M. Mazhar, and S.A. Qureshi, **Acta Cryst., C56,** 327 (2000).
22. A. Kalsoom, M. Mazhar, S. Ali, M.F. Mahon, K.C. Molloy and M.I. Choudhary, **Appl. Organomet. Chem., 11,** 47 (1997).

23. M.A. Choudhary, M. Mazhar, S. Ali, U. Salma, S. Ashraf and A. Malik, **Turk. J. Chem., 26,** 125 (2002).
24. F. Ahmad, S. Ali, M. Parvez, A. Munir, M. Mazhar, K.M. Khalid and T.A. Shah, **Heteroatom Chem., 13,** 638 (2002).
25. T. Lebel, J. Holecek and A. Lycka, **Sci. Pap Univ. Pardubice Ser., A2,** 5, (1996).
26. J.R. Homes and H.D. Kasez, **J. Am. Chem. Soc., 83,** 3903, (1961).
27. H.O. Kalinowski, S. Berger and S. Brown, **"^{13}C NMR Spektroskpie"**, Thieme Verlag, Stuttgart, Germany, (1984).
28. T.P. Lockart, W.F. Manders and E.M. Holt, **J. Am. Chem. Soc., 108,** 6611, (1986).
29. T.P. Lockart, **Organometallics, 7,** 1438, (1988).
30. A. Lycka, J. Holecek and D. Mickak, **Collect. Czech. Chem. Commun., 62,** 1169, (1997).
31. M. Danish, H.G. Alt, A. Badshah, S. Ali, M. Mazhar and N. Islam, **J. Organomet. Chem., 486,** 51, (1995).
32. B.W. Fitzmans, N.J. Seeley and A.W. Smith, **J. Chem. Soc.,** A-143, (1969).
33. B. Wrackmeyer, in G. A. Webb (ed.), **Ann. Rep. on NMR Spectroscopy,** ^{119}Sn NMR Parameters, Academic Press London, 73, (1985).
34. B. Wrackmeyer, **Ann. Rep. NMR Spectrosc., 38,** 203, (1999).
35. A. Ruzicka, V. Pejchal, J. Holecek, A. Lycka and K. Jacob, **Collect. Czech. Chem. Commun., 63,** 977, (1998).