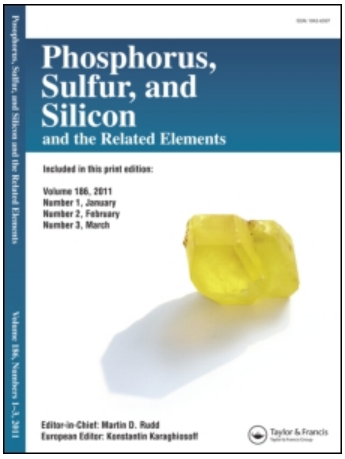

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THE SYNTHESIS, CHARACTERISATION AND MICROBIAL STUDIES OF ORGANOSILICON(IV) COMPOUNDS OF AZOMETHINES

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A new class of coordination compounds of organosilicon(IV) moiety derived from azomethines having a general formulae, $Ph_2SiCl.L$ and Ph_2SiL_2 (where L = anion of azomethine), have been synthesized and characterised spectroscopically. The inferences based on elemental analysis, molecular weight determinations, conductance measurements, UV, IR (^1H, ^{13}C and ^{29}Si) NMR studies suggest trigonal bipyramidal and octahedral geometries for $Ph_2SiCl.L$ and $Ph_2Si.L_2$ types of complexes, respectively. The microbial studies of a specific azomethine and its substituted silicon complexes have also been evaluated against some pathogenic fungi and bacteria.

Key words: Organosilicon(IV) compounds; azomethine; microbial studies; ^{13}C NMR and ^{29}Si NMR spectra.

INTRODUCTION

The organic substrates having nitrogen and sulphur/oxygen as donor systems[1–3] and their transition/non-transition metal chelates[4–6] which possess a variety of applications[7–9] in different aspects of life, are attracting the attention of a large number of chemists. However, little is known about the chelating behaviour of silicon and particularly with N⁀OH type of systems. To address this situation, we report the synthesis of selected organosilicon(IV) derivatives containing this ligand type and a study of their structures along with their biological activity.

RESULTS AND DISCUSSION

The reactions of diphenyldichlorosilane with the sodium salts of monobasic bidentate ligands derived by the condensation of heterocyclic aldehydes with semicarbazide hydrochloride have been carried out in 1:1 and 1:2 stoichiometric proportions in dry methanol. The reactions proceed as follows:

$$Ph_2SiCl_2 + N⁀ONa \rightarrow Ph_2Si(N⁀O)Cl + NaCl$$
$$Ph_2SiCl_2 + 2N⁀ONa \rightarrow Ph_2Si(N⁀O)_2 + 2NaCl$$

(Where N⁀O represents the donor system of the azomethine molecule LH). The azomethines used are 3-Indolecarbaldehyde semicarbazone, Indol.SczH (**1**); 2-Thiophenecarbaldehyde semicarbazone, Thiop.SczH (**2**); 2-Pyridinecarbaldehyde semicarbazone, Pyd.SczH (**3**); 2-Furaldehyde semicarbazone, Fur.SczH (**4**); and Cinnamaldehyde semicarbazone, Cinn.SczH (**5**).

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The resulting compounds $Ph_2Si(Indol.Scz)Cl$ (**6**), $Ph_2Si(Indol.Scz)_2$ (**7**), $Ph_2Si(Thiop.Scz)Cl$ (**8**), $Ph_2Si(Thiop.Scz)_2$ (**9**), $Ph_2Si(Pyd.Scz)Cl$ (**10**), $Ph_2Si(Pyd.Scz)_2$ (**11**), $Ph_2Si(Fur.Scz)Cl$ (**12**), $Ph_2Si(Fur.Scz)_2$ (**13**), $Ph_2Si(Cinn.Scz)Cl$ (**14**) and $Ph_2Si(Cinn.Scz)_2$ (**15**) are coloured solids and are soluble in common organic solvents. Their molar conductances of 10^{-3}M solutions in methanol reveal their non-electrolytic nature. The monomeric nature of these complexes is confirmed by their molecular weight determinations. The stereochemistry of these complexes has been determined spectroscopically using infrared, ultraviolet and NMR (^1H, ^{13}C and ^{29}Si) spectral data.

