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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND BIOLOGICAL EVALUATION OF SOME INNOVATIVE SILICON SCHIFF BASE COMPOUNDS

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ABSTRACT

A new series of bio effective organosilicon, (IV) complexes were isolated as coloured solids soluble in most of the organic solvents. These compounds were prepared by the reaction of trimethylsilicon chloride and triphenylsilicon chloride with the hydrazinecarboxamide and hydrazinecarbothioamide ligands of Schiff bases in 1:1 stoichiometry give complexes having general formula [R3Si(LlH)], [R3Si(L2H)], [R3Si(L3H)], [R3Si(L4H)], where R= triphenyl and trimethyl. Their molecular weight determinations show that the complexes are monomeric in nature. Conductivity measurement values in DMF lie in the range of 10-12 ohm-1 cm2 mol-1 indicate them to be non-electrolyte. The coordination behaviour and bonding pattern of these compounds are discussed by the support of electronic, infrared and multinuclear magnetic resonance (1H, 13C and 29Si NMR) spectral studies. These analyses suggest that the ligands act in a bidentate manner, coordinating metal through the oxygen/sulphur and nitrogen atoms. Trigonal bipyramidal geometry is assigned for 1:1 metal complexes. All the schiff base ligands and their corresponding organosilicon complexes have also been screened for their antifungal and antibacterial activities against Gram-positive bacterial strain (Staphylococcus aureus) and Gram-negative bacterial strains (Escherichia coli and Pseudomomas cepacicala).

KEYWORDS: Triorganosilicon (IV) complexes; thio- and semi-ligands; spectral studies; biochemical studies.

INTRODUCTION

Metal complexes of organosilicon(IV) and organotin(IV) halides with N,O, and S donor ligands have been received much more attention during the last few years1-4 because of the most important industrial5 and environmental applications6. N, O, and S donor ligands7 have been used to enhance the biological activities of organosilicon and organotin derivatives. The interest in organsilicon(IV)8 compounds is generated due to their versatile applicability in pharmaceutical and in chemical industries. It has been reported that the activity of sulphur containing ligand increases on complexation9−11.

The diverse steric and substitution patterns available to organosilicon compounds provide opportunities to design and control stability, solubility, and pharmacokinetic properties.

Numerous methods have been developed for the synthesis of new silicon-containing molecules and silicon derivatives of known drugs12−14.

Organosilicon(IV) complexes have been subjected of interest for their versatile applications in pharmaceutical and chemical industries. Organosilicon compounds of nitrogen and sulphur containing ligands are well known for their anticarcinogenic, antibacterial, antifungal, tuberculostatic, insecticidal, and a caricidal activities15–18. Generally, organosilicon complexes seem to owe their antitumor properties to the immune-defensive system of the organism 19. It has been reported that the activity of sulphur-containing ligand increases on complexation 20–24. The medical applications and effectiveness of the silatranes in the treatment of wounds and tumours are thought to be related to the role of silicon in the growth of epithelial and connective tissues and hair, where its function is to impart strengths, elasticity, and impermeability to water. Hetero nuclear Schiff base complexes have been found in applications as magnetic materials, catalysts, and in the biological engineering field25,26.

In view of this, it was considered worthwhile to synthesize organosilicon complexes of some stereo chemical as well as biological interest. Some of the organosilicon(IV) metal complexes of biologically potent Schiff bases are reported and their characterization has been made by elemental analysis and spectroscopic (UV, IR, ^{1}H, ^{13}C and ^{29}Si NMR) studies. Their antibacterial and antifungal activities have been screened against various fungi and bacteria.

EXPERIMENTAL

Physical Measurements

All the chemicals were dried and purified and the reactions were carried out with a distillation assembly, fitted with condensor and protected from moisture. Nitrogen was estimated by the Kjeldahl's method and sulphur was estimated by the Messenger's method. Silicon was determined gravimetrically as SiO_2. The conductance was measured by conductivity bridge type 304 Systronics model and the molecular weights were determined by the Rast Camphor method. IR spectra were recorded on FTIR spectrophotometer; model IR-550 as nujol mulls using KBr optics.^{1}H and ^{19}F NMR spectra were recorded in DMSO-D_6, ^{13}C and ^{29}Si spectra were recorded in methanol, using TMS as the internal standard. C_6F_6 was used as the external reference for the ^{19}F NMR spectra.

