

Synthetic, Structural and Biological Studies of Organotin(IV) Complexes of Schiff Bases Derived from Pyrrol-2-carboxaldehyde

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Some new organotin(IV) complexes having general formulae $R_2MCl[L]$ and $R_2M[L]_2$ were synthesized by the reactions of Me_2MCl_2 with Schiff bases [5-Mercapto-4-(pyrrolcarboxalideneamino)-s-triazole, 5-Mercapto-3-methyl-4-(2-pyrrolcarboxalideneamino)-s-triazole, 3-Ethyl-5-mercapto-4-(2-pyrrolcarboxalideneamino)-s-triazole] in 1:1 and 1:2 molar ratios. All of the compounds were characterized by elemental analysis, molar conductance, IR, UV, 1H , ^{13}C and ^{119}Sn NMR spectral studies. The IR and 1H NMR spectral data suggest the involvement of azomethine nitrogen in coordination with the central metal atom. With the help of the above-mentioned spectral studies, penta and hexacoordinated environments around the central metal atoms in the 1:1 and 1:2 complexes, respectively, have been proposed. Finally, the free ligands and their metal complexes were tested *in vitro* against some pathogenic bacteria and fungi to assess their antimicrobial properties.

Keywords: Organotin(IV) complexes, s-Triazoles, Schiff bases, Antifungal and antibacterial activities

INTRODUCTION

The use of organotin compounds has increased dramatically over the last thirty years as a result of their wide range of technical applications and their favorable environmental and toxicological properties [1]. At the present time, the industrial uses of non-toxic organotin compounds (R_2SnX_2 and R_2SnX_3 types) account for almost two-thirds of the total world consumption, although the other major use of these derivatives as selective biocides and pesticides (R_2SnX_3) has increased rapidly in recent years [2-5].

There has been considerable interest in the chemistry of penta- and hexacoordinated organotin(IV) complexes derived from various organic ligands due to their structural and stereochemical properties, in marked contrast to the well-

documented chemistry of organotin(IV) complexes [6-8]. Organotin(IV) complexes are put to use in various fields [9-11] and exhibit potential biological applications [12-14] such as insecticidal, fungicidal and antitumor activities. Organotin compounds are now the active components in a number of biocidal formulations, finding applications in such diverse areas as fungicides, miticides, molluscicides, marine antifouling paints, surface disinfectants and wood preservatives [15-19].

In recent years, investigations have been carried out to test their antitumor activity and it has been observed that indeed several diorganotin and triorganotin species show potential as antineoplastic agents [20-21]. These developments in mind, we report here the synthesis of organotin(IV) metal complexes of Schiff bases derived from condensation of pyrrol-2-carboxaldehyde with different triazoles whose characterization has been made by elemental analysis and spectroscopic (UV,

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IR, ^1H , ^{13}C and ^{119}Sn NMR) studies. Their antibacterial and antifungal activities have been screened against various fungi and bacteria.

EXPERIMENTAL

All the apparatus used during the experimental work were fitted with quick fit interchangeable standard ground joints. All the reagents *viz.* pyrrol-2-carboxaldehyde (HiMedia) and dimethyltin dichloride (ACROS) were used as received. Strict anhydrous conditions were maintained during the synthesis of the metal complexes, since the dimethyltin dichloride and the product complexes were moisture-sensitive.

Tin was determined gravimetrically as tin dioxide. Melting points were determined on a capillary melting point apparatus. Molar conductance measurements of 10^{-3} M solution of metal complexes in dry DMF were measured at 25 ± 1 °C with a conductivity bridge type 305 systronic model. The electronic spectra of ligands and their metal complexes were recorded in the region 1100-200 nm on a HITACHI U-2000 spectrophotometer, in dry methanol. The IR spectra were recorded on BUCK scientific M500 grating spectrophotometer in the range of 4000-250 cm^{-1} . Multinuclear magnetic resonance spectra (^1H , ^{13}C and ^{119}Sn) were recorded on BRUKER 400ACF spectrometer.

