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Synthesis, Characterization and Antimicrobial Studies of Some New Organosilicon (IV) Complexes with Semicarbazones and Thiosemicarbazones

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ABSTRACT

The organosilicon (IV) complexes have been synthesized by the reaction of diethoxydimethyl silane with Schiff bases in 1:1 molar ratio using tetrahydrofuran as reaction medium. Ligands used in these studies have been prepared by the condensation of diketones with semicarbazide hydrochloride and thiosemicarbazide in 1:2 molar ratio in ethanol. The resulting organosilicon (IV) complexes were characterized by elemental analyses, IR, ¹H, ¹³C and ²⁹Si NMR spectral datas. On the basis of spectro scopic evidences all complexes have octahedral geometry. Si (IV) compounds have been found to be more active than their uncomplexed ligands as both of them screened for antibacterial and antifungal activities.

Keywords: Coordination compounds, antibacterial, antifungal, silicon (IV) complexes, Schiff bases.

INTRODUCTION

Schiff bases are nitrogen analogue of carbonyl compounds, in which the carbonyl group has been replaced by an imines or azomethine group.

$$R-CH_2-NH_2 + (R)_2C=O \rightarrow R-CH_2-N=C(R)_2+ H_2O$$

The azomethine group containing ligands are easily synthesized and form complexes with almost all metal ions [1] and their coordination compounds have gained importance because of their application in various fields as- biological, biochemical, analytical, antibacterial and antifungal activities [2]. There is lot of Schiff bases in coordination chemistry used as insecticidal, fungicidal, herbicidal [3]. Many Schiff bases are noted to have catalytic and medicinally importance. Some heteronuclear Schiff base complex act as magnetic material so used in biological engineering [4-7].

Its well known that the presence of metal ion bonded to biologically active ligands enhance their activity [8-11], Therefore the organosilicon compounds raised attention continuously due to their versatile applicability in the pharmaceutical industries and also to owe their antitumor properties in immunodefensive system of living organism [12]. Owing to their complexing activities of semicarbazone and thiosemicarbazone with silicon contributes their importance to growth of epithelial and connective tissue [13] and used in the treatment of wound and tumor. Silicon compounds are useful to impart strength elasticity and impermeability to water [14].

The present paper is an humble effort to describe the bonding pattern and antimicrobial activities of some newly synthesized organosilicon (IV) complexes with Schiff bases.

MATERIALS AND METHODS

Chemical and instrumentation: The solvent and chemicals used in experimental work were analytical grade and dried by standard procedure. 1-Phenyl butane-1,3- dione, pentane -2,4-dione, ethanedione, were purchased from HIMEDIA, Diethoxy-dimethylsilane was purchased from HIMEDIA. Reactions were carried out under anhydrous condition. Molecular weight was determined by Rast camphor method. Fourier Transform Infrared spectra of synthesized metal complexes were recorded on SHIMADZU FTIR spectrometer in the range of 4000-400Cm⁻¹ using KBr disc. The CHN elemental analysis was determined using a Thermo Finnigan CE 125 CHN analyzer. ¹H NMR and ¹³C NMR spectra were obtained on a Jeol Al 300 MHz spectrometer. DMSO-d6 used as solvent and reference nuclei was tetramethyl silane. Nitrogen was estimated by Kjeldal's method. Chlorine was estimated by Volhard's method. Silicon was estimated gravimetrically and sulphur was estimated by the messenger method. Perkin Elmer UV visible Spectrophotometer in the range 200-600 nm was used for UV spectra.

Synthesis of ligand: Schiff bases were synthesized by the condensation of 1-phenyl butane-1,3-dione, ethanedial and pentane 2,4-dione with thiosemicarbazide and semicarbazide hydrochloride in the presence of sodium acetate. This reaction was carried out in 1:2 molar ratio using ethanol as reaction medium. The solution was refluxed on a water bath for 2h and then allowed to cool at room temperature. The crystalline solid were separated out and purified by recrystalization from the same solvent and dried over anhydrous calcium chloride under vacuum. Physical properties and analysis of ligands are recorded in table1.