Infra Red Spectra

In the infrared spectra of free ligands a broad and medium intensity band attributable to $\nu(OH)/\nu(NH)$ modes in the region 3200–3100 cm^{-1} disappears in the silicon complexes suggesting the possible deprotonation on complexation. Further, the bands at 1615 ± 15 cm^{-1} in the ligands due to the (C=N) stretching frequency shifts to lower frequencies and clearly indicates the coordination of the silicon atom through the azomethine nitrogen atom. The formation of the resulting complexes has also been supported by the presence of new bands due to ν(Si—O)[10] and ν(Si ← N)[11] appearing at 740 ± 10 and 515 ± 15 cm^{-1}, respectively. The appearance of a new band at 445 ± 15 cm^{-1} and medium to strong intensity bands around 1450–1400, 1130–1085, 800–685 and 690–620 cm^{-1} have been assigned due to ν(Si—Cl)[12] and (Si—C_6H_5) modes,[13] respectively (Table I).

Electronic Spectra

In the electronic spectrum of **1** there appears a band at 355 nm due to the n-π^* transitions of the azomethine group.[14] This band shifts to a lower wavelength in the complex and appears at 325 nm and 330 nm in the 1:1 and 1:2 products, respectively, and which clearly indicates the coordination of azomethine nitrogen to the silicon atom. Further, the bands at 315 nm and 260 nm due to π-π^* transitions in the ligand remain unchanged in the spectra of silicon complexes.

^1H NMR Spectra

The bonding pattern of the ligand to metalloid is further supported by the ^1H NMR spectral studies. The spectrum of one representative ligand (Table II) exhibits NH proton signal at δ 11.52 ppm which disappears in the spectra of complexes, showing thereby its deprotonation. The azomethine proton signal appearing at δ 8.16 ppm shifts downfield in the spectra of complexes due to the formation of a coordinate linkage between nitrogen and silicon atom and appears at δ 8.80 in 1:1 complex and δ 8.86 ppm in 1:2 complex. The new complex multiplet centered at δ 6.0 ppm and δ 6.18 ppm in the silicon complexes are due to the phenyl protons[13] of the diphenyldichlorosilane.

^{13}C NMR Spectra

The ^{13}C NMR spectra of **1** and its corresponding silicon complexes (Table III) were also recorded in methanol. The considerable shifts in the position of carbons in-

TABLE I

IR Spectral data (cm^{-1}) of azomethines and their silicon complexes

Compound	νOH/νNH	>C=N	νSi-O	νSi-N	νSi-Cl			Si-C_6H_5	Modes
1	3100-3140	1610	-	-	-			-	
2	3100-3150	1600	-	-	-			-	
3	3140-3200	1630	-	-	-			-	
4	3100-3160	1600	-	-	-			-	
5	3100-3200	1620	-	-	-			-	
6	-	1590	740	520	445	1440	1120	720	690
7	-	1580	740	500	450	1400	1110	710	680
8	-	1585	745	525	445	1415	1110	690	660
9	-	1580	740	530	460	1412	1105	690	650
10	-	1590	740	530	455	1430	1100	685	620
11	-	1580	750	530	460	1425	1085	795	650
12	-	1580	740	525	430	1450	1130	790	650
13	-	1585	730	530	440	1430	1110	795	660
14	-	1600	740	520	440	1430	1100	800	680
15	-	1595	740	510	455	1425	1090	790	680

TABLE II

^{1}H NMR Spectral data (δ, ppm) of ligand and its corresponding silicon complexes

Compound	Aromatic (m)	-NH (bs)	Azomethine (s)	$-NH_2$ (bs)	$Si-C_6H_5$ (m)
1	7.76-6.32	11.52	8.16	2.56	-
6	8.08-7.18	-	8.80	2.53	6.00
7	8.10-7.20	-	8.86	2.54	6.18

s = singlet, bs = broad singlet and m = complex multiplet

TABLE III

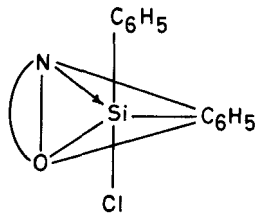
^{13}C NMR Spectral data of azomethine 1 and its silicon complexes

