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**Research Article**

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# Studies on synthesis, characterization, antifungal and antibacterial activities of organosilicon derivatives

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**ABSTRACT**

*This paper deals with the synthesis, spectral, and biological studies of organosilicon (IV) complexes derived from the reaction of organosilicon(IV) chlorides with the sodium salts of 1-(4-chloro-2-oxo-2H-chromen-3-yl)-methylene)-thiosemicarbazide ($L^1H$) 1-(4-chloro-2-oxo-2H-chromen-3-yl)-methylene)-semicabazide ($L^2H$) in 1:1 and 1:2 molar ratios and investigated using a combination of elemental analysis, melting point determinations, molecular weight determinations, IR, $^1$H-NMR ,$^{13}$C NMR, $^{29}$Si NMR, studies. Ligands and their silicon complexes have been screened for antimicrobial and antifungal activities. Spectral studies confirm ligands to be monofunctional bidentate and trigonal bipyramidal and octahedral environments around silicon ions.*

**Keywords:** Silicon(IV) complexes, spectral studies, antifungal activity, antibacterial activity.

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## INTRODUCTION

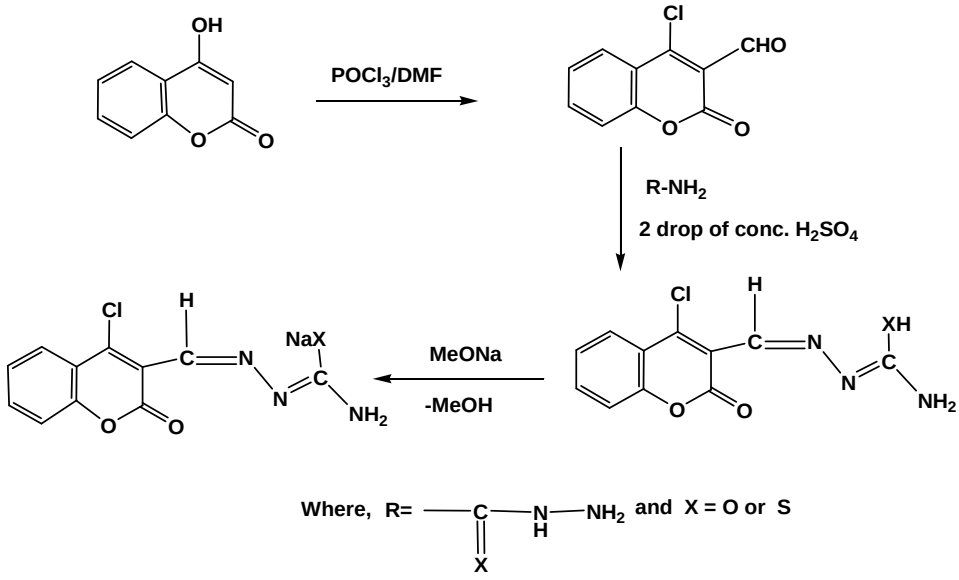
Schiff base complexes have an important and popular area of research due to their simple synthesis, versality and diverse range of applications.[1] The Schiff bases play a significant role in the area of coordination chemistry. The study of a range of coordination compounds is linked to the coordination of metals with the Schiff base ligands. The schiff bases are widely used ligands to synthesize their metal complexes due to their facile synthesis, significant and good solubility in common organic solvents. Thus, they have played a important applicable role in research and development of coordination chemistry as they readily form stable metal complexes in different oxidation states[2]. The schiff base complexes of main group elements containing ligands such as semicarbazones and thiosemicarbazones have remained a topic of significant current research interest[3]. This is mainly because of biological applications not only of ligands but also of compounds derived from them. Semi- and thiosemicarbazones can act as neutral or charged ligands. They can show tautomerism and can exist in keto/thione or enol/thiol form. semicarbazones and thiosemicarbazones have also attracted attention due to their biological activities. These compounds present a wide variety of biological activities such as antitumoral[4,6] fungicidal[7,8] bactericidal[9] and antiviral. It is known that some drugs have increased activity when administered in the form of the metal complexes[10] and a number of metal chelates inhibit tumor growth.[11] In the treatment of cancer, the active species is not the semicarbazones or thiosemicarbazones but their metal chelates.[11,12] The rapid rise in the industrial, agricultural, biological, and medical applications of organosilicon(IV) compounds during the last few decades have led to their accumulation in the environment and in biological systems. Organosilicon compounds of sulfur containing ligands have attracted much attention recently due to their biological importance. The sulfur containing ligands are well known for their anticarcinogenic, antibacterial, tuberculostatic, antifungal and acaricidal effect. It has been reported that the activity of sulfur-containing ligands increases on complexation.[13]