Synthesis of the Ligands, L_1H, L_2H, L_3H and L_4H

Ligands (L_1H and L_2H) were prepared by the condensation of heterocyclic ketones 1,3-dihydro-3-[2-(phenyl)-2-oxo-ethylidene]-2H-indol-2-one (5.2g) and 2-phenyl-3-(3-phenyl-3-oxoprop-1-enyl)-indol (6.5g) with hydrazine carboxamide (1.57g and 1.51g respectively) in the presence of sodium acetate in equimolar ratio (1:1) in absolute ethanol.

Similarly ligands (L_3H and L_4H) were synthesized by the condensation of above described heterocyclic ketones with hydrazine carbothioamide in appropriate 1:1 ratios. 1,3-dihydro-3-[2-(phenyl)-2-oxo-ethylidene]-2H-indol-2-one (5.2g) and 2-phenyl-3-(3-phenyl-3-oxoprop-1-enyl)-indol (6.0g) with hydrazine carbothioamide (1.90g and 1.69g respectively) in the presence of sodium acetate in equimolar ratio (1:1) in absolute ethanol.

These mixtures were heated under reflux for 45 minutes. The solvent was then removed and the residue was dried in vacuum under reduced pressure. The products were purified by recrystallization from the same solvent. The analysis and physical properties of these ligands are enlisted in (Table-1).

Synthesis of the Complexes

A calculated amount of the sodium salt of the ligand in dry methanol was added to the weighed amounts of Me_3SiCl and Ph_3SiCl in a round bottom flask in 1:1 molar ratios The reaction was refluxed over a ratio-head for 16-18 hours and the white precipitate of sodium chloride obtained, was removed. Compounds were dried under reduced pressure for 3-4 hours. These were purified by repeated washing with n-hexane and methanol. All the compounds were isolated as powdered solids. The details of these reactions and the analysis of the resulting products are recorded in (Table-1).

RESULTS AND DISCUSSION

Reactions of triorganosilicon (IV) halides with monobasic bidentate ligands in 1:1 molar ratio in methanol may be represented by the following equations:

$$Me_3SiCl + (N\frown S).Na \xrightarrow{1:1} Me_3Si(N\frown S) + NaCl$$

$$Ph_3SiCl + (N\frown S).Na \xrightarrow{1:1} Ph_3Si(N\frown S) + NaCl$$

$$Me_3SiCl + (N\frown O).Na \xrightarrow{1:1} Me_3Si(N\frown O) + NaCl$$

$$Ph_3SiCl + (N\frown O).Na \xrightarrow{1:1} Ph_3Si(N\frown O) + NaCl$$

(where, N S and N O = donar set of the ligands)

IR Spectra

The infrared spectra of the ligands and their silicon complexes were recorded and important features may be summarized as follows:

The IR spectra of the ligands show broad and medium intensity bands in region 3280-3100cm^{-1} due to *ν*NH mode. These disappear in the spectra of metal complexes thereby showing the deprotonation of the group. The two sharp bands around 3450 and 3350 cm^{-1} due to asymmetric and symmetric vibrations of the NH_2 group in the ligands, remain almost at the same positions in the metal complexes, showing non-involvement of this group in the complexation.

The bands of medium intensity appearing in the region 3300 cm^{-1} and 2700 cm^{-1} may be assigned to *ν*NH[27] and *ν*SH vibrations, respectively, which suggest that the ligands exist as in keto-enol tautomerism. These disappear in the corresponding tin complexes.

The band due to >C=N of free azomethine group in the ligands get shifted to the lower wave number ($\Delta\nu$= 15−20 cm^{-1}) in the silicon complexes indicating coordination through azomethine nitrogen[28]. The *ν*C=O band in hydrazinecarboxamide and *ν*C=S in hydrazinecarbothioamide appear at 1690 cm^{-1} and 1035 cm^{-1}, respectively. These bands disappear on complexation, which is due to the covalent bond formation of the ligand with the silicon metal through the oxygen or sulphur atoms.

