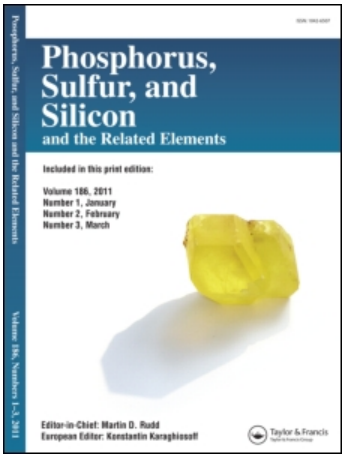

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SYNTHETIC, SPECTRAL AND BIOLOGICAL STUDIES OF ORGANOSILICON (IV) COMPLEXES WITH SCHIFF BASES OF SULFA DRUGS

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SYNTHETIC, SPECTRAL AND BIOLOGICAL STUDIES OF ORGANOSILICON (IV) COMPLEXES WITH SCHIFF BASES OF SULFA DRUGS

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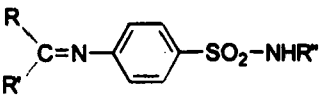
In the present paper synthetic and structural studies of six-coordinated $Me_2Si(\widehat{NN})_2$ type of organosilicon(IV) complexes of Schiff bases $(\widehat{NN})$ have been described. The complexes were characterized by elemental analyses, conductance measurements, molecular weight determinations and electronic, infrared, ^1H, ^{13}C and ^{29}Si NMR spectral studies. A few representative complexes were also screened for antimicrobial activity and found to be quite active in this respect.

Keywords: Heterocyclic aldehydes/ketones; diethoxydimethylsilane; sulpha drugs; microorganisms; spectral studies

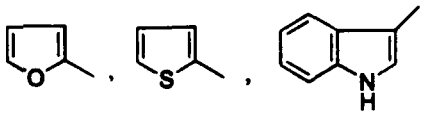
INTRODUCTION

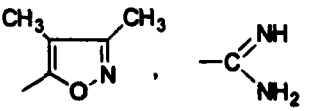
Sulphonamides have long been used as drugs for diseases like cancer[1], tuberculosis[2], diabeties[3], malaria[4] and leprosy[5] etc. They have been found to be active against different types of bacteria and virus. It has now been observed that some of these drugs show increased activity when administered in the form of metal complexes[6–8]. In view of this it was considered of interest to synthesize and characterize the Schiff bases derivatives of Si(IV) and result of these investigation are reported in this paper. During the course of present investigation Schiff bases used are as follows.

* Corresponding Author.



where R = H, CH_3

R' = 

R" = 

RESULT AND DISCUSSION

The reactions of diethoxydimethylsilane with these ligands have been carried out in 1:2 molar ratio in benzene medium as

$$(CH_3)_2Si(OC_2H_5)_2 + 2\,\widehat{NN}H \longrightarrow (CH_3)_2Si(\widehat{NN})_2 + 2C_2H_5OH$$

On refluxing for about 5 hours, the resulting complexes are obtained as coloured solids. The molar conductance value of 10^{-3} M solutions of the complexes (10–15 ohm^{-1} cm^2 mol^{-1}) in DMF showed them to be non-electrolytes. The monomeric nature of these complexes was confirmed by their molecular weight measurement. The physical characterstics of these complexes are recorded in Table I and II.

Electronic Spectra

In the electronic spectra a band due to >C=N chromophore[9] in the ligands at 385 nm shifts to a shorter wavelength in the complexes and appears at ~350 nm. This clearly indicates the coordination of azomethine nitrogen to the silicon atom.

IR Spectra

In the IR spectra of the ligands a broad and strong band in the region, 3400–3200 cm^{-1} due to νNH does not appears in the spectra of the corre-

sponding silicon complexes. A sharp and strong band at ~1615 cm^{-1} due to (>C=N)[10] group in the ligands shifts to the lower frequency region in the silicon complexes and appeared at ~1600 cm^{-1} in 1:2 complexes, which further gets support by the appearance of a new ν(Si ← N)[11] band at ~570 cm^{-1} in all the complexes. Several new bands of strong to medium intensity in the spectra of the complexes at ~1265 and ~760 cm^{-1} may be due to the asymmetric deformation[12] modes of CH_3-Si and stretching vibrations[13] of Si-C, respectively.

