PESTICIDAL AND NEMATICIDAL PROPERTIES OF ORGANOSILICON (IV) DERIVATIVES OF NITROGEN–NITROGEN DONOR SULPHONAMIDE IMINE

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ABSTRACT

Biologically potent new tri– and di–organosilicon (IV) derivatives of sulphonamide imine have been prepared by the reaction of the corresponding tri– and di–organosilicon (IV) chlorides with the sodium salt of sulphonamide imine 1:1 and 1:2 molar ratios, in refluxing methanol. These derivatives have been characterised by element analyses, molecular weight determinations, conductivity measurements, melting point determinations, and UV, IR and NMR (^{1}H and ^{29}Si) spectral studies. All the complexes are monomeric and non–electrolytic in nature and are soluble in most of the organic solvents. IR and NMR spectral data of these complexes show the bidentate behaviour of sulphonamide imine and five–or six–coordinated structures for tri or diorganosilicon (IV) derivatives, respectively. The pesticidal and nematicidal activities of all the complexes have been studied by screening them against organisms and the results have been compared.

Key words: Pesticidal, Nematicidal, Organosilicon (IV), Sulphonomide imine, Nitrogen, Nitrogen–donor

INTRODUCTION

Organosilicon complexes with N,O and N,S donor ligands have been reported[1–3], and are widely used in medicinal and pharmaceutical chemistry[4,5]. Certain organosilicon compounds have been extensively used in chemical vapours deposition[6] and deoxygenation reactions in organic transformations[7]. Moreover, they are valuable synthons for a wide variety of useful chemicals[8].

The predominating factor, which appears to govern the formation of higher coordinated derivatives in the case of silicon is the shape and diffused character of the 3d orbitals[9]. However, certain amount of concentration of these orbitals due to some positive charge on the silicon atoms being induced by even weakly electronegative substituents appears to be essential for their participation in suitable bond formation[10]. Organosilicon compounds of several types have been found to possess significant biological activities and are used as fungicides[11], bactericides[12,13] and antitumour[4] agents. Keeping these facts in mind, we have synthesized

some organosilicon (IV) complexes with a biologically potent ligand 2–acetylnaphthalene sulphapyridine and screened them for their pesticidal and nematicidal activities.

EXPERIMENTAL

All the chemicals and solvents were dried and purified by standard methods. The reactions were carried out under strictly anhydrous conditions.

Preparation of the Ligand

The ligand was prepared by the condensation of 2–acetylnaphthalene with sulphapyridine in 1:1 molar ratio by refluxing the reacting species for 5–6 hours in alcohol. The important physical properties and analytical data have been given in Table 1.

Table 1. Analytical data and physical properties of the ligand and its complexes

Compound	Colour and M.P. (°C)	Yield (%)	Analysis (%) Found (Calcd.)						Mol. Wt. Found (Calcd.)
			C	H	N	Si	S	Cl	
LH	White 162–164	72	68.69 (68.80)	4.71 (4.76)	10.38 (10.46)	–	7.87 (7.98)	–	371 (401.49)
Me$_2$SiCl(L)	Peach 115–117	71	60.73 (60.77)	4.82 (4.89)	8.44 (8.50)	5.61 (5.68)	6.43 (6.48)	7.13 (7.17)	464 (494.09)
Me$_2$Si(L)$_2$	Cream 161–163	70	67.02 (67.10)	4.88 (4.92)	9.73 (9.78)	3.19 (3.26)	7.39 (7.46)	–	833 (859.12)
Ph$_2$SiCl(L)	Brown 156–158	75	67.90 (67.99)	4.49 (4.56)	6.75 (6.79)	4.48 (4.54)	5.13 (5.18)	5.68 (5.73)	592 (618.23)
Ph$_2$Si(L)$_2$	Cream 153–155	71	70.79 (70.84)	4.62 (4.71)	8.49 (8.54)	2.79 (2.85)	6.47 (6.52)	–	961 (983.26)
Ph$_3$Si(L)	White 217–219	73	74.53 (74.62)	4.98 (5.04)	6.31 (6.36)	4.18 (4.25)	4.80 (4.85)	–	621 (659.88)

Preparation of the Complexes

To a weighed amount of Me$_2$SiCl$_2$, Ph$_2$SiCl$_2$ and Ph$_3$SiCl was added the sodium salt of 2–acetylnaphthalene sulphapyridine ligand in 1:1 and 1:2 molar ratios in dry methanol. The resulting solution was refluxed for 15–16 hours, filtered to remove sodium chloride and the excess of the solvent was removed under reduced pressure. The products were purified by repeated washing with *n*–hexane and ether.