Several new bands in the complexes at 620, 580 and 425 cm^{-1}, are due to ν(Si-O), *ν*(Si N) and *ν*(Si−S) respectively, which are absent in the spectrum of the ligand, further supporting the participation of the oxygen/sulphur atom and the azomethine nitrogen in complexation.

Electronic Spectra

A band due to the >C=N chromophore in the spectrum of the ligand at 365 nm shifts to a higher wavelength in the silicon complexes. This clearly indicates the coordination of the azomethine nitrogen to the tin atom. Such a shift in n- π * transition band is probably due to the donation of lone pair of electrons by the nitrogen of the ligand to the central metal atom indicating the delocalization of the electronic charge within the chetate ring and thus stabilizing of the resulting complexes. Further, two bands at 260 nm and 305 nm are due to π- π * transitions, these are assigned to the benzenoid ring and (>C=N) band of the azomethine group respectively. The K band π- π * showed a red shift due to the overlap of the central metal d-orbital with the p-orbital of the donor atom, which causes an increase in conjugation and the B-band undergoes a hypsochromic shift in the complexes.

^{1}H NMR Spectra

The proton magnetic resonance spectra[29] of the ligands and their corresponding silicon complexes were recorded in DMSO-d_6 using TMS as the internal standard. The chemical shift values (δ, ppm) of the different protons are given in (Table 2). The ^{1}H NMR spectra of the ligands exhibit peaks around of δ value 11.24−10.12 (1H) were characteristic of −NH of the isatin ring. The peaks found around δ value 7.74−6.36 (7H) may be due to aromatic protons, while that observed at δ value 10.08−10.04 (1H) due to −NH of thiosemicarbazone/semicarbazone. The disappearance of signal which is due to −NH of thiosemicarbazone/semicarbazone in the silicon derivatives indicate the coordination of the azomethine nitrogen atom as well as covalent bond formation between metal and sulphur/oxygen due to deprotonation of the ligands. In the spectra of the complexes, a downfield shift in the position of -CH_3 and aromatic protons indicate deshielding, as well as the coordination of azomethine nitrogen to the silicon atom. This is probably due to the donation of the lone pair of electrons by the nitrogen to the central metal atom, resulting in the formation of a coordinate linkage (Si N). The appearance of a signal around 2.98−2.54 δ value due to −NH_2 group at the same positions in the ligand and its silicon complexes, showing non-involvement of this group in coordination. The ^2J [^{1}H,^{29}Si] values for various tri organosilicon compounds indicate that the compounds have 5-coordinated environment[30] around them.

^{13}C NMR Spectra

The ^{13}C NMR spectra of the ligands and their corresponding tin complexes were also recorded in dry MeOH. Substantial shifts in the positions of carbon atoms attached to the azomethine nitrogen, thiolic sulphur or amido oxygen support the proposed coordination in these complexes. The heterocyclic moiety carbon signals, especially those of the carbon atoms directly bonded to the heteroatom, undergo slight upfield shifts relative to the other carbon atoms which remain almost undisturbed. The shift towards upfield in the signal of the thiolo carbon and azomethine carbon in the complexes suggest participation of these groups in coordination to the silicon atom. The heteronuclear coupling constant values viz ^1J [^{13}C,^{29}Si], ^2J [^{13}C, ^{29}Si] and ^3J [^{13}C,^{29}Si] for few compounds are also scrutinized which are very useful in providing the information regarding the geometry[31]of organosilicon complexes. The different δ values of all the carbon atoms of aromatic and phenyl group are listed in (Table 3and 4).

^{29}Si NMR Spectra

In the case of the silicon complexes $Ph_3Si(L_1)$ and $Me_3Si(L_2)$ signals at δ—96.5 ppm and δ−92.04 ppm for 1:1 complexes, respectively which stated for coordination number five[32] around the silicon atom. On the basis of the above spectral studies, possible trigonal bipyramidal geometry has been suggested for pentacoordinated state for all the 1:1 metal complexes (Figure 1).

EXAMINATION OF MICROBIAL ACTIVITY

Bioefficacies of the Schiff base ligands and their complexes were tested in *in vitro*, as well as in *in vivo*. The paper disc method[33] has been used for the antibacterial activity and percent disease incidence (PDI)[34] for antifungal screening.