^{1}H NMR Spectra

In the ^{1}H NMR spectrum of the above ligand the broad signal due to the NH proton at δ ~10.15 ppm disappears in the silicon(IV) complexes indicating the coordination of nitrogen through a covalent bond formation by the nitrogen with the silicon atom.

The signals at δ ~1.90 ppm and δ ~9.2 ppm observed in the spectra of ligands are assigned to the methyl protons [-C(CH_3)=N] and azomethine protons (CH=N) respectively, which are shifted downfield in the spectra of silicon complexes (~0.18 ppm) in comparison to their original position indicating the coordination of azomethine nitrogen to the silicon atom. Further, new signals at δ ~1.60 ppm in the complexes are due to the methyl protons of Me_2Si group.

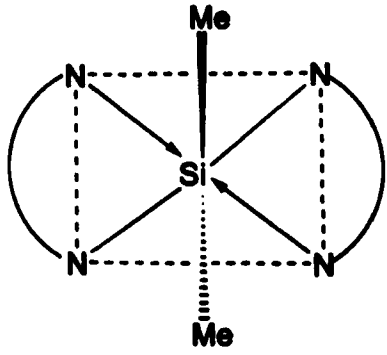
^{13}C NMR Spectra

The ^{13}C NMR spectra of indole-3-carboxylaldehyde sulphaguanidine or furfuraldehyde sulphaguanidine and its corresponding silicon complexes have been recorded in dry DMSO. A considerable shift (Table III) in the position of carbons attached to the different participating group clearly indicates the bonding of azomethine nitrogen and amido nitrogen to the silicon atom.

^{29}Si NMR Spectra

Further the ^{29}Si NMR spectra of silicon complexes gives a sharp signal at δ-42.63 to −39.75 ppm clearly indicating the six-coordinated environment

around the silicon. On the basis of the above spectral studies the following octahedral[14] geometries has been suggested for the silicon(IV) complexes.



Antimicrobial activity

All of the synthesized compounds were tested[15] for their antimicrobial activities at a concentration of 1 mg/disc. Streptomycin and Mycostatin were used as the reference compounds for antibacterial and antifungal activities respectively. *Bacillus tumefaciens, S. aureus, K. pneumoniae, E. coli* (bacteria) or *A. niger, A. flavus, R. phaseoli* and *P. crysogenous* (fungi) were used as the test organisms. Results have been recorded in the form of inhibition zone (diameter mm) and activity index in Table IV.

Further the silicon complexes are more active as compared to the free ligands and which indicates that metallation increases the activity and the preliminary results achieved have led us to conclude that this type of compounds should be studied in detail for their applications in diverse areas.

EXPERIMENTAL

Materials and Methods

Chemical and solvents used were dried and purified by standard method and moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes. The ligands were prepared by the literature method[16]. The complexes were prepared, purified and analyzed by similar method to those reported in our earlier publications[17–19].

TABLE I Physical Properties and Analytical Data of Ligands

S. No.	Ligands	Colour & State	M.P. °C	Analysis %				
				C Found (Calcd.)	H Found (Calcd,)	N Found (Calcd,)	S Found (Calcd.)	Mol. wt. Found (Calcd.)
1.	Indole-3-carbaldehyde sulfisoxazole (L^1H)	Cream	148	60.72	4.54	14.01	8.03	380
	$C_{20}H_{18}N_4O_3S$	solid		(60.91)	(4.60)	(14.21)	(8.12)	(394)
2.	Indole-3-carbaldehyde sulphaguanidine (L^2H)	Creamish	154	56.22	4.36	20.44	9.33	328
	$C_{16}H_{15}N_5O_2S$	pink shining		(56.30)	(4.43)	(20.53)	(9.38)	(341)
3.	Thiophene-2-carbaldehyde sulfisoxazole (L^3H)	Light brown	165	53.11	4.11	11.52	17.69	353
	$C_{16}H_{15}N_3O_3S_2$	solid		(53.18)	(4.19)	(11.63)	(17.73)	(361)
4.	Thiophene-2-carbaldehyde sulphaguanidine (L^4H)	Light brown	186	46.67	3.90	18.04	20.27	301
	$C_{12}H_{12}N_4O_2S_2$	solid		(46.75)	(3.93)	(18.18)	(20.39)	(308)
5.	Furfuraldehyde sulphaguanidine (L^5H)	Light brown	175(d)	49.21	4.05	19.10	10.88	280
	$C_{12}H_{12}N_4O_3S$	solid		(49.31)	(4.14)	(19.18)	(10.76)	(292)
6.	2 Acetylthiophene sulphaguanidine (L^6H)	Creamish white	108	48.29	4.33	17.35	19.70	302
	$C_{13}H_{14}N_4O_2S_2$	solid		(48.44)	(4.38)	(17.39)	(19.87)	(322)
7.	2 Acetylthiophene sulfisoxazole (L^7H)	Brown	160(d)	54.43	4.50	11.17	17.00	367
	$C_{17}H_{17}O_3N_3S_2$	solid		(54.54)	(4.58)	(11.23)	(17.11)	(374)
8.	2 Acetylfuran sulfisoxazole (L^8H)	Cream	158–160	56.75	4.72	11.51	8.78	350
	$C_{17}H_{17}O_4N_3S$	solid		(56.82)	(4.77)	(11.69)	(8.91)	(359)