The resulting monomeric complexes are coloured solids (Table 1). They are soluble in methanal, chloroform, DMF and DMSO. Conductance measurements in annydrous DMF at 10^{-3} M concentration show them to be non–electrolytes.

IR spectra were recorded as KBr pellets or Nujol mulls on a FT IR spectrophotometer, model magna IR–550. ^{1}H NMR spectra were recorded on JEOL FX 90Q spectrometer in DMSO–d_6 using TMS as an internal standard. ^{29}Si NMR spectra were recorded in methanol. Nitrogen and sulphur were determined by Kjeldahl's and Messenger's methods, respectively. Silicon was estimated as SiO_2.

RESULTS AND DISCUSSION

Spectral Studies

The IR spectra of the complexes do not show any band in the region 3250–3100 cm^{-1} and 1610 cm^{-1} which could be assigned to vNH and δN–H. This clearly indicates the deprotonation of the ligand as a result of complexation with the silicon atom. Sharp band at 1635 cm^{-1} which shifted to the lower frequency (*ca.* 15 cm^{-1}) in case of silicon compounds, indicating the coordination of the azomethine nitrogen to the silicon atom. New bands are observed in the spectra of the silicon complexes at *ca* 575±5 cm^{-1} and 437 and 422 cm^{-1} for v (Si ← N) and v(Si–Cl) vibrations, respectively. These remain absent in the spectrum of the ligand (Table 2).

Table 2. I.R. absorption, bands (in cm^{-1}) of the ligand and its silicon complexes

Compound	v(NH)	v(C=N)	δ (N–H)	v(M←N)	v(M–Cl)
Ligand	3250–3100 m	1635 vs	1610 w	–	–
Me$_2$SiCl(L)	–	1628 vs	–	575 w	422 m
Me$_2$Si(L)$_2$	–	1630 vs	–	578 w	–
Ph$_2$SiCl(L)	–	1624 vs	–	572 w	437 m
Ph$_2$Si(L)$_2$	–	1621 vs	–	575 w	–
Ph$_3$Si(L)	–	1623 vs	–	570 w	–

m = medium, vs = very strong, w = weak

The proton magnetic resonance spectral data have been recorded in DMSO–d_6. The chemical shift values relative to the TMS peak are listed in Table 3. The disappearance of –NH proton signals from compounds clearly indicates the deprotonation of the NH group after the substitution reaction. Further, in the spectra of the complexes, a downfiled shift in the position of the aromatic protons also indicates the coordination of the azomethine nitrogen to the silicon atom.

Table 3. ^{1}H NMR and ^{29}Si NMR Spectral data of the ligand and its complexes (δ, ppm)

Compound	CH₃	M–CH₃/C₆H₅	NH	Aromatic protons	^{29}Si
Ligand	2.11 (s,3H)	–	10.65 (br, 1H)	8.96–7.56(m)	–
Me₂SiCl(L)	2.23 (s,3H)	1.08s	–	8.20–7.65(m)	–94 ppm
Me₂Si(L)₂	2.20 (s,6H)	1.20s	–	8.58–7.10(m)	–126 ppm
Ph₂SiCl(L)	2.22 (s,3H)	7.98m*	–	8.34–6.9(m)*	–91 ppm
Ph₂Si(L)₂	2.18 (s,6H)	8.17m*	–	8.38–7.10(m)*	–105 ppm
Ph₃Si(L)	2.21 (s,3H)	8.09m*	–	8.35–6.9(m)*	–90 ppm

m* = merged together

The ^{29}Si NMR spectra of the complexes give sharp signals at δ–94 to –90 and δ–126 to –105 ppm which are in good agreement with penta coordinated and hexa coordinated states around the silicon atoms for 1:1 and 1:2 molar reactions, respectively (Fig.1).
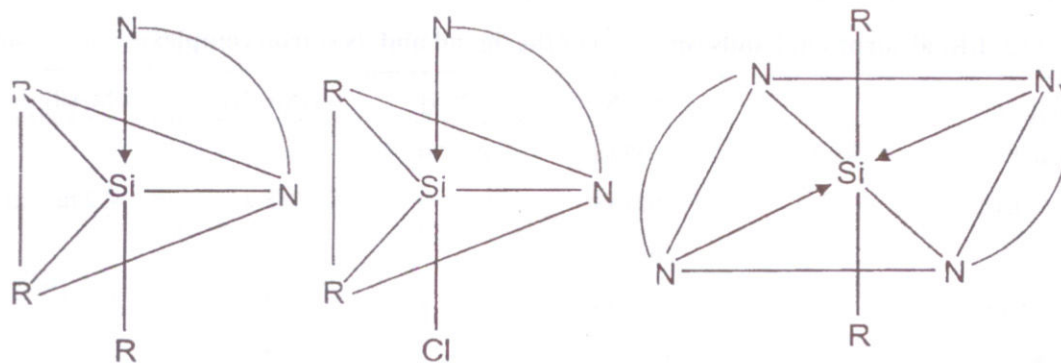
Figure 1

Biocidal Studies

The antifungal activity was evaluated against *Aspergillus niger, Macrophomina phaseolina, Fusarium oxysporum,* and *Alternaria alternata,* by the agar plate technique[15] (Table 4) and the activity against bacteria was evaluated by the Inhibition Zone Technique[16]. The organisms used in these investigations included *E. coli, Klebsiella acrogenous, Pseudononas cepacicola* and *Staphylococcus aureus* (Table 5).