Antibacterial Screening *(in vitro)*

Bacterial strains, *Staphylococcus aureus(+),Pseudomomas cepacicala(-)* and *Escherichia coli* (-) are selected for this study and the technique used is paper disc method[35]. In this technique sterilized hot nutrient agar and paper disc of Whatman No.1 were used. The discs having a diameter of 5 mm were soaked in the solutions of test compounds in methanol (500 and 1000 ppm concentrations). These discs were placed on agar medium previously seeded with bacterial suspension in petri plates and stored in an incubator at 30 ± 1°C. The inhibition zone around each disc was measured after 24-30 hours. Results have been recorded in the form of inhibition zones (diameter, mm) reported in (Table 5).

Antifungal Screening *(in vivo)*

Those chemicals which are found most effective against fungal and bacterial strains, tested in *in vitro*, were also tested in field for controlling the Rust in **Pearl millet** (*Pennisetum glaucum*) caused by *Puccinia substriata*. Field experiments were laid out in randomized block design plots with three replications. The crops (20 plants) were raised in each plot. Compounds with a standard fungicide, Bavistin, [2-(methoxycarbamyl) benzimidazole] were tried. After sowing of 45 days, the plants were inoculated artificially by spraying the conidial suspension. The suspension was prepared by crushing the infected leaves in water. The first spray of the respective fungicide was given, when lesions were first seen and were repeated after ten days. Disease intensity was analysed for statistical significance and (%) disease control on test compounds was worked out.

$$\text{PDI} = \frac{\text{Sum of score of infected plants} \times 100}{\text{Total number of plants observed} \times \text{Maximum rating of score (10)}}$$

The effectiveness of the chemicals were calculated using the following formula

$$\%\ \text{Disease control} = \frac{\text{PDI in treated plants} - \text{PDI in untreated plants}}{\text{PDI in untreated plants}} \times 100$$

The results of these findings are given in (Table 6).

Mode of Action

Metal based fungicides inhibit a wide range of enzymes involved in various metabolic pathways, ultimately causing cell death. Early work on the mode of action of fungicides showed that these compounds inhibit cell division. It was later[36] shown that the specific site of action is β-tubuline, a polymeric protein found in microtubules - an essential component of the cytoskeleton. Phenyl and amine groups in the complexes affect nucleic acid, synthesis and mitochondrial electron transport also.

This activity might be due to the presence of a hydroxyl and phenyl groups[37]. The increased activity in the organotin complexes may be due to the coordination and polarity of a silicon (IV) atom with oxygen of the ligand[38]. The order of increasing activities is; ligand<Me_3SiL<Ph_3SiL, the results matched with the previously reported data. The novel synthesized compounds are cost effective and are easy to synthesize. It is likely that the new complexes might be more environments friendly. There have been several reports dealing with the impact of organosilicon chemistry in the biosphere.

We might then expect at least the following regulatory processes to be operative.
Chelation theory[39] accounts for the increased activity of the metal complexes. Chelation reduces the polarity of the metal atom, mainly because of partial sharing of its positive charge with the donor groups and possible π electron delocalisation within the whole chelate ring. The chelation increases the lipophilic nature of the central atom, which subsequently favours its permeation through the lipid layer of the cell membrane.
An additional theory is based on penetration of cell wall[40]**.** It suggests chitinases and a another compound, β-1,3-glucanase, defense system of the plants, hydrolyze fungal cell walls and inhibit the rapid growth of fungal pathogens.

CONCLUSION

The results of fungicidal and bactericidal screening of the tin complexes against some pathogenic fungi and bacteria are recorded in Tables 5 and 6. The results show that the activity is enhanced on undergoing chelation. It is a well-known fact that the concentration plays a vital role in increasing the degree of inhibition. Hence as the concentration increases, the activity also increases.

The screening results have shown that the triorganosilicon(IV) complexes have better antibacterial activity than the free ligands. Furthermore, it has been shown that the triphenylsilicon(IV) derivatives exhibit significantly better activities than the trimethylsilicon(IV) derivatives.