S.N	Compounds	Colour/ State	Mol.	M.P	Eleme	ntal analysis	s (%)
	Compounds	Colour/ State	Wt.	(°c)	С	Н	N
1	Pentane-2,4 dione Semicarbazone (L ¹ H)	Milky White/solid	213.16 (214.24)	275	39.24 (38.94)	6.58 (6.34)	39.23 (39.00)
2	Pentane-2,4 dione thiosemicarbazone (L ² H)	Shiny yellow/solid	245.18 (246.36)	230	34.12 (33.98)	5.72 (5.70)	34.12 (34.10)
3	1-phenyl-butane-1,3-dione semicarbazone (L ³ H)	White/solid	275.36 (276.30)	260	52.15 (52.05)	6.25 (6.02)	30.42 (30.37)
4	1-phenyl-butane-1,3-dione thiosemicarbazone (L ⁴ H)	Slightly yellow/solid	307.38 (308.42)	210	46.72 (46.60)	5.22 (5.21)	27.25 (27.23)
5	Ethanedial semicarbazone (L ⁵ H)	Pale yellow/ Powder	171.15 (172.16)	280	27.90 (27.88)	4.68 (4.66)	48.82 (48.56)
6	Ethanedial thiosemicarbazone (L ⁶ H)	Yellow/ Powder	203.28 (204.28)	235	23.51 (23.47)	3.94 (3.89)	41.14 (41.06)

Table 1. Analytical and physical data of ligands

Synthesis of metal complexes: Metal complexes were prepared in 1:1 [M:L] molar ratio by the addition of diethoxy-dimethyl silane in tetrahydrofuran solution of ligands. The mixture was refluxed on a fractional column. The reactions were carried out in round bottom flask for 5-6 h. The resulting derivatives were recovered by filtration, washed with same solvent and dried in vacuum. The purity of the compounds was checked by TLC using silica gel-G as an adsorbent. The physical properties and analytical data of complexes are listed in table 2.

CN	Complexes empirical formula	Colour and state	M.P	M 1 W	Elemental Analysis				
S.N.		Colour and state	(°c)	Mol.Wt	С	Н	N	Si	
1	C ₉ H ₁₈ N ₆ O ₂ Si	Off White/solid	280	300.689 (303.07)	35.91% (36.10)	5.98% (6.70)	18.62% (18.90)	9.31% (9.50)	
2	$C_9H_{18}N_6S_2Si$	Light Yellow/Solid	215	332.689 (334.79)	32.46% (34.05)	5.41% (6.90)	16.83% (17.05)	8.41% (8.75)	
3	C ₁₄ H ₂₀ N ₆ O ₂ Si	White/solid	270	376.73 (378.09)	44.59% (47.10)	5.30% (5.79)	14.98% (15.30)	7.49% (7.80)	
4	$C_{14}H_{20}N_6S_2Si$	Yellow/solid	190	408.73 (410.70)	41.10% (45.10)	4.89% (5.10)	13.70% (14.50)	6.85% (7.10)	
5	$C_6H_{12}N_6O_2Si$	White/Solid	290	309.31 (310.35)	23.27% (25.20)	3.87% (4.15)	18.10% (18.79)	9.05% (9.55)	
6	$C_6H_{12}N_6S_2Si$	Yellow/Solid	200	341.31 (344.50)	21.09% (23.57)	3.51% (4.5)	16.40% (16.80)	8.20% (8.55)	

Table 2 Analytical and Physical data of Si (IV) complexes.

RESULTS AND DISCUSSION

By the addition of Schiff bases and diethoxydimethyl silane in 1:1 (M:L) molar ratio using THF as a reaction medium, the metal complexes were obtained. The reaction of starting material of metal with Schiff base has been shown by the following general equation.

$$Si(OC_2H_5)_2(CH_3)_2 + L^{1-6}H \longrightarrow [Si(L^{1-6}H)(CH_3)_2]$$

Solid form of the complexes was obtained, and could be separated by filtration. The molecular weight of the newly synthesis complexes were determined by Rast camphor method showed them to be monomers. The proposed structure of ligands and metal complexes on the basis of elemental analysis and spectral characterization are shown under scheme 1.