Table 4. Fungicidal screening data of ligand and its silicon complexes, percent growth inhibition after 4 days at 25± 2°C. (25, 50 and 100 conc. in ppm)

Compound	Aspergillus niger			Macrophomina phaseolina			Fusarium oxysporum			Alternaria alternata		
	25	50	100	25	50	100	25	50	100	25	50	100
Ligand	37	45	63	38	46	64	41	53	60	43	55	62
Me$_2$SiCl(L)	38	51	67	41	51	67	44	57	67	46	59	67
Me$_2$Si(L)$_2$	45	58	76	48	59	78	47	62	76	49	62	79
Ph$_2$SiCl(L)	43	54	73	43	56	73	45	59	72	47	60	72
Ph$_2$Si(L)$_2$	47	58	79	49	61	80	48	63	78	50	63	81
Ph$_3$Si(L)	44	55	75	44	57	78	46	59	74	48	61	75

Table 5. Bactericidal screening data of ligand and its silicon complexes, percent inhibition after 24 hrs. at 28± 2°C. (25,50 and 100 conc. in ppm)

Compound	E. coli (–)		Klebsiella aerogenous (–)		Pseudomonas cepacicola (–)		Staphylococcus aureus (+)	
	500	1000	500	1000	500	1000	500	1000
Ligand	6	9	6	9	10	12	11	13
Me$_2$SiCl(L)	8	11	9	11	11	14	12	15
Me$_2$Si(L)$_2$	11	12	11	12	14	15	13	17
Ph$_2$SiCl(L)	9	12	10	11	12	14	13	16
Ph$_2$Si(L)$_2$	12	14	13	15	15	17	15	17
Ph$_3$Si(L)	10	13	11	12	13	15	14	16

The enhanced pesticidal activity of silicon chelates over their corresponding chelating agent may be explained by the chelation theory[17]. The chelation reduce the polarity of the silicon atom mainly because of partial sharing of its positive charge with the donor groups and possible π–electron delocalisation within the whole chelating ring. The chelation increase the lipophilic nature of the central atom which subsequently favours its premeation through the lipid layer of the cell membrane. The complexes screened exhibited considerable fungitoxicity even at lower

concentrations and it has been found that the fungal growth is directly dependent on the concentration of the complexes.

Nematicidal Activity

There are numerous estimates of the economic losses caused by nematodes in crop production in the world as a whole and also for individual countries. The magnitude of the loss depends upon the pathogenic nature of nematode spp., the degree in invasion, the species of the host plant and the condition of the cultivation. Besides causing quantitative losses, nematodes known to reduce vitamins and minerals in edible plant parts. It is estimated that 50% crop losses are caused by all kind of pest together and nematode share[18] in this may be about 5%.

Eggmasses were separated from heavily infected brinjal roots, washed from running water and cut into small 1–2 cm pieces. These were shaken in 500 ml of 1% NaOCl and at last sieving through 150 and 400 mesh sieves[19]. The treating solutions were prepared by water + methanol + chemicals and only water was taken in control plate. Only one eggmass in each petri dish, with different conc. of solutions (25, 50 and 100 ppm) was taken. The experiment was done under temperature range 30 ± 2^oC. The period which was fixed for experiment is 24 hrs. (one day). The spp. was used .

Meloidogyne incognita

These chemicals act by impairing nematode neuro–muscular activity, thereby reducing their movement, invasion, feeding and consequently the rate of the development and reproduction[20, 21]. It was observed that two thirty eggs were hatched in larvae in control plate and the result indicates that increasing the concentration of solution retards the hatching percentage.

Table 6. Hatching percentage in *Meloidogyne incognita* (25, 50 and 100 conc. in ppm)

Compound	25	50	100
Ligand	23.6	19.0	14
$Me_2SiCl(L)$	21.0	16.5	–
$Me_2Si(L)_2$	19.2	14.6	–
$Ph_2SiCl(L)$	20.5	16.0	–
$Ph_2Si(L)_2$	17.4	12.4	–
$Ph_3Si(L)$	18.9	15.2	–

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