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Table 1. Physical properties of the ligands and their organosilicon (IV) complexes

Compound	Colour and state	Molar ratio	M.P. (°C)	Analysis (%) Found (Calcd.)				
				C	H	N	S	Si
L_1H $C_{17}H_{14}N_4O_2$	Red Crystalline Solid		180-181	66.51 (66.66)	4.56 (4.61)	18.08 (18.29)	-	-
$Me_3Si(L_1)$ $C_{20}H_{22}N_4O_2Si$	Red Solid	1:1	132-134	63.32 (63.46)	5.73 (5.86)	13.92 (14.8)	-	7.28 (7.42)
$Ph_3Si(L_1)$ $C_{35}H_{28}N_4O_2Si$	Red Solid	1:1	141-143	74.30 (74.44)	4.89 (5.00)	9.78 (9.92)	-	4.80 (4.97)
L_2H $C_{24}H_{20}N_4O$	Red Crystalline Solid		176-178	75.61 (75.77)	5.18 (5.30)	14.60 (14.73)		-
$Me_3Si(L_2)$ $C_{27}H_{28}N_4OSi$	Brown Solid	1:1	137-138	71.52 (71.65)	6.12 (6.24)	12.22 (12.38)		6.11 (6.21)
$Ph_3Si(L_2)$ $C_{42}H_{34}N_4OSi$	Red Solid	1:1	148-150	78.82 (78.96)	5.24 (5.36)	8.63 (8.77)		4.25 (4.40)
L_3H $C_{17}H_{14}N_4OS$	Red Crystalline Solid		175-177	63.20 (63.34)	4.25 (4.38)	17.23 (17.38)	9.81 (9.95)	
$Me_3Si(L_3)$ $C_{20}H_{22}N_4OSSi$	Red Solid	1:1	160-162	60.63 (60.88)	5.45 (5.62)	13.85 (14.2))	8.01 (8.13	7.00 (7.12)
L_4H $C_{24}H_{20}N_4S$	Orange Solid		180-182	72.56 (72.70)	4.91 (5.08)	14.00 (14.13)	7.89 (8.09)	
Me_3Si (L_4) $C_{27}H_{28}N_4SSi$	Red Solid	1:1	162-164	69.02 (69.19)	5.78 (6.02)	11.84 (11.95)	6.75 (6.84)	5.85 (5.99)

Table 2. 1H NMR spectra data of the ligands and their organosilicon (IV) complexes

Compound	-NH ring(bs)	-NH free(bs)	$-NH_2$ (bs)	=CH-C=N (s)	Aromatic (indole ring) (m)	Si-Me/Ph $^2J(^1H-^{119}Sn)$ *Hz*	Aromatic (Phenyl) (m)
L_1H	12.32	10.08	2.36	8.08	7.24-6.08	-	7.38-7.01
$Me_3Sn(L_1)$	12.24	-	2.30	8.12	7.64-6.65	0.98 **^2J [6.6]**	7.45-7.32
$Ph_3Sn(L_1)$	12.08	-	2.28	8.16	7.88-7.16	6.24	7.90-7.40
L_2H	11.04	9.08	2.55	8.24	7.94-6.16	-	7.40-7.25
$Me_3Sn(L_2)$	10.92	-	2.34	8.63	7.88-6.56	1.08 **^2J [5.5]**	7.75-7.34
$Ph_3Sn(L_2)$	11.12	-	2.58	8.77	8.18-7.12	6.24	8.10-7.63
L_3H	12.80	10.32	3.46	8.64	7.94-7.54	-	7.38-7.22
$Me_3Sn(L_3)$	12.96	-	3.34	8.84	7.98-7.64	*0.*56 **^2J [6.5]**	7.58-7.22
L_4H	10.04	9.72	3.16	8.24	8.15-6.96	-	7.75-7.268

$Me_3Sn(L_4)$	10.98	-	3.12	8.64	8.36-7.08	0.96 ^2J **[6.2]**	7.96-7.58

Table 3. 13C NMR spectra data of the ligands and their organosilicon (IV) complexes

