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Synthesis, Characterization and Antimicrobial Studies of Organosilicon(IV) Complexes Derived from Heterocyclic Sulphonamide Imines

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Abstract

This paper deals with the synthesis, spectral, and antimicrobial studies of organosilicon (IV) complexes derived from the interaction of organosilicon(IV) chlorides with the sodium salts of 1-(1-(2-oxo-2H-chromen-3-yl)ethylidene) sulphathiazole in 1:1 and/or1:2 molar ratios and characterized on the basis of analytical, conductance, and spectroscopic techniques. Probable trigonal bipyramidal and octahedral structures for the resulting derivatives have been proposed on the basis of electronic, IR, ^{1}HNMR, and ^{29}Si NMR spectral studies. The free ligand and its metal complexes have been tested *in vitro* against a number of pathogenic microorganisms in order to assess their antimicrobial properties. Both the ligand and its complexes were found to possess appreciable antifungal and antibacterial properties.

Keywords: Silicon(IV) complexes, Schiff bases, spectral analysis , antimicrobial studies.

Contents

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1. Introduction

Sulpha drugs are a group of compounds used for eliminating a wide range of infections in human and other animal systems[1]. Many chemotherapeutically important sulpha drugs, like sulphadiazine, sulphathiazole, possess SO_2NH moiety which exhibit an important toxophoric function[2]. Sulfa drugs are extensively used for the treatment of certain infections caused by Gram positive and Gram negative microorganisms[3]. Metal complexes of sulpha drugs have been found to be more bacteriostatic than the drug themselves[4].Schiff bases and their metal complexes have exhibited biological activity as antibiotics, antiviral, and antitumor agents because of their specific structures. Schiff base complexes have been found applications as magnetic materials, catalysts and in the biological engineering field[5-6]. Organosilicon compounds of sulphur-containing ligands have attracted much attention recently due to their biological importance. The sulphur containing ligands are well known for their anticarcinogenic, antibacterial, tuberculostatic, antifungal, insecticidal, and acaricidal activities[7-8]. It has been reported that the activity of sulphur-containing ligand increases on complexation[9-11]. The interest in organosilicon(IV) compounds is due to

their antitumour properties to the immuno defensive system of the organism[12]. The preparation and characterization of one biologically active sulphonamide imine derived from 3-acetylcoumarin with sulphathiazole and its silicon(IV) complexes form the subject of this paper.

2. Materials and Methods

All the reagents and the solvents used were dried, distilled, and purified using standard methods. Metal salts Ph_2SiCl_2 , as well as 1-(1-(2-oxo-2H-chromen-3-yl)ethylidene) and sulphathiazole were purchased from Alfa Aesar and used as such.

Synthesis of the Ligand

The ligand was prepared by the condensation of 1-(1-(2-oxo-2H-chromen-3-yl)ethylidene) with sulphathiazole 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.

Synthesis of the Complexes

For the preparation of Ph_2SiCl_2 complexes, methanol solutions of Ph_2SiCl_2 were mixed with the corresponding sodium salts of the ligand in equimolar ratio using methanol as a solvent. The solution was refluxed for a period of 15–17 hours. The white precipitate of sodium chloride formed during the course of the reaction was removed by filtration, and the filtrate was dried under reduced pressure. The resulting product was repeatedly washed with a mixture of methanol and *n*-hexane (1 : 1) and then finally dried for 3–4 hours. The purity was further checked by thin layer chromatography with silica gel-G using DMSO as a solvent.

3. Results and Discussion

The synthesized ligand and complexes respectively are soluble in DMF and DMSO. The reactions were carried out in perfectly dry methanol.