## EXPERIMENTAL SECTION

All the synthetic reactions were performed under moisture free conditions. All the chemicals used were of reagent grade. Solvents (E Merck) were dried by standard methods before use. Metal salts, $Ph_2SiCl_2$ as well as 4-hydroxy coumarin were purchased from Alfa Aesar and used as such.

**Preparation of 3-Formyl-4-chlorocoumarin**:- Phosphorus oxychloride (10 mL) was added dropwise to a solution of dimethylformamide (DMF) (20 mL) keeping the temperature below 5◦C. Solution of 4-hydroxycoumarin (4.0 g) in DMF (10mL) was then gradually added to the mixture with constant stirring and maintaining the temperature of the reaction mixture below 5◦C. The reaction mixture was then allowed to stand at room temperature for 2 h and then heated on a steam bath for 1h. After cooling, the reaction mixture was poured onto crushed ice and neutralized with sodium carbonate. A solid product was immediately formed which was crystallized from ethanol to give a yellow solid (80%), MP 115◦C [14].

**Preparation of ligands:-** The ligand was prepared by the condensation of 3-formyl-4-chlorocoumarin (0.02 mol) with semi and thiosemicarbazide in 1:1 ratio and the contents were refluxed for nearly 3-4 h. The residue formed was separated out, filtered off, washed with water, recrystallized from ethanol and finally dried in vacuum over fused calcium chloride.




**Scheme 1. Synthesis of ligand**

**Preparation of the silicon complexes**

For the preparation of complex , a calculated amount of $Ph_2SiCl_2$ in about 30 ml of methanol in a round bottom flask were taken, and a requisite amount of sodium salt of the ligand in the same solvent was added to this solution. The contents were refluxed over a fractionating column for 12–14 h. After the completion of the reaction, the excess of the solvent was removed and NaCl was precipitated out and removed by filtration. The complexes were subsequently dried for 3–4 h and then repeatedly washed with methanol and n-hexane so as to ensure their purity and then dried a second time under reduced pressure. The synthetic details and elemental analyses of the resulting silicon complexes are listed in Table I.