Synthesis of Ligands

4-Amino-5-mercapto-*s*-triazole (AMT), 4-Amino-5-mercapto-3-methyl-*s*-triazole (AMMT) and 4-Amino-3-ethyl-5-mercapto-*s*-triazole (AEMT) were synthesized by a reported method [22]. The ligands were synthesized by the condensation of pyrrol-2-carboxaldehyde with AMT, AMMT and AEMT in the medium of ethanol. The solutions mixture were refluxed on heating mantle for 3-4 h and allowed for cooling to room temperature. The products were filtered, washed, and recrystallized from the same solvent and dried. Their elemental analysis and physical properties are given in Table 1.

Synthesis of Metal Complexes

To a weighed amount of Me_2SnCl_2 was added the calculated amount of the sodium salt of the ligand in 1:1 and 1:2 molar ratios, in methanol as reaction medium in dry

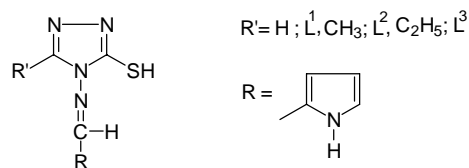


Fig. 1. Structure of the ligands used.

atmosphere. On refluxing for about 12 h, the resulting complexes were obtained as colored solids. The excess of the solvent was removed under reduced pressure and the complexes were dried in vacuo at 35 ± 5 °C after repeated washing with dry cyclohexane. The analysis and physical properties of these complexes are reported in Table 1.

RESULTS AND DISCUSSION

All the newly synthesized complexes were colored solids and soluble in DMSO, DMF and methanol. The conductivity values measured for 10^{-3} M solutions in anhydrous DMF were in the range 10-15 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, showing them to be non-electrolytes. The analytical data were in good agreement with the proposed stoichiometry of the complexes. The physical and analytical data of the ligands and their metal complexes are presented in Table 1.

Electronic Spectra

Electronic spectra of the ligands (L^1 and L^2) and their metal complexes of Sn(IV) were taken. The test solutions were prepared by dissolving the ligands and their complexes in dry methanol. The electronic spectra of the ligands L^1 and L^2 exhibited maxima at 387 nm and 358 nm, which could be assigned to the $n-\pi^*$ transition of the azomethine group. These bands show a blue shift in the Sn (1:1 and 1:2) complexes and appear at 362 nm ($\text{Me}_2\text{Sn}L^1\text{Cl}$), 337 nm ($\text{Me}_2\text{Sn}\{L^1\}_2$), 336 nm ($\text{Me}_2\text{Sn}L^2\text{Cl}$), 311 nm ($\text{Me}_2\text{Sn}\{L^2\}_2$), respectively. This clearly indicates the coordination of the azomethine nitrogen atom with the metal atom. Furthermore, two medium intensity bands at 284 nm and 221 nm due to $\pi-\pi^*$ transitions in the ligands remain unchanged in the spectra of the metal complexes.

IR Spectra

The ligands exhibit a broad and strong band in the region

Table 1. Physical Characteristics and Analytical Data of Ligands and Their Metal Complexes

Ligands and metal complexes	Empirical formula	Color	M.P. (°C)	Calculated (Found)				
				C	N	H	S	Sn
L ¹	C ₇ H ₇ N ₅ S	Grey	168-170	43.52 (43.02)	36.26 (36.17)	3.62 (3.37)	16.58 (16.11)	-
Me ₂ SnCl(L ¹)	C ₉ H ₁₂ N ₅ SnClS	Light brown	187-189	28.72 (27.80)	18.61 (18.23)	3.19 (3.03)	8.51 (8.22)	31.64 (30.60)
Me ₂ Sn(L ¹) ₂	C ₁₆ H ₁₈ N ₁₀ S ₂ Sn	Brown	179-181	36.02 (35.79)	26.26 (26.0)	3.37 (3.15)	12.0 (11.85)	22.32 (21.96)
L ²	C ₈ H ₉ N ₅ S	Light violet	165-168	46.37 (45.87)	33.81 (33.26)	4.34 (4.05)	15.45 (15.30)	-
Me ₂ SnCl(L ²)	C ₁₀ H ₁₄ N ₅ SnClS	Light yellow	193-195	30.76 (30.18)	17.94 (17.40)	3.58 (3.22)	8.20 (8.0)	30.50 (29.73)
Me ₂ Sn(L ²) ₂	C ₁₈ H ₂₂ N ₁₀ SnS ₂	Yellow	181-183	37.17 (37.05)	24.09 (23.41)	3.71 (3.30)	11.01 (10.95)	26.48 (26.22)
L ³	C ₉ H ₁₁ N ₅ S	Grey	218-220	48.86 (48.52)	31.67 (31.09)	4.97 (4.62)	14.47 (14.00)	-
Me ₂ SnCl(L ³)	C ₁₁ H ₁₆ N ₅ SnClS	Light brown	236-238	32.67 (32.12)	17.32 (17.10)	3.96 (3.65)	7.92 (7.68)	29.45 (28.27)
Me ₂ Sn(L ³) ₂	C ₂₀ H ₂₆ N ₁₀ SnS ₂	Brown	227-229	40.74 (40.36)	23.76 (23.29)	4.41 (4.14)	10.86 (10.26)	20.20 (19.80)