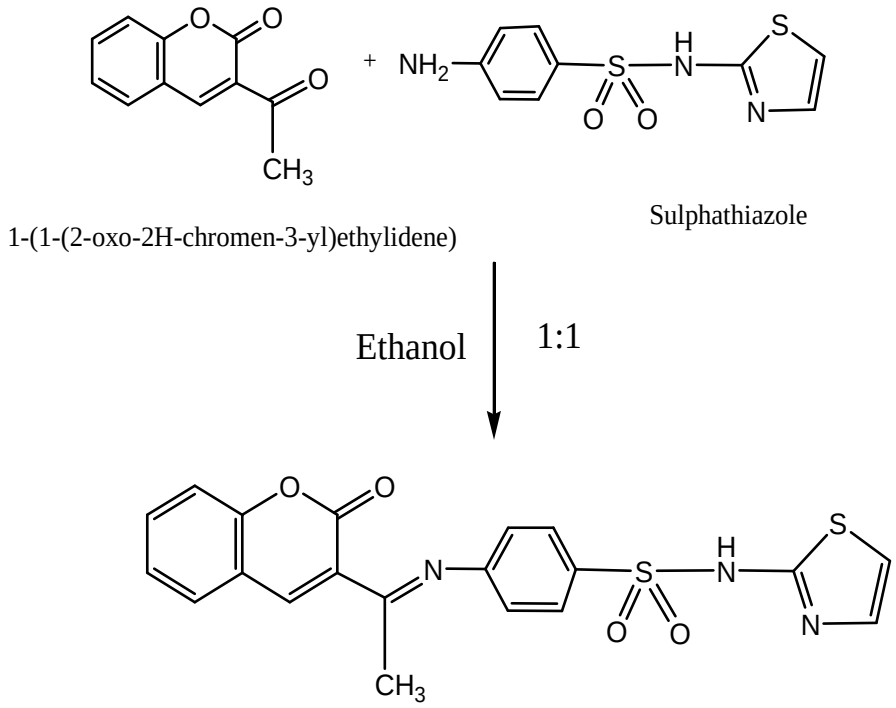


Figure 1. Synthesis of ligand

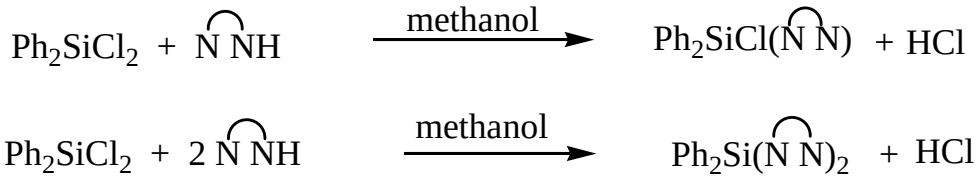


Figure 2. Synthesis of complexes

Physical Measurements and Analytical Methods

Molecular weights of the synthesized ligands and their metal complexes were determined by the Rast Camphor method. Nitrogen was estimated by the Kjeldahl's method and sulfur were estimated by the Messenger's methods[13]. Silicon was determined gravimetrically as SiO_2.

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

Compounds	Color	M.P.	Elemental analysis (%)				Molar mass (Calc.) Found
			N	S	Cl	Si	
L	Light yellow	130-135	(9.87) 8.12	(15.07) 14.67	--	--	(425.48) 421
$Ph_2SiCl(L)$	brown	145-150	(6.67) 5.23	(10.17) 9.58	5.62 (4.51)	4.45 (3.56)	(642.21) 640.00
$Ph_2Si(L)_2$	brown	155-160	(8.24) 7.12	(12.58) 12.14	--	2.76 (1.98)	(1031.24) 1015.14

Electronic spectra

The electronic spectrum of the ligand recorded in methanol display two maxima at ~276 and ~326 nm which are due to π-π* electronic transitions and remain almost unchanged in the spectra of the silicon complexes. The band around 370 nm is due to the n-π* transitions of the >C=N chromophore which undergoes a blue shift in the complexes due to the polarization within the >C=N chromophore caused by the silicon–ligand electron interaction during the chelation. The shift of this band in the spectra of the complexes suggests the coordination of nitrogen to metal atom.

IR Spectra

The infrared spectra of the starting materials and their silicon(IV) complexes were recorded and important features are discussed. The broad band due to -(NH) vibrations in the regon 3200-3050 cm^{-1}, disappears in the spectra of the complexes, indicating the deprotonation of this group on coordination with the silicon atom. The IR spectra of the free ligand display absorption bands at 1600–1610 due to >C= N , shifts to the lower frequency (ca. 10 cm^{-1}) in the silicon complexes, and this indicates the coordination of the azomethine nitrogen to the silicon atom. The spectra of the free ligand display two sharp bands at 3400–3500 and 3250–3300cm^{-1} due to asym and sym vibrations of NH_2 group, respectively, which remains at the same position in the spectra of metal complex. New bands in the regions 580–585 cm−1, and 560–565 cm−1 are due to *ν*(Si ← N), and *ν*(Si-N) modes, respectively, which further support the coordination through azomethine nitrogen to the metal atom and bonding of oxygen with the metal atom[14-15].