d=decomposition.

TABLE II Synthesis and Analysis of Si(IV) Complexes

	Reactants		*Molar ratio*	*Products Colour & State M.P. °C*		*Analysis %*					
	Silicon	*Ligand*				*C Found (Calcd.)*	*H Found (Calcd.)*	*N Found (Calcd.)*	*S Found (Calcd.)*	*Si Found (Calcd.)*	*Mol. Wt. Found (Calcd.)*
1.	$C_6H_{16}O_2Si$	$C_{20}H_{13}N_4O_3S$	1:2	$C_{42}H_{40}N_8O_6S_2Si$	115	59.02	4.70	13.03	7.44	3.25	830
				Light brown		(59.71)	(4.74)	(13.27)	(7.58)	(3.32)	(844)
2.	$C_6H_{16}O_2Si$	$C_{16}H_{15}N_5O_2S$	1:2	$C_{34}H_{34}N_{10}O_4S_2Si$	146	55.09	4.55	18.80	8.50	3.75	724
				Light yellow solid		(55.28)	(4.61)	(18.91)	(8.67)	(738)	(738)
3.	$C_6H_{16}O_2Si$	$C_{16}H_{15}N_3O_3S$	1:2	$C_{34}H_{34}N_6O_6S_4Si$	162	52.38	4.30	10.00	16.35	3.53	765
				Cream solid		(52.44)	(4.37)	(10.19)	(16.45)	(3.61)	(778)
4.	$C_6H_{16}O_2Si$	$C_{12}H_{12}N_4O_2S_2$	1:2	$C_{26}H_{28}N_8O_4S_4Si$	202	49.79	4.08	16.48	19.00	4.00	658
				Greenish yellow		(50.00)	(4.17)	(16.67)	(19.04)	(4.18)	(672)
5.	$C_6H_{16}O_2Si$	$C_{12}H_{12}N_4O_3S$	1:2	$C_{26}H_{28}N_8O_6S_2Si$	178	52.41	4.22	17.25	9.81	4.31	621
				Pinkish violet		(52.50)	(4.37)	(17.50)	(10.00)	(4.39)	(640)
6.	$C_6H_{16}O_2Si$	$C_{13}H_{14}N_4O_2S_2$	1:2	$C_{28}H_{32}N_4O_8S_4Si$	172	42.22	4.01	14.01	16.01	3.50	778
				Off white		(42.39)	(4.04)	(14.13)	(16.14)	(3.54)	(792)
7.	$C_6H_{16}O_2Si$	$C_{17}H_{17}N_3O_3S_2$	1:2	$C_{36}H_{38}N_6O_6S_4Si$	137.138	47.86	4.15	9.22	14.08	3.03	876
				Light brown		(48.04)	(4.22)	(9.34)	(14.23)	(3.12)	(899)
8.	$C_6H_{16}O_2Si$	$C_{17}H_{17}N_4O_3S$	1:2	$C_{36}H_{38}N_8O_6S_2Si$	177–178	49.74	4.30	9.50	7.31	3.18	851
				Light brown solid		(49.82)	(4.38)	(9.69)	(7.38)	(3.23)	(867)