$$Ph_2SiCl_2 + LNa \xrightarrow[-NaCl]{methanol} Ph_2Si(L)Cl \quad 1:1$$

$$Ph_2SiCl_2 + 2\,LNa \xrightarrow[-2\,NaCl]{methanol} Ph_2Si(L)_2 \quad 1:2$$

**Where, L= $L^1$ or $L^2$**

**Table 1. Analytical data and physical properties of the ligands and their silicon complexes**

| Compound | Colour | Melting Point($^0$C) | Found (Calcd.)(%) | | | | | Mol.Wt Found (Calcd.) |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | S | Si | |
| **$L^1H$** | Yellow | 127 | 45. 95 (46.90) | 2.65 (2.86) | 14.72 (14.92) | 11.12 (11.38) | - | 278.15 (281.71) |
| **$L^2H$** | White | 133 | 48.01 (49.73) | 2.98 (3.04) | 15.56 (15.82) | - | - | 261.32 (265.65) |
| **$Ph_2SiCl(L^1)$** | Brown | 141-145 | 54.02 (55.42) | 3.39 (3.43) | 7.56 (8.43) | 5.56 (6.43) | 4.25 (5.63) | 496.75 (498.37) |
| **$Ph_2SiCl(L^2)$** | Dark brown | 130-135 | 56.05 (57.27) | 3.06 (3.55) | 7.56 (8.71) | - | 5.02 (5.82) | 481.03 (482.32) |
| **$Ph_2Si(L^1)_2$** | Yellow | 215-218 | 55.85 (56.27) | 3.02 (3.33) | 10.56 (11.58) | 7.85 (8.83) | 3.02 (3.87) | 724.23 (725.62) |
| **$Ph_2Si(L^2)_2$** | Brown | 250-255 | 56.03 (57.38) | 2.01 (2.26) | 10.56 (11.81) | - | 3.01 (3.9) | 710.03 (711.57) |

## ANTI-MICROBIAL STUDIES

### Antibacterial activity

The newly prepared compounds were screened for their antibacterial activity against *Escherichia coli* (ATCC25922) and *Bacillus subtilis* (ATCC6633) by paper disc plate method. Each compound was dissolved in DMSO and solutions of the concentrations (500 and 1000 ppm) were prepared separately. Paper discs of Whatman filter paper (No. 42) of uniform diameter (2 cm) were cut and sterilized in an autoclave. The paper discs soaked in the desired concentration of the complex solutions were placed aseptically in the Petri dishes containing nutrient agar media (agar 20 gþbeef extract 3 gþpeptone 5 g) seeded with *Escherichia coli* and *Bacillus subtilis* .The antibacterial activity of common standard antibiotic Imipinem was also recorded using the same procedure as above at the same concentrations and solvent. The medium with DMSO as solvent was used as a negative control whereas media with Imipinem (standard antibiotics) were used as positive control. The experiments were performed in triplicates.[15]

### Antifungal activity

The newly prepared complexes were also screened for their antifungal activity against *Fusarium oxysporum* (ATCC7808) and *Rhizopus nigricans* (ATCC6227b) in DMSO by agar diffusion method[16]. The fungi were grown in potato-dextrose agar medium (glucose- 20 g, starch- 20 g, agar-agar- 20 g and 1000 mL of water) and the complexes after being dissolved in requisite concentration in DMSO were mixed in this medium. Several series of concentrations were prepared. The medium was then poured into Petri plates and small disc (0.7 cm) of the fungus culture was cut into a sterile cork borer and transferred aseptically in the centre of a Petri plate containing the medium with a certain amount of the compound. Suitable checks were kept where the culture plates were grown under the same conditions on PDA without the compound. These Petri plates were wrapped in polythene bags containing a few drops of alcohol and were placed in an incubator at 25±2˚C. Two replicates were used in each case. The colony diameter, after 96 h. was compared with the check. The result was compared with standard fungicide Bavistin. The percentage inhibition was calculated as-

% inhibition = 100(C-T)/C

Where, C and T are the diameters of the fungal colony in the control and the test plates, respectively.

## RESULTS AND DISCUSSION

The ligand and complexes synthesized are soluble in DMF and DMSO. Molecular weights were determined by the Rast Camphor method. Silicon was determined gravimetrically as $SiO_2$. Nitrogen was estimated by the Kjeldahl's method and sulfur was estimated by the Messenger's method[17]. Carbon and hydrogen analyses of the ligands and their silicon complexes were carried out at CDRI, Lucknow. U.V. Spectra of the ligands and their complexes were recorded in Methanol with the help of 752 UV spectrophotometer. Infrared spectra of the ligands and their complexes were recorded with the help of Nicolet Megna FTIR-550 spectrophotometer on KBr pellets. $^1$H NMR and $^{29}$Si NMR spectra were recorded on a JEOL-AL-300 FTNMR spectrometer in DMSO-$d_6$ using TMS as the internal standard.

