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Synthesis, characterization and antimicrobial activity of organotin and organosilicon complexes of substituted hydrazones

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A few organotin and organosilicon complexes of substituted hydrazones have been synthesized and characterized by their elemental analyses, conductivity measurement and infrared and ^{1}H NMR spectral data. The ligand and their complexes have been evaluated for fungicidal activity against phytopathogenic fungi, viz., *Alternaria alternata, Colletotrichum capsicum, Fusarium oxysporum* and *Rhizoctonia solani* at 37°C and bactericidal activity against *Bacillus subtilis* and *Escherichia coli* at 28°C. Organotin complexes are found to be more potent than organosilicon complexes and parent ligands.

Organotin or organosilicon compounds exhibit a broad spectrum of biological activity which includes bactericidal[1,2], fungicidal[3], antitumor[4] and acaricides[5]. In continuation of our earlier research on biologically active metal complexes[6-8] of pyrazoles and acid hydrazides, where the activity of ligand was enhanced several folds on coordination with suitable metal ion, an attempt has now been made to synthesize the complex of hydrazones with organotin/silicon halides [$R_{4-n}ML_{1-II}Cl_n$; M=Sn or Si, R=Me or Ph; n=1 or 2; L_I, L_{II}=substituted hydrazones] with a view to studying the effect of coordination on antimicrobial activity and explore the possibility of their use as potential biocidal agents. The fungi and bacteria were selected keeping in view their economic importance.

Experimental

All operations were carried out under dry nitrogen atmosphere. Solvents used were dried by conventional methods. Infrared spectra were recorded as nujol mull using NaCl/polyethylene optics on Perkin Elmer 1430 ratio recording spectrophotometer. The ^{1}H NMR spectra of ligands and their complexes were recorded on Varian EM 390-90 MHz spectrometer in $CDCl_3$ using TMS as an internal reference. Elemental analyses were obtained using Perkin Elmer 2400 CHN elemental analyzer. Molecular weights were determined cryoscopically in nitrobenzene.

Preparation of hydrazone

3-Substituted benzoyl prop-2-ene-1-oic acid hydrazides were prepared in good yield by condensing corresponding ester with hydrazine hydrate in ethanol. The hydrazones were synthesized by refluxing the ethanolic solutions of respective hydrazides with *o*-hydroxy acetophenone in 1:1 molar ratio for 3 h. The reaction mixture was allowed to cool at room temperature and separated solid was filtered and crystallized from ethanol to give the required ligand.

Preparation of complexes

To a solution of substituted hydrazone in dry benzene, was added dropwise equimolar amount of organotin/silicon chloride in the same solvent under dry nitrogen atmosphere. The mixture was stirred vigorously for 1 h. The solid was filtered and washed repeatedly with dry benzene and dried *in vacuo* over P_2O_5. The analytial data of these complexes are given in Table 1.

Antimicrobial assay

All the synthesized ligands and their organotin/silicon complexes were evaluated for *in vitro* growth inhibitory activity against phytopathogenic fungi viz. *Alternaria alternata, Colletotrichum capsicum, Fusarium oxysporum* and *Rhizoctonia solani* and bacteria viz. *Bacillus subtilis* and *Escherichia coli*. Adequate temperature, requisite nutrients and growth media free from other microorganisms were employed for the growth of cultures of both fungi and bacteria[9]. The stock solutions were prepared by dissolving the compounds in DMSO and testing was carried out using two-fold serial dilution technique[10]. The lowest

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Table 1—Characterization data of ligands and their organosilicon/tin complexes

Compounds	M.P. (°C)	Found (Calcd), % C	H	N	Cl	Sn/Si
L_I	188	69.7(70.1)	4.9(5.2)	9.3(9.1)	-	-
$Me_2SiCl_2L_I$	212	55.2(54.9)	4.8(5.0)	6.1(6.4)	16.5(16.3)	6.8(6.4)
$Me_2SnCl_2L_I$	230	45.3(45.5)	3.9(4.2)	5.0(5.3)	13.7(13.5)	22.1(22.5)
Ph_3SnClL_I	211	61.9(62.3)	4.7(4.5)	4.5(4.4)	4.8(5.1)	16.9(17.2)
L_{II}	195	70.3(70.8)	5.3(5.6)	9.0(8.7)	—	—
$Me_2SiCl_2L_{II}$	160	55.7(55.9)	5.1(5.3)	5.9(6.2)	16.2(15.8)	5.9(6.2)
$Me_2SnCl_2L_{II}$	196	46.8(46.5)	4.1(4.4)	4.8(5.2)	12.8(13.2)	22.3(22.0)
Ph_3SnClL_{II}	241	63.1(62.8)	4.7(4.6)	4.3(4.0)	4.9(5.0)	16.5(16.8)

concentration of compound which resulted in complete inhibition of the visible mycelium growth (except for bacteria *B. subtilis*, which was seen under microscope) after incubation, was recorded as MIC (minimum inhibitory concentration) values. The incubation period for the fungi and bacteria was 72 h at 37°C and 48 h at 28°C respectively. The conventional fungicide, 2-(methoxy carbomyl)benzimidazole (bavistin) and bactericide, streptopencillin, were used as standards for comparing the activity of the compounds.