^{1}H NMR Spectra

The proton magnetic resonance spectra of the complexes were recorded in DMSO-d_6 . The broad signal (10.15 ppm) 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 free ligand shows a complex multiplet at δ 8.76-7.56 ppm for the aromatic protons and this remains at the same position in the spectrum of the organosilicon(IV) complexes. The methyl (-CH_3) proton signal appears at *δ* 2.10 ppm in the ligand. Further, a downfield shift in the position of methyl (-CH_3) proton in the spectra of the complexes also indicates the coordination of the azomethine nitrogen to the silicon atom. The additional signal in the region *δ* (7.90 and 8.20 ppm) are observed due to Ph_2Si group.

^{29}Si NMR Spectra

In order to confirm the geometry of the complexes, ^{29}Si NMR spectra were recorded in Methanol. The signals at δ -95 to - 91 and -101 to 120 ppm are indicative of penta- and hexacoordinated states of the silicon atom in the ^{29}Si NMR spectra of the complexes of $Ph_2SiCl(L)$ and $Ph_2Si(L)_2$ respectively[16].

Microbial Assay

In- vitro 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[17]. Each compound was dissolved in DMSO and solutions of the concentrations (500 and 1000 ppm) were

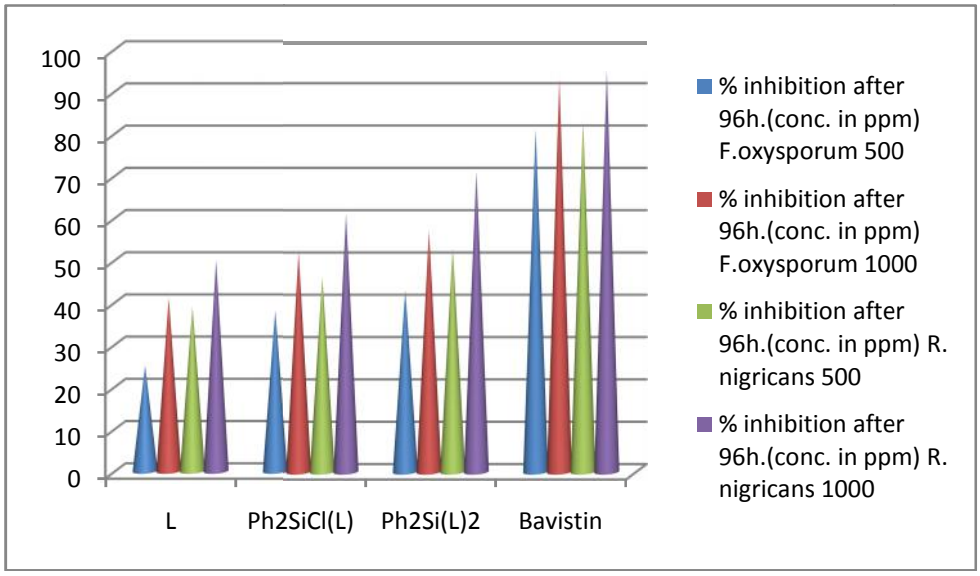
prepared separately. Paper discs of Whatman filter paper (No. 42) of uniform diameter (5 mm) were cut and sterilized in an autoclave. The paper discs soaked in the desired concentration of the complex solutions were placed aseptically in the petri dishes containing nutrient agar media (agar 20 g + beef extract 3 g + peptone 5 g) seeded with *E. coli* (ATCC25922) and *B. subtilis* (ATCC6633) bacteria strains separately. The petri dishes were incubated at 37°C and the inhibition zones were recorded after 24 h of incubation. 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.