TABLE III ^{13}C NMR Spectral data (δ ppm) of ligands and its organosilicon(IV) complexes

	Chemical shift values														
Compounds	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*Si-CH_3*
L^2H	137.1	135.4	1235	122.8	120.4	119.2	110.7	167.7	125.8	121.3	115.2	115.1	162.8	–	
$Me_2Si(L^2)_2$	136.7	135.5	124.7	123.6	121.3	119.9	118.1	111.8	158.2	125.4	122.0	115.0	116.2	154.3	15.6
L^5H	150.6	134.6	114.7	146.2	170.1	126.6	122.2	119.3	116.9	164.5	–	–	–	–	–
$Me_2Si(L^5)_2$	151.3	133.0	112.5	146.0	161.7	126.0	122.4	119.0	117.1	156.2	–	–	–	–	15.8

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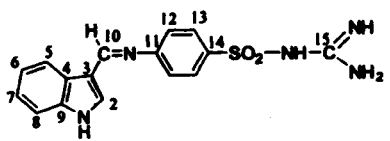

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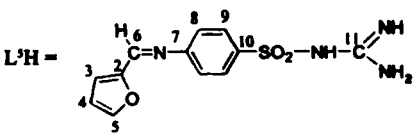

TABLE IV Antimicrobial Activity of ligands and its Silicon(IV) complexes

Microorganisms		*Compounds*					
		L^2H	$Me_2Si(L^2)_2$	L^3H	$Mi_2Si(L^3)_2$	L^4H	$Me_2Si(L^4)_2$
B. tumefaciens	IZ	8.6	10	7.2	9	11	12.8
	(AI)	(0.61)	(0.79)	(0.52)	(0.65)	(0.79)	(0.92)
S. aureus	IZ	9.0	12.8	8.2	10	9	11.4
	(AI)	(0.82)	(1.16)	(0.75)	(0.91)	(0.82)	(1.04)
K. pneumoniae	IZ	6.0	11	6.1	8	8	9.9
	(AI)	(0.46)	(0.85)	(0.47)	(0.62)	(0.62)	(0.77)
E. coli	IZ	9.0	12.0	8.2	10	10	11.2
	(AI)	(0.75)	(1.0)	(0.68)	(0.84)	(0.84)	(0.94)
A. niger	IZ	6.0	9.0	6.4	8	8	8.9
	(AI)	(1.00)	(1.50)	(1.07)	(1.34)	(1.34)	(1.48)
A. flavus	IZ	6.1	6.8	6.0	7	5	6
	(AI)	(0.76)	(0.85)	(0.75)	(0.88)	(0.63)	(0.75)
R. phaseoli	IZ	6.0	6.3	4	6.9	7	7.8
	(AI)	(0.75)	(0.79)	(0.5)	(0.86)	(0.88)	(0.98)
P. crysogenous	IZ	5.0	9.2	4.1	7.9	5	8
	(AI)	(0.71)	(1.31)	(0.59)	(1.13)	(0.71)	(1.14)

IZ = Inhibition zone (in mm), AI = Activity index = Inhibition zone of test compounds/Inhibition zone of standard.

Spectral measurements

The electronic spectra were recorded in methanol on a Toshniwal spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer 577 grating IR spectrophotometer in the region 4000–200 cm^{-1} using KBr optics. ^{1}H NMR spectra were recorded on a Perkin-Elmer RB-12 spectrometer in DMSO-d_6 using TMS as an internal standard at 90 MHz. ^{13}C and ^{29}Si NMR spectra recorded on a Jeol Fx-90 Q a spectrometer in dry DMSO using TMS as an internal standard at 22.49 MHz and 17.75 MHz respectively.

Synthesis of Si(IV) Complexes

To a weighed amount of diethoxydimethylsilane in dry benzene was added the calculated amount of ligand in 1:2 molar ratio. The reactants were refluxed for about 5–6 hours to complete the reaction. The ethanol liberated in the reaction was removed azeotropically with benzene, the excess of the solvent was removed under reduced pressure and the complexes were subsequently dried for 3–4 h. These were then repeatedly washed with dry cyclohexane so as to ensure their purity and again dried under reduced pressure. The synthetic and analytical data of the resulting complexes are recorded in Table II.

Acknowledgements

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