Scheme1 Proposed structure of Ligand and their corresponding Si (IV) complexes

Spectroscopic Characterization

IR Spectra: FT-IR studies have been done to recognize the functional group present in the ligands and metal complexes. A study and comparison of IR spectra of ligands and its metal complexes (Table 5) infer that the metal is coordinated through N, S or O of the ligands. In the ligands there are two bands at 3400 and 3440cm⁻ appears which are characteristic of -NH₂ stretching modes. Both of two bands remain unchanged in the spectra of complexes. A broad band due to -NH vibration in the region 3300-3150cm⁻ appears in ligand and disappeared in the complexes. Most of the IR spectral bands appears in ligand are practically unchanged in the complexes but the appearances of some new bands with medium to weak intensity in the spectra of complexes in the region 575-550 cm⁻, 620-600 cm⁻ and 440-410 cm⁻ due to Si-N, Si-O and Si-S respectively. The absorption at 1615 cm⁻ in free ligand can be attributed to (C=N) stretching vibration of imine nitrogen. The negative shift (10-20 cm⁻) of new (C=N) bonds observed in all complexes indicates the involvement of azomethine nitrogen upon complexation.

Table 5 IR Spectral data of Ligand and their corresponding silicon (IV) complexes

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S/N	Compounds	v(C=N) (Cm ⁻¹)	v (Si-S) (Cm ⁻¹)	v (Si-O) (Cm ⁻¹)	v (Si-N) (Cm ⁻¹)
1	$C_4H_8O_2N_6$	1630	_	_	_
2	$C_6H_{12}N_6O_2Si$	1634	430	615	545
3	$C_{12}H_{16}N_6S_2$	1645	_	_	_
4	$C_{14}H_{20}N_6S_2Si$	1647	450	620	575
5	$C_4H_8S_2N_6$	1625	_	-	-
6	$C_6H_{12}N_6S_2Si$	1630	425	595	525
7	$C_{12}H_{16}O_2N_6$	1620	_	_	_
8	$C_{14}H_{20}N_6O_2Si$	1626	455	630	567

Electronic Spectra: The electronic spectra of ligands and their corresponding Si(IV) complexes were recorded in ethanol on a Perkin Elmer UV Visible spectrophotometer in the range 200-600nm. A broad band at 373nm observed in the spectra of ligand and it can be assigned to the $(n-\pi)$ transition of the azomethine group. The bond undergoes hypsochromic shift due to the coordination through nitrogen atom and appearing at 349 nm. Two bonds observed at 245 nm and 270 nm in the ligand due to $(\pi-\pi)$ transition within the benzene ring and (C=N) of the azomethine group respectively remain unchanged on the complexation.

²⁹Si spectra: The NMR spectra of ²⁹Si were recorded in CDCI₃ to confirm the coordination behavior of complexes. All complexes were assigned sharp signal at δ -97 to -140ppm. One sharp singlet observed in each case and the δ value indicates that complexes have hexacoordination behavior. In order to increasing the coordination number of nuclei chemical shift moves to lower frequency.

¹H NMR Spectra: The ¹H NMR spectra of ligands and their corresponding metal complexes recorded in DMSO-d6. TMS was used as internal reference. A broad peak at δ7.90-7.30ppm due to –NH-CO proton and disappeared in the spectra of complexes. However, disappearance of these signals in complexes indicates the covalent bond formation between silicon and oxygen/ sulphur due to deprotonation [15]. The azomethine proton signal (H-C=N) was detected at δ8.45ppm, which appears at δ8.55ppm in the spectra of complexes due to the coordination of azomethine nitrogen to the metal atom. The appearance of signal

due to $-NH_2$ proton at approximate same position in the ligand and its complexes shows that this group does not involve in coordination [16]. A complex multiplet shows by the ligands as well as by the organosilicon (IV) complexes in the region at $\delta 7.28-8.39$ ppm for the aromatic protons. The NMR spectral data of ligands and their corresponding metal complexes are listed in table 6.