at $\sim 2750\text{ cm}^{-1}$ due to the $\nu(\text{S-H})$ [23]. The deprotonation of the thiol group is indicated by the absence of the band in metal complexes at $\sim 2750\text{ cm}^{-1}$, which appears due to $\nu(\text{S-H})$ in the spectra of the ligands indicating complexation through sulfur atom. A band appears at $\sim 747\text{ cm}^{-1}$ which is assigned to $\nu(\text{C-S})$ and which further confirms the coordination of the ligand through the sulfur atom. Metal sulfur bond formation is further supported by a band at $\sim 455\text{ cm}^{-1}$ for $\nu(\text{Sn-S})$ [24-25]. A sharp and strong band at $\sim 1600 \pm 5\text{ cm}^{-1}$ assignable to $\nu(\text{N=C})$ [26], is shifted to higher wavelength number $\sim 1610 \pm 5\text{ cm}^{-1}$ in the spectra of the metal complexes, indicating coordination through the azomethine nitrogen with the metal atom. This can be explained by a reduction of the carbon nitrogen double bond character in the azomethine group.

Formation of a metal nitrogen bond is further supported by the presence of a band at $\sim 535\text{ cm}^{-1}$ for $\nu(\text{Sn-N})$ [27], indicating the coordination of the ligand with the central metal

atom through the azomethine nitrogen atom. A strong band in the region of $485\text{-}431\text{ cm}^{-1}$ was assigned to $\nu(\text{M-Cl})$ [28] in 1:1 metal complexes. A characteristic band was observed at $\sim 3250\text{ cm}^{-1}$ due to $\nu(\text{N-H})$ of pyrrole in the spectra of ligands and their metal complexes.

¹H NMR Spectra

To further confirm the bonding pattern in these complexes, ¹H NMR spectra of the ligands and their metal complexes were recorded in DMSO-d₆ using TMS as the internal standard. The ¹H NMR spectra of the ligands show -SH proton signal at $\delta 13.70 \pm 0.15\text{ ppm}$. Disappearance of this signal due to -SH protons in the spectra of the metal complexes indicates the deprotonation of the thiol group which supports the coordination of ligand through sulfur atom with the metal atom. A signal at $\delta 9.7 \pm 0.10\text{ ppm}$ is observed in the spectra of metal complexes due to the azomethine protons, which

moves downfield in comparison to its original position in the free ligands, thereby indicating the coordination through the azomethine nitrogen with the metal atom. A sharp singlet due to -NH proton (pyrrole) is also observed at δ 11.5-12.0 ppm in the spectra of ligands which remains unaltered in the spectra of metal complexes. Some additional signals at δ 3.5-4.0 ppm (s, -H, triazole), δ 2.0-3.5 ppm (s, -CH₃, triazole), δ 2.0-3.0 ppm (q, -CH₂CH₃, triazole) and δ 1.0-2.0 ppm (t, -CH₂CH₃, triazole) are observed in the ligands and their metal complexes. One more signal due to (s, CH₃-Sn-CH₃) in the range of δ 0.5-1.5 ppm appeared in the spectra of metal complexes. The ¹H NMR spectroscopic data of the ligands and their metal complexes are given in Table 2.