### IR Spectra

The IR spectra of the free ligands display absorption bands at 3200-3150, 1600–1620 and 1060/1670cm$^{-1}$ due to -(NH), (>C= N), and (>C= S)/(>C=O), respectively. The bands at ca. 1710-1715 cm$^{-1}$ due to (>C=O) of lactone moiety of the ligands remain almost unchanged in the complexes indicating their non-involvement in complexation. The broad band due to -(NH) vibrations, disappears in the spectra of the complexes, indicating the deprotonation of

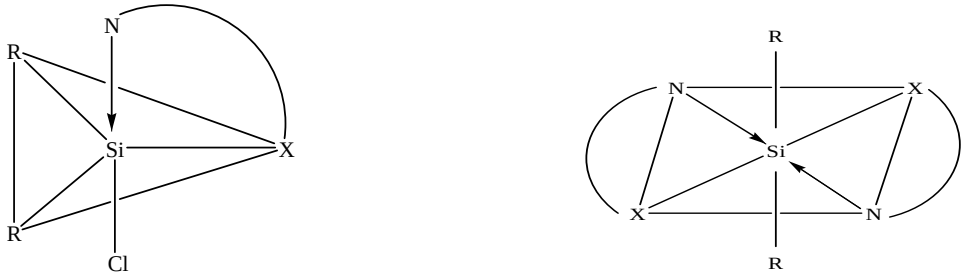
this group on coordination with the silicon atom. The negative shift (10–20cm$^{-1}$) of (>C=N) band observed in all the complexes indicates the involvement of azomethine nitrogen upon complexation. The bands due to (>C=S) and (>C=O) are shifted towards lower frequencies in the complexes indicating coordination of sulfur and oxygen to the central silicon atom.

**$^{1}$H NMR Spectra**

The broad signal due to the −NH proton in the ligand disappears in the case of silicon complexes showing the coordination of silicon to nitrogen after the deprotonation of the functional group. The ligands show a complex pattern in the region $\delta$ 8.22– 6.35 ppm for the aromatic protons and this is observed in the region $\delta$ 9.40–6.95 ppm in the spectra of the organosilicon(IV) complexes. This shifting also supports the coordination through the nitrogen atom.

**$^{29}$Si NMR Spectra**

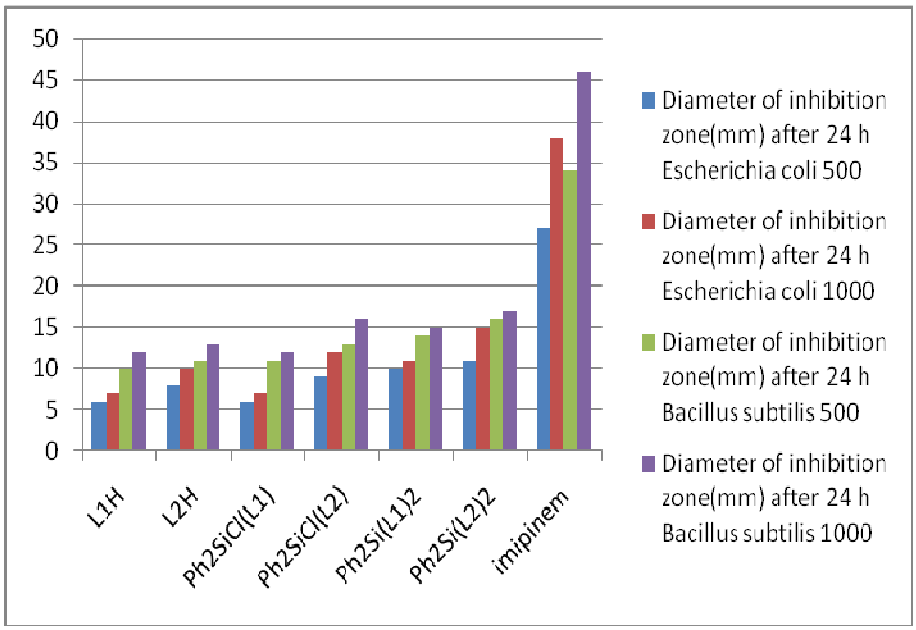
The $^{29}$Si NMR spectra of $Ph_2SiCl((L^1)$ and $Ph_2SiCl((L^2)$ give sharp signals at $\delta$-93 to $\delta$- 97 ppm and the spectra of $Ph_2Si(L^1)_2$ and $Ph_2Si(L^2)_2$ give sharp signals at $\delta$-120 to $\delta$-108 ppm , which clearly indicates the penta- and hexa-coordinated environments, respectively, around the silicon atom.