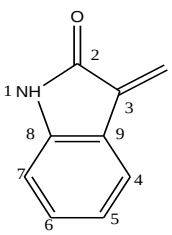
Compound	**Chemical Shift Values (δ, ppm)**					
	Amido/ thiolo	**Azomethine**	**-NH-C=O/ - NH-C-Ph**	**Aromatic * (indole ring)**	**Sn-Me/Ph**	**Phenyl ring ***
L_1H	170.52	159.92	165.86	141.24, 140.22, 126.16, 128.94, 129.94, 125.12, 124.08, 139.66	-	137.12, 128.29, 125.56, 131.15
$Me_3Sn(L_1)$	165.94	154.16	163.98	143.36, 142,01, 127.08, 129.92, 130.12, 126.72, 125.44, 140.11	14.98	139.98, 134.59 130.25, 132.25
L_2H	169.88	156.51	162.16	143.68, 142.28, 128.34, 123.34, 127.85, 125.66, 121.56, 141.92	-	140.93, 133.95 130.25, 133.51
$Ph_3Sn(L_2)$	166.58	151.36	163.32	146.72, 146.12, 129.38 125.11, 130.36,130.98, 125.72, 148.23	131.68, 130.16, 128.11, 127.58	144.11, 139.82 132.95, 136.95
L_3H	167.65	158.92	165.86	143.66, 140.22, 126.72, 129.10, 123.52, 123.18, 120.66, 141.29	-	136.1, 128.9, 127.5, 131.5
$Me_3Si(L_3)$	166.16	156.04	165.04	146.04, 150.01, 128.11, 129.28, 125.68, 131.52 126.72, 130.72	16.38	139.23, 132.19 128.25, 132.25
L_4H	168.58	157.64	168.50	143.66, 146.04, 135.72, 123.34, 120.23, 127.85, 126.54, 136.92	-	138.90, 131.95 128.5, 133.5
$Me_3Si(L_4)$	159.98	152.92	163.58	151.16, 148.98, 137.08 136.89, 132.52, 130.64, 126.72, 145.52	18.04	141.81, 132.12 130.85, 133.62

For compound $Ph_3Si(L_4)$ $^1J(^{13}C\text{-}^{119}Si)$ = *112.6Hz – 110.5Hz,*
$^2J(^{13}C\text{-}^{119}Si)$ = *4.6Hz- 4.2Hz* $^3J(^{13}C\text{-}^{119}Si)$ = *2.8Hz -2.5 Hz*

***** Detailed Values of aromatic and phenyl carbons are given in below table 4.

Table 4

Compound	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}
L_1H	141.24	140.22	129.94	128.94	126.16	125.12	124.08	139.66	128.29	137.12	131.15	130.05
$Me_3Sn(L_1)$	143.36	140.11	130.12	129.92	127.08	126.72	125.44	142.01	139.98	134.59	132.25	130.25
L_2H	143.68	142.28	128.34	127.85	125.66	123.34	121.56	141.92	140.93	133.95	133.51	130.25
$Ph_3Sn(L_2)$	148.23	146.12	130.98	130.36	129.38	125.11	125.72	146.72	144.11	139.82	132.95	136.95



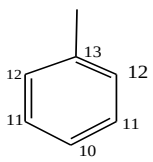


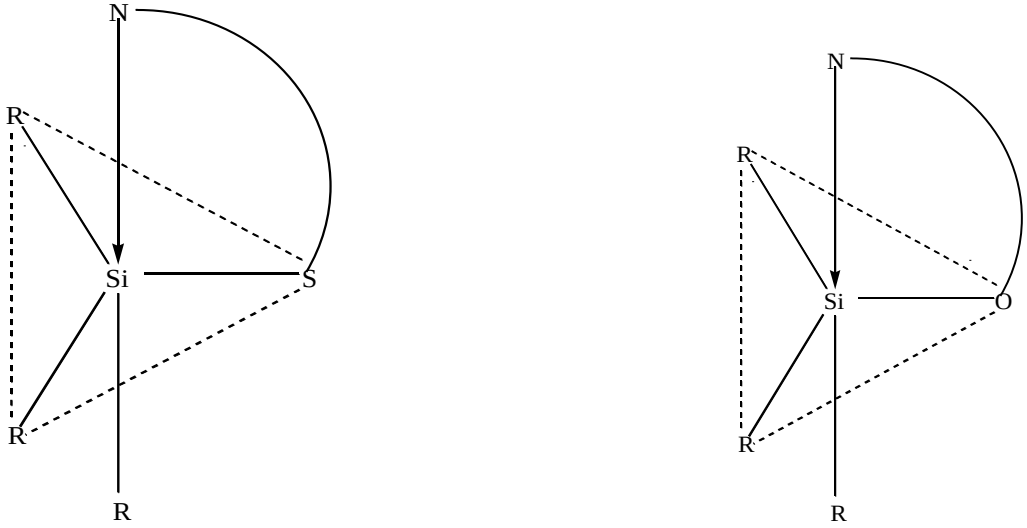
Table 5. Bactericidal screening data of the ligands and their Silicon complexes