¹³C NMR Spectra

The ¹³C NMR spectral data of ligand [L¹] and its corresponding 1:1 and 1:2 metal complexes have been recorded and given in Table 3. The signal due to the carbon atom attached to the azomethine group in the ligand appears at δ 151.61 ppm. However, in the spectra of the corresponding metal complexes the signal appears at higher δ values. The considerable shifting in the carbon atom attached to azomethine nitrogen indicates the coordination of nitrogen with the central metal atom in 1:1 and 1:2 metal complexes. Moreover, the shifting of the ¹³C resonance which is attached to sulfur atom in the spectra of 1:1 and 1:2 tin complexes compared to the free ligands indicates the coordination through sulfur with the metal atom. Additional signals in ¹³C NMR spectra of the metal complexes were observed at δ 15.30

ppm and δ 18.27 ppm (Sn-C) in 1:1 and 1:2 metal complexes, respectively.

¹¹⁹Sn NMR Spectra

The value of $\delta^{119}\text{Sn}$ spectra reflects the coordination number of the nucleus in the corresponding metal complexes [29-31]. In general, ¹¹⁹Sn chemical shifts move to lower frequency with increasing coordination number of the nuclei. In order to confirm the geometry of the complexes, ¹¹⁹Sn NMR spectra were recorded. The spectra in each case show only a sharp singlet, indicating the formation of a single species. The ¹¹⁹Sn NMR spectra of 1:1 and 1:2 tin [Me₂SnCl(L²) and Me₂Sn(L²)₂] complexes give sharp signals at δ -143.93 ppm and δ -240.30 ppm, respectively, which is indicative of penta and hexacoordinated environment around the tin atom.

On the basis of the above evidences, it is suggested that the geometries around the tin atom in the complexes investigated be characterized as trigonal bipyramidal and octahedral in 1:1 and 1:2 ratios, respectively, as shown in Fig. 2.

Biological Aspects

The fungicidal and bactericidal activities of free ligands L¹, L² and L³ and their organotin(IV) complexes against various fungi and bacteria are given in Tables 4 and 5 using the following methods [32].

In vitro Antifungal Activity

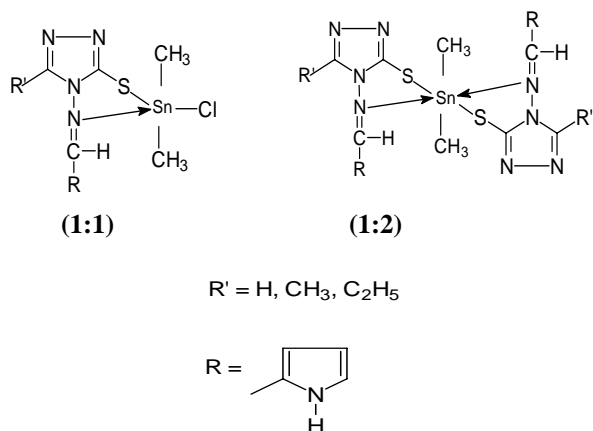
Potato dextrose agar medium (PDA) was prepared in flasks

Table 2. ¹H NMR Chemical Shifts of the Ligands and Their Metal Complexes

Ligands and metal complexes	Aromatic-H	-NH (pyrrole)	-SH	Azomethine-H	-H, -CH ₃ , -C ₂ H ₅	Sn-CH ₃
L ¹	6.5-8.0	11.2	13.2	9.7	3.4(s)	-
Me ₂ SnCl(L ¹)	6.6-8.1	11.1	-	9.5	3.3(s)	1.2(s)
Me ₂ Sn(L ¹) ₂	6.6-8.3	11.1	-	9.4	3.2(s)	1.0(s)
L ²	6.5-8.1	11.4	13.8	9.8	2.3(s)	-
Me ₂ SnCl(L ²)	6.7-8.2	11.2	-	8.9	2.2(s)	0.85(s)
Me ₂ Sn(L ²) ₂	6.7-8.2	11.3	-	9.1	2.1(s)	0.76(s)
L ³	6.4-8.8	11.8	13.7	9.4	2.4(q), 1.7(t)	-
Me ₂ SnCl(L ³)	6.6-8.2	11.6	-	9.2	2.3(q), 1.5(t)	0.88(s)
Me ₂ Sn(L ³) ₂	6.6-8.7	11.6	-	9.0	2.3(q), 1.4(t)	0.65(s)