S/N	Compounds	-NH ₂ (ppm)	NH-CO (ppm)	H-CN (ppm)	Aromatic Protone(ppm)	=CH ₂ (ppm)	²⁹ Si (ppm)
1	$C_{12}H_{16}N_6S_2$	3.10	7.30		7.00-8.20	3.67	
2	$C_{14}H_{20}N_6S_2Si$	3.18			6.67-8.40	3.75	-89.20
3	$C_4H_8S_2N_6$	3.05	7.34	8.45			
4	$C_6H_{12}N_6S_2Si$	3.10		8.50			-89.00
5	$C_{12}H_{16}O_2N_6$	3.23	7.42		6.50-7.90	3.36	
6	$C_{14}H_{20}N_6O_2Si$	3.23			6.99-8.23	4.22	-91.00

Table 6 ¹H and ²⁹Si NMR spectral data of ligands and their corresponding metal complexes

¹³C NMR spectra: ¹³C spectra of ligands and their corresponding Si(IV) complexes were recorded in dry DMSO. The signal has been shifted downfield [17] due to the attachment of azomethine nitrogen to carbon atom. The shifting supports the involvement of this group in complexation. The signals appeared at 117.5-151.7 ppm [18] due to the aromatic carbon atom. The azomethine carbon atom observed at 176.4 ppm in ligand and in complex it observed at 149.4-152.13 ppm. The carbon atom attached to sulfur and oxygen atom show [19] considerable shift, which indicates the involvement of oxygen and sulfur atom with the silicon atom.

APPLICATIONS

Antibacterial Activity: In order to find out the bactericidal property of the newly synthesized Schiff bases and their corresponding Si (IV) complexes, all were screened in vitro [20] against four of the test organism-Escherichia coli, B. Thurigiensis, Proteus mirabilis and staphylococcus aureus, bacterial strain using a paper disc diffusion method [21]. The compounds under investigation were dissolved in methanol to the given concentration of 500 and 1000 ppm. The nutrient agar medium and 5 mm diameter paper disc of Whatman filter paper no.1 were used. The filter paper soaked in these solution dried and then placed in Petri plates were incubated for 24 h at 28° and the inhibition zone around each disc was measured. The results are quite promising. The antibacterial activity displayed by various compounds against pathogenic bacteria is shown in table 3. It is also noted that sulphur containing ligands as well as their complexes are more active than their oxygen containing counterpart. Streptomycin was used as a reference compound for antibacterial activity.

Proteus milamilis E.Coli **B.**Thurigensis S. Aureus S/N Compounds $C_7H_{14}O_2N_6$ $C_9H_{18}N_6O_2Si$

Table 3 Antibacterial screening data of shiff bases and their silicon (IV) complexes in (ppm)

3	$C_{12}H_{16}N_6S_2$	16	20	14	15	16	20	13	15
4	$C_{14}H_{20}N_6S_2Si$	17	26	18	24	17	28	16	21
5	$C_4H_8S_2N_6$	13	15	12	14	18	21	12	13
6	$C_6H_{12}N_6S_2Si$	15	21	17	19	23	26	14	21
7	Streptomycin	12	14	14	16	15	17	15	16

Antifungal Activity: All synthesized ligands and their organosilicon (IV) complexes were screened against some fungus as Aspergillus flavus, Aspergillus Niger Fusarium oxyporum, and Rhizopus phaseolin. The samples were mixed with DMF and then mixed with the medium. For antifungal activities agar plate technique have been used. The linear growth of the fungus was recorded by measuring the diameter of colony after 96 h and the percentage inhibition was calculated as 100cc, where cc are the diameter of the fungus colony in the control and test plates. The data of antifungal activity was listed in table 4.

Table 4 Antifungal activity of Schiff bases and their Silicon(IV) complexes in(ppm)

S/N	Compounds	R. Phaseoli		A. Flavus		F. Oxyporum		A. Niger	
5/IN		100	200	100	200	100	200	100	200
1	$C_7H_{14}O_2N_6$	42	47	34	38	33	37	45	53
2	C ₉ H ₁₈ N ₆ O ₂ Si	51	56	40	46	38	45	51	62
3	$C_{12}H_{16}N_6S_2$	43	46	36	39	49	52	43	52
4	$C_{14}H_{20}N_6S_2Si$	50	59	39	44	53	59	52	60
5	$C_4H_8S_2N_6$	45	49	41	47	35	40	44	50
6	$C_6H_{12}N_6S_2Si$	47	52	46	52	48	53	51	61

CONCLUSIONS

Biologically active Schiff bases and their Si (IV) complexes have been synthesized. It has been found out that the complexes show moderate activity as compared to standard bactericide and fungicides. The activity of complexes against pathogens indicated that the complexation to metal enhance the activity of the ligand. Octahedral geometry of complexes has been found out on the basis of spectral evidences.

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