*Where, X= O or S and R = Me or Ph*

**Fig 2 Structures of silicon(IV) complexes**

**Graph 1: Antibacterial screening data of the ligands and their organosilicon complexes**

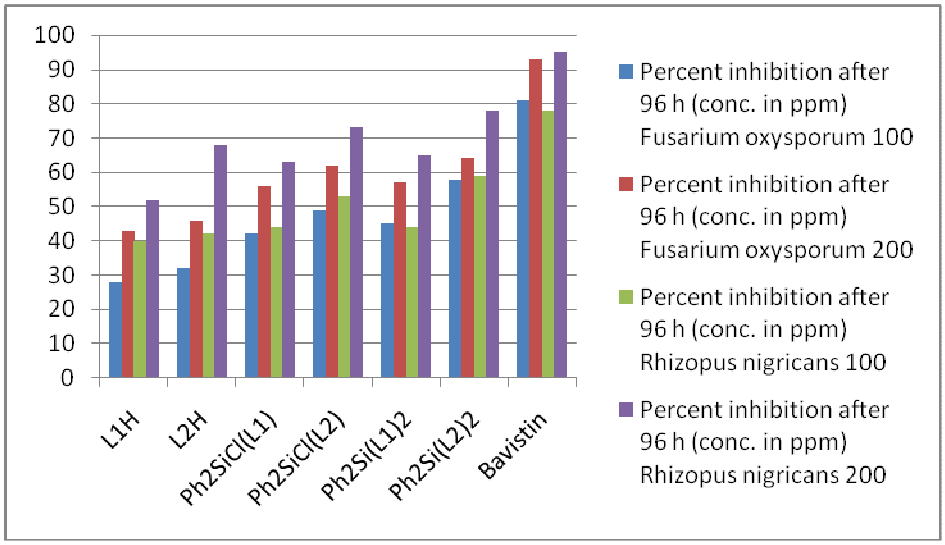



**ANTIMICROBIAL ASSAY**

The biological activity of the ligands exhibited a markedly enhancement on coordination with the metal ions against all the test bacterial/fungal strains (Graph1 and 2). The results show that the coordination compounds have enhanced activity compared with the ligand, which indicates that the coordinated metals have an influence on the antimicrobial effects. However, the higher activity of the complexes, compared with the free ligand, can be understood in terms of the chelating theory. Moreover, coordination reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor groups[18,19] within the chelate ring system formed during coordination. This process, in turn, increases the lipophilic nature of the central metal atom, which favors its permeation more efficiently through the lipid layer of the micro-organism[20] thus destroying them more aggressively. It has been suggested that the ligands with nitrogen and oxygen donor systems inhibit enzyme activity,

since the enzymes which require these groups for their activity appear to be especially more susceptible to deactivation by metal ions on coordination.

**Graph 2: Antifungal screening data of the ligands and their organosilicon complexes**




## CONCLUSION

We have synthesized biologically relevant ligands and their Si(IV) complexes. Based on various physicochemical investigations the penta- and hexa-coordinated environment, around the silicon atom has been proposed. The complexes showed higher antibacterial and antifungal activities as compared to the parent ligands. A large number of other coordination complexes of nitrogen/oxygen/sulfur donor ligands have been extensively screened for their biological activity. The complexes show better biological activities compared to the parent ligands. The compounds inhibit the growth of fungi and bacteria to a greater extent as the concentration is increased.

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