Table 3. ^{13}C NMR Chemical Shifts of the Ligands and Their Metal Complexes

Ligand and metal complexes	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	M-CH ₃
	125.52	124.45	110.37	118.10	151.61	161.26	155.82	-
	125.55	124.31	110.22	118.12	155.90	161.30	152.27	15.30
	125.30	124.20	110.32	118.22	156.03	161.35	152.36	18.27
R =	and		R' = H					


Fig. 2. Proposed structures of the 1:1 and 1:2 complexes.

and sterilized and poured into petri plates. Requisite quantity (100 $\mu\text{g ml}^{-1}$) of the standard antibiotic (ampicilline) was added just before pouring in the medium to check the growth of bacteria. Test samples were prepared in different concentrations (10 μg , 50 μg and 100 $\mu\text{g ml}^{-1}$) in Dimethylsulfoxide (DMSO) and 200 μl of each sample was

added to PDA plates containing mycelial discs, taken from the 5-7 days old culture of (*Aspergillus flavus* and *A. niger*) fungi. These plates were incubated for 5-7 days at 28 ± 1 °C. Control plates were given the same treatment except for the addition of the test samples. The efficacy of each sample was determined by measuring radial mycelial growth. The radial growth of the colony was measured in two directions at right angle to each other and the average of two replicates was recorded in each case. Data were expressed as percent inhibition over control from the size of colonies, and subjected to two-way analysis of variance. The percent inhibition given in the table was calculated using the formula:

$$\% \text{Inhibition} = (C - T) \times 100 / C$$

where C = diameter of fungus colony in the control plate after 96 h incubation; T = diameter of the fungus colony in the tested plate after the same incubation period.

In vitro Antibacterial Assay

The newly synthesized ligands and their metal complexes were screened for their antibacterial activity against test

Table 4. Antifungal Screening (Average Percentage Inhibition after 96 h) Data of the Ligands and Their Metal Complexes (Percent Inhibition)

Ligands and metal complexes	Concentration	AF*	AN*
C ₇ H ₇ N ₅ S	control	nil	nil
	10 µg	nil	nil
	50 µg	nil	nil
	100 µg	05.98	09.54
C ₉ H ₁₂ N ₅ SnClS	control	nil	nil
	10 µg	11.20	08.21
	50 µg	27.30	15.57
	100 µg	50.15	47.29
C ₁₆ H ₁₈ N ₁₀ S ₂ Sn	control	00.00	00.00
	10 µg	23.71	20.03
	50 µg	48.14	79.43
	100 µg	65.22	74.82
C ₈ H ₉ N ₅ S	control	nil	nil
	10 µg	10.00	12.10
	50 µg	22.01	09.60
	100 µg	34.10	17.75
C ₁₀ H ₁₄ N ₅ SnClS	control	00.00	00.00
	10 µg	25.54	20.39
	50 µg	44.72	38.64
	100 µg	79.40	77.21
C ₁₈ H ₂₂ N ₁₀ SnS ₂	control	00.00	00.00
	10 µg	22.79	25.33
	50 µg	37.89	58.32
	100 µg	66.41	72.62
C ₉ H ₁₁ N ₅ S	control	00.00	00.00
	10 µg	09.56	10.45
	50 µg	12.06	08.55
	100 µg	38.97	28.43
C ₁₁ H ₁₆ N ₅ SnClS	control	00.00	00.00
	10 µg	10.87	09.30
	50 µg	27.33	19.50
	100 µg	52.57	47.86
C ₂₀ H ₂₆ N ₁₀ SnS ₂	control	00.00	00.00
	10 µg	15.40	20.21
	50 µg	43.25	31.43
	100 µg	54.20	45.22

AF* - *Aspergillus flavus*, AN* - *Aspergillus niger*.**Table 5.** Antibacterial Screening Data of the Ligands and Their Metal Complexes