Compound	Diameter of inhibition zone (mm)					
	Staphylococcus aureus (+) (Concentration in ppm)		*Escherichia coli* (-) Concentration in ppm)		*Pseudomomas cepacicala(-) (Concentration in ppm)*	
	500	1000	500	1000	500	1000
L_1H	7	10	6	10	5	9
$Me_3Si(L_1)$	9	13	9	11	6	10
$Ph_3Si(L_1)$	11	14	10	12	8	12
L_3H	8	12	7	11	7	11
$Me_3Si(L_3)$	11	13	9	12	8	12
$Ph_3Si(L3)$	13	15	10	13	9	14
Streptomycin	15	17	17	18	14	16

Table 6. Efficacy of the compounds against Rust in Pearl millet (Pennisetum glaucum) was evaluated using the Percent Disease Incidence Technique (PDI)

Compound	PDI in treated plants	% Disease control
L_1H	12	57.1
$Me_3Si(L_1)$	9	67.8
$Ph_3Si(L_1)$	7	75.0
L_2H	10	64.2
$Me_3Si(L_2)$	9	67.8
$Ph_3Si(L_2)$	6	78.5
Bavistin	3	89.3

Figure 1. Suggested structures for the complexes; R= Me or Ph and N S and N O = donar set of the ligands



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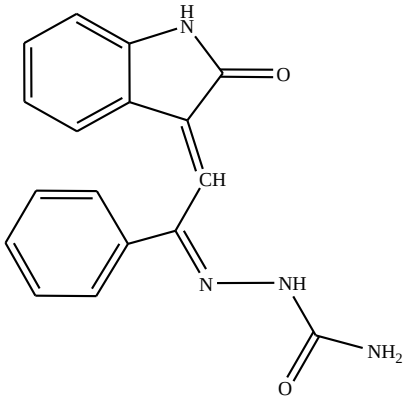
Structure of Ligands



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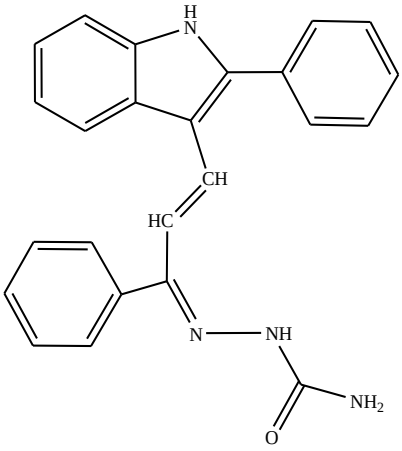

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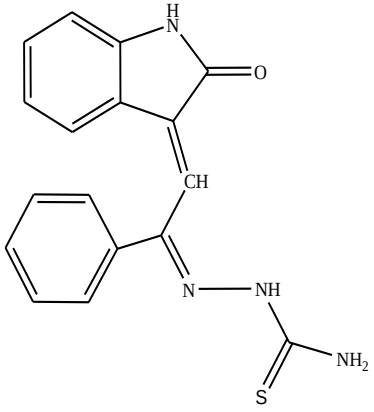

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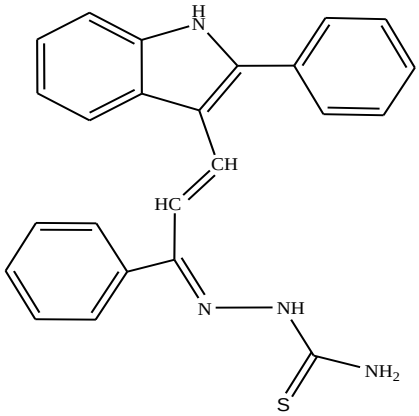

L_4H