Results and discussion

The ligands and their complexes with organotin/silicon chloride were synthesized and characterized by elemental analyses (Table 1) and spectroscopic techniques. The low molar conductance values (7.0-21.0 ohm^{-1} cm^2 mol^{-1}) of the complexes indicated their non-electrolytic nature. Molecular weight determination of the complexes of hydrazones of organotin/silicon chlorides suggested the general formula $R_{4-n}ML_I$-$L_{II}Cl_n$.

The IR spectra of the ligands exhibited two bands ~3220-3200 and 1660-1640 cm^{-1} which were assigned to νNH and νC = O vibrations respectively. The strong band at 1615-1600 cm^{-1} was assigned to the combination of νC=N and νC=C mode. In the spectra of the ligands, a broad band centered at 3450 cm^{-1} indicated the existence of νOH group on the acetophenone. Also, the broadness of this band suggested the presence of a hydrogen bond between the azomethine nitrogen of the hydrazone and OH group. Moreover, a weak band in the region 2810-2790 cm^{-1} was attributed to the intramolecular hydrogen bond OH group[11]. The spectra of organotin and organosilicon complexes revealed negative spectral shifts in the νC=O and νC=N modes relative to the free ligands which appeared at 1635-1620 and 1605-1585 cm^{-1} respectively. These data are indicative of the donation through oxygen and nitrogen atoms of the carbonyl and azomethine groups. Of the two nitrogens of azomethine group, coordination through N(2)[nitrogen of terminal azomethine group] is suggested as it gives rise to stable five-membered ring with lesser strain as compared to that of four membered ring which would be formed on coordination through other nitrogen. The bands in the region 1060-1040, 840-820, 500-470, 710-690 and 400-390 cm^{-1} were assigned to νSi–O, νSi–C, νSi-O(C), νSi–N and νSi–Cl respectively[12-14]. Similarly the regions 590-570, 560-550, 410-390 and 320-305 cm^{-1} were assigned to νSn–O, νSn-C, νSn–N and νSn–Cl vibrations respectively[15,16].

In ^1H NMR spectra of the ligands, signals observed at 10.8, and 8.3 ppm were attributed to protons of intramolecularly hydrogen bonded OH group, and NH group respectively. The multiplet in the region 7.5-7.0 ppm was due to aromatic protons. Two olefinic protons appeared as doublets at 6.7 and 8.1 ppm were assigned trans configuration on the basis of coupling constant (16 Hz). The protons of methyl group attached to phenyl ring and azomethine group were observed as singlets at 2.5 and 2.2 ppm respectively. In the spectra of complexes proton signals due to azomethine and NH group were shifted to 9.4 and 8.6 ppm respectively confirming the involvement of N(2) nitrogen in coordination. No shift was observed in the signal due to proton of OH indicating the non-reactivity of *o*-hydroxy group of acetophenone during coordination. A sharp singlet observed at 1.1 to 1.3 ppm was attributed to methyl protons attached to tin moiety while in the case of corresponding silicon complexes, it was observed at 0.5-0.8 ppm. Similar

changes in the signal positions were observed in the spectra of the organosilicon complexes. The integral proton ratio of various groups in the spectrum of each compound was well in agreement with the proposed structure.

A perusal of the fungicidal and bactericidal data indicated that most of the compounds exhibited promising activity against all the tested organisms. The activity of most of the ligands was appreciably enhanced on complexation with organotin/silicon halides. Complexes of triorganotin halide was found to be more potent than their diorganotin counterparts which is in conformity with the earlier reports[17].

Rhizoctonia solani was least affected organism by the ligands (MIC values 100) but the activity increased on complexation with organotin/organo-silicon chlorides. Organosilicon complexes were found to be less active as comapred to the ligands against *Fusarium oxysporum* but organotin complexes showed better growth inhibition upto 3.215 ppm. Not much variation was observed in the activity of ligands and their organo-silicon complexes against *Alternaria alternata* but among their organotin counterparts, Ph_3SnL_ICl showed MIC value of 3.215 ppm. *Colletotrichum capsicum* was moderately effected organism by the ligands (MIC values varied between 100 to 50 ppm) but their complexes were quite active.

The ligands showed complete inhibition at more than 100 ppm against gram negative *Escherichia coli* but their complexes were more active. Among the complexes, $Ph_3SnL_{II}Cl$, exhibited growth inhibition upto 6.25 ppm. Bactericidal activity of ligands and their complexes against gram positive *Bacillus subtilis* varied between 12.5-50 ppm. All the ligands and complexes were less toxic than conventional bactericide, streptopencillin, used for the comparison of results.

No definite activity pattern was observed with the change of substituents on the ligands. However, complexes of organotin chlorides were found to be more potent than organosilicon complexes and free ligands. The complexes of triorganotin chlorides possessed higher activity than the diorganotin complexes.

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