***In- vitro* Antifungal Activity**

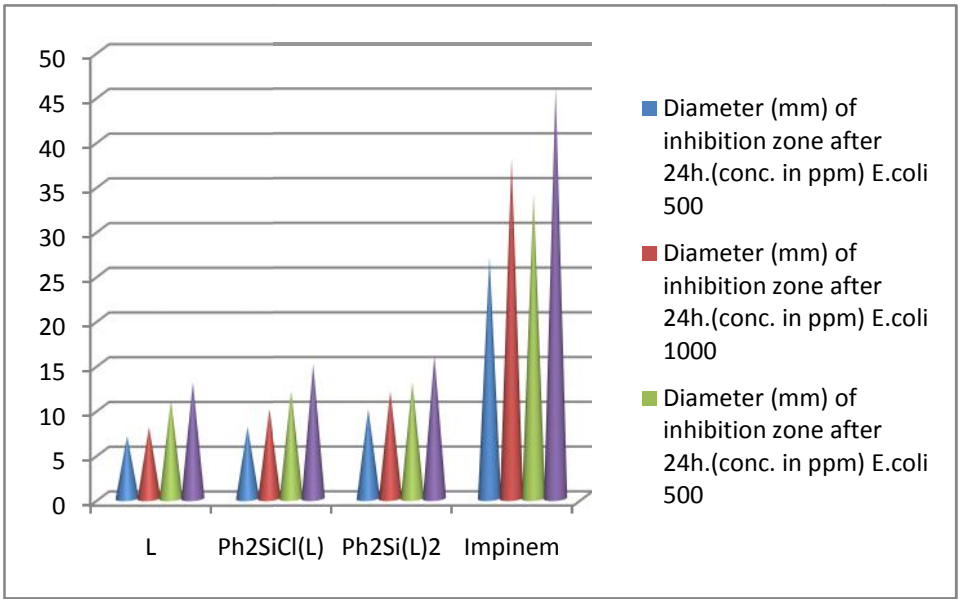
The newly prepared complexes were also screened for their antifungal activity against *Fusarium oxysporum* (ATCC7808) and *Rhizopus nigricans* (ATCC6227b) in DMSO by agar diffusion method[18]. Agar media was prepared by dissolving peptone (10 g), D-glucose (40g) and agar (20 g) in distilled water (1000 mL) and adjusting pH to 5.7. Normal saline water was used to make suspension spore of fungal strain lawning. A loopful of particular fungal strain was transferred to 3 mL saline to get suspension of corresponding species. Twenty milliliters of agar media were poured into each petri dish. Excess of suspension was decanted and plates were dried by placing in an incubator at 37° C for 1 h using an agar punch, wells were made and each well was labeled. A control was also prepared in triplicate and maintained at 37° C for 96 h. The fungal activity of each compound was compared with Bavistin as standard drug. The medium with DMSO as solvent was used as a negative control whereas media with Bavistin (standard antifungal) were used as positive control. The experiments were performed in triplicates. The cultures were incubated for 96 h at 35°C and the growth was monitored and the percentage of inhibition was calculated by equation:

$$\% \text{ inhibition} = 100(C-T)/C$$

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



Graph I. Antifungal screening of the Ligand and its complexes.



Graph II. Antibacterial screening of the Ligand and its complexes

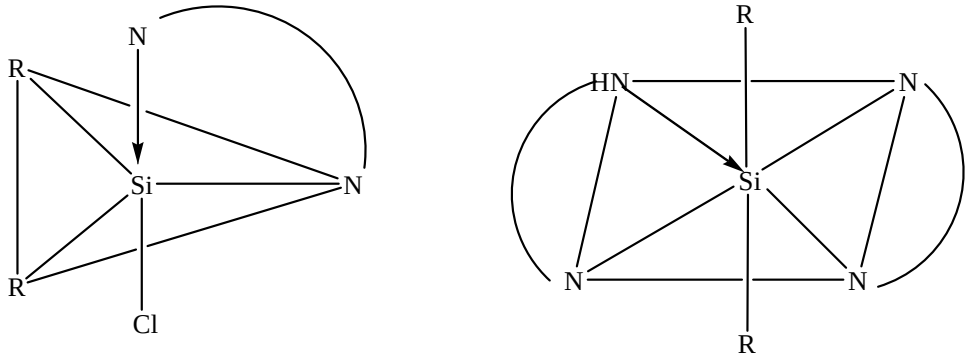


Figure 3. Structures of Silicon(IV) complexes

4. Conclusion

We have synthesized biologically relevant ligands and its Si(IV) complexes. Thus, on the basis of the above spectral features, as well as the analytical data, a penta-coordinated trigonal bipyramidal and hexa-coordinated octahedral geometries shown in Fig 3 have been suggested for the organosilicon(IV) complexes. The antimicrobial results indicated that the complexes showed promising antibacterial and antifungal activities. Both the ligand and their respective Si(IV) complexes were found to be sensitive against all the fungal and bacterial strains and the silicon complexes are more potent antimicrobial agents than the free ligand.

5. Acknowledgement

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