Ligands and metal complexes	Concentration (µg ml ⁻¹)	Percentage inhibition	
		EC*	BS*
C ₇ H ₇ N ₅ S	50	nil	nil
	100	11	17
	500	24	22
C ₉ H ₁₂ N ₅ SnClS	50	16	31
	100	47	62
	500	82	70
C ₁₆ H ₁₈ N ₁₀ S ₂ Sn	50	28	32
	100	40	51
	500	83	75
C ₈ H ₉ N ₅ S	50	18	16
	100	22	30
	500	67	88
C ₁₀ H ₁₄ N ₅ SnClS	50	28	38
	100	63	73
	500	91	84
C ₁₈ H ₂₂ N ₁₀ SnS ₂	50	22	30
	100	48	52
	500	66	83
C ₉ H ₁₁ N ₅ S	50	nil	nil
	100	21	29
	500	55	60
C ₁₁ H ₁₆ N ₅ SnClS	50	20	13
	100	48	55
	500	78	67
C ₂₀ H ₂₆ N ₁₀ SnS ₂	50	24	30
	100	59	74
	500	76	85

BS* - *Bacillus stearothermophilus*, EC* - *Escherichia coli*.

bacteria, namely, *E.coli* (MTCC 51) and *Bacillus stearothermophilus* determined by reported methods [33]. Turbidity of the control was adjusted to 0.5 McFarland standards [34]. All the test cultures were streaked on nutrient agar medium (g l⁻¹) (Peptone, 10; yeast extract, 03; NaCl, 05; Agar, 2%) (NAM) and incubated overnight at 37 °C. By preparing bacterial suspension of 3-5 well-isolated colonies of

similar morphological type selected from a NAM plate, cultures were further diluted to 10 folds to get inoculum size of 1.2 CFU/ml. A stock solution of 500 $\mu\text{g ml}^{-1}$ of each compound was prepared in DMSO and was appropriately diluted to obtain final concentration of 100 and 50 $\mu\text{g ml}^{-1}$. Requisite quantity of antifungal compound (cyclohexamide) was added to medium to get its desirable final concentration of 100 $\mu\text{g ml}^{-1}$. Each appropriately diluted 100 μl test sample was spread over the solidified NAM. Separate flasks were used for each test dilution. The test bacterial culture was spotted in a predefined pattern by aseptically transferring 5 μl of each bacterial culture on the surface of solidified agar-agar plates and incubated at 35 °C for 24 h.

Observations

The free ligands and their metal complexes were screened against various fungi and bacteria to assess their potential as antimicrobial agents. The antimicrobial data reveals that the complexes are superior compared to the free ligands. The activity increased as the concentration was increased. Efficacy of these complexes was found to be more potent inhibitors of bacterial growth as compared to fungal culture. These complexes were more inhibitory for the growth of *E. coli* among test bacterial cultures and nearly equally sensitive for test fungal cultures. Thus, it can be postulated that further studies of these complexes in this direction and biocides could lead to more interesting results. Details of antifungal and antibacterial screening data are given in Tables 4 and 5, respectively.

