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, fungicidal, antitumor and acaricides. In continuation of our earlier research on biologically active metal complexes 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 $[R_{1-a}M_{1-a}L_{a}Cl]_{n}$; $M=$Sn or Si; $R=$Me or Ph; $n=$1 or 2; $L_1, L_2=$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 benzoal prop-2-ene-1-0ic 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$_2$O$_5$. The analytical 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. The stock solutions were prepared by dissolving the compounds in DMSO and testing was carried out using two-fold serial dilution technique. The lowest
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, streptomycin, 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 (7.0-2.0 ohm·cm²·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 R₄-nML₁Clₙ.

The IR spectra of the ligands exhibited two bands ~3220-3200 and 1660-1640 cm⁻¹ which were assigned to vNH and vC=O vibrations respectively. The strong band at 1615-1600 cm⁻¹ was assigned to the combination of vC=N and vC=C mode. In the spectra of the ligands, a broad band centered at 3450 cm⁻¹ indicated the existence of vOH 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. The spectra of organotin and organosilicon complexes revealed negative spectral shifts in the vC=O and vC=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 vSi-O, vSi-C, vSi-O(C), vSi-N and vSi-Cl respectively.

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 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.

*Rhizoctonia solani* was least affected organism by the ligands (MIC values 100) but the activity increased on complexation with organotin/silicon chlorides. Organosilicon complexes were found to be less active as compared 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, Ph3SnL2Cl showed MIC value of 3.215 ppm. *Colletotrichum capsicum* was moderately affected 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, Ph3SnL2Cl, 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, streptopenicillin, 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.

References

5. Ascher K R S & Nissim S, World Review of Pest Control, 3 (1964) 188.