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REFERENCES

- [1] A.G. Davis, P.J. Smith, *Adv. Inorg. Chem., Radio Chem.* 1 (1980) 23.
- [2] M. Jain, S. Maanju, R.V. Singh, *Appl. Organomet. Chem.* 18 (2004) 471.
- [3] D.D. Nhan, D.T. Loan, I. Tolosa, S.J. De Mora, *Appl. Organomet. Chem.* 19 (2005) 811.
- [4] A. Chaudhary, M. Aggarwal, R.V. Singh, *Appl. Organomet. Chem.* 20 (2006) 295.
- [5] U.N. Tripathi, G. Venubabu, S.F. Ahmad, S.S. Rao Kolisetty, A.K. Srivastava, *Appl. Organomet. Chem.* 20 (2006) 669.
- [6] C. Pettinari, F. Marchetti, R. Pettinari, D. Martini, A. Drozdov, S. Troyanov, *Inorg. Chim. Acta* 325 (2001) 103.
- [7] L.E. Khoo, B. Yan, N.K. Goh, S.W. Ng, *Main Group Metal Chem.* 24 (2001) 817.
- [8] C. Pettinari, F. Marchetti, R. Pettinari, A. Gindulyte, L. Massa, M. Rossi, F. Caruso, *Eur. J. Inorg. Chem.* 2002 (2002) 1447.
- [9] A.H. Penninks, P.M. Punt, M. Bol-Schoenmakers, H.J.M. Van Rooijen, W. Seinen, *Silicon, Germanium, Tin and Lead Compounds* 9 (1986) 367.
- [10] Y. Kondo, D. Uchiyama, T. Sakamoto, H. Yamanaka, *Tetrahedron Lett.* 30 (1989) 4249.
- [11] S.J. Blunden, P.A. Cusack, R. Hill, *The Industrial Uses of Tin Chemicals*, Royal Society of Chemistry, London, UK, 1985.
- [12] P.M. Samuel, D. de Vos, D. Raveendra, J.A.R.P. Sarma, S. Roy, *Bioorg. Med. Chem. Lett.* 12 (2002) 61.
- [13] T.S. Basu Baul, S. Dutta, E. Rivarola, M. Scopelliti, S. Choudhuri, *Appl. Organomet. Chem.* 15 (2001) 947.
- [14] A. Ruzicka, L. Dostal, R. Jambor, *Appl. Organomet. Chem.* 16 (2002) 315.
- [15] A. Chaudhary, A. Phor, G.K. Aggarwal, R.V. Singh, *Heterocycl. Commun.* 10 (2004) 181.
- [16] M. Gielen, *Tin-Based Antitumor Drugs*, NATO ASI Series, (Springer-Verlag, Berlin, 1990, p. 37.
- [17] R. Malhotra, J. Mehta, J.K. Puri, *Cent. Eur. J. Chem.* 3 (2007) 5.
- [18] G. Eng, D. Whalen, P. Musingarimi, J. Tierney, M. Derosa, *Appl. Organomet. Chem.* 12 (1998) 25.
- [19] M. Jain, S. Gaur, S.C. Joshi, R.V. Singh, A. Bansal, *Phosphorus, Sulfur and Silicon* 179 (2004) 1517.
- [20] Q. Xie, Z. Yang, L. Jiang, *Main Group Metal Chem.* 19 (1996) 509.
- [21] M. Gielen, A. Bouhdid, F. Kayser, M. Biesemans, D.

- Devos, B. Mohien, Willem R, Appl. Organomet. Chem. 9 (1995) 251.
- [22] S. Bala, R.P. Gupta, M.L. Sachdeva, A. Singh, H.K. Pujari, Ind. J. Chem. 16 (1978) 481.
- [23] G. Singh, P.A. Singh, K. Singh, D.P. Singh, R.N. Handa, S.N. Dubey, Proc. Nat. Acad. Sci. Ind. 72A (2002) 87.
- [24] S. Belwal, R.V. Singh, Appl. Organomet. Chem. 12 (1998) 39.
- [25] K. Singh, K. Singh, J.P. Tondon, Polyhedron 7 (1988) 151.
- [26] K. Singh, D.P. Singh, M.S. Barwa, P. Tyagi, Y. Mirza, J. Enz. Inh. Med. Chem. 21 (2006) 749.
- [27] T. Daniel, K. Natrajan, Trans. Met. Chem., (Drodrecht Neth.) 25 (2000) 311.
- [28] A. Chaudhary, R.V. Singh, Phosphorus, Sulfur and Silicon 178 (2003) 615.
- [29] M. Jain, R.V. Singh, Appl. Organomet. Chem. 17 (2003) 616.
- [30] M. Jain, S. Nehra, P.C. Trivedi, R.V. Singh, Metal Based Drugs 9 (2002) 53.
- [31] M. Pellei, G.G. Lobbia, M. Ricciutelli, L. Santini, J. Coord. Chem. 58 (2005) 409.
- [32] Y.L. Nene, P.N. Thapliyal, in: Fungicides in Plants Disease Control, 3th ed., Oxford and IBH Publishing, New Delhi, 1993, p. 531.
- [33] NCCLS, Method for Dilution Antimicrobial Susceptibility Test for Bacteria That Grow Aerobically Approved Standard, 5th ed., National Committee for clinical Laboratory Standards, Villanova, PA, 2000.
- [34] J. McFarland, J. Am. Med. Assoc. 14 (1907) 1176.