Compound	Chemical shifts in (δ, ppm)										
	Azomethine	>C=O	Aromatic								Si-C
1	155.9	166.7	136.9	136.4	123.5	122.8	120.4	119.1	117.8	110.7	-
6	145.4	153.8	136.8	136.4	124.7	123.6	121.3	119.8	117.9	111.0	14.5
7	147.1	155.3	137.3	136.8	124.9	124.1	121.8	120.1	118.3	111.8	16.2

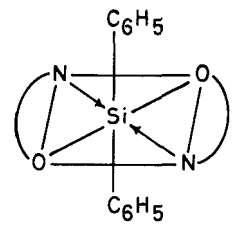
volved in complex formation clearly indicate the bonding of the azomethine nitrogen and ketonic/enolic oxygen to the silicon atom. Thus, based on these spectral studies trigonal bipyramidal and octahedral geometries have been suggested for the resulting 1:1 and 1:2 complexes, respectively.

^{29}Si NMR Spectra

In the ^{29}Si NMR spectra of **6** and **7** complexes, the signals at δ-36.60 ppm and δ-46.30 ppm are in good agreement with the values for penta- and hexa-coordinated states around the silicon atom.



(1:1 Product)



(1:2 Product)

BIOCIDAL ACTIVITY

The results of antibacterial and antifungal activities of ligand, **2** and its silicon complexes against different bacteria and fungi have been recorded in Tables IV and V. These were screened by the methods reported earlier.[15,16] The results reveal

TABLE IV

Antibacterial activity of 2 and its silicon complexes

Name of Bacteria	Gram Reaction	Diameter of inhibition zone (mm)		
		2	8	9
E. coli	(-)	8	19	21
Staphylococcus	(+)	7	16	17
Streptococci	(+)	13	25	28
B. subtilis	(+)	12	21	23

TABLE V

Antifungal activity of 2 and its silicon complexes

Compound	Average percentage inhibition after 96 hours							
	Rhizopus oryzae		**Helminthosporium graminium**		**Aspergillus flavus**		**Alternaria solani**	
	Cond.	used	Conc.	Used	Conc.	used	Conc.	used
	0.01%	0.1%	0.01%	0.1%	0.01%	0.1%	0.01%	0.1%
2	33	38	35	38	39	48	28	30
8	58	64	59	63	61	63	48	51
9	61	66	57	64	63	62	51	50

TABLE VI

Physical properties and analytical data of silicon(IV) complexes

Compound	Colour	Yield (%)	M.P. (°C)	Elemental Analysis (%)					Mol.Wt.
				C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	Cl Found (Calcd.)	Si Found (Calcd.)	Found (Calcd.)
6	Dark brownish	73	250	63.07 (63.29)	4.57 (4.81)	13.37 (13.08)	8.46 (8.21)	6.70 (6.51)	417.96 (400.10)
7	Creamish white	69	315d	65.73 (65.91)	4.83 (5.09)	19.16 (18.89)	-	4.80 (4.53)	584.72 (568.81)
8	Off yellow	65	230	56.02 (56.29)	4.18 (4.45)	10.89 (10.61)	9.19 (8.91)	5.42 (5.19)	518.70 (503.61)
9	Light yellow	71	258	55.58 (55.81)	4.27 (4.53)	16.20 (16.00)	-	7.28 (7.00)	385.95 (363.53)
10	Off white	70	235d	59.91 (60.18)	4.50 (4.78)	14.71 (14.48)	9.31 (9.08)	7.37 (7.05)	380.92 (358.17)
11	Yellowish white	67	205	61.40 (61.63)	4.76 (4.98)	22.03 (21.81)	-	5.52 (5.23)	508.62 (489.23)
12	Dark grey	63	290d	58.45 (58.72)	4.36 (4.59)	11.36 (11.14)	9.58 (9.27)	7.59 (7.36)	369.89 (350.87)
13	Dark yellow	68	240d	59.00 (59.25)	4.95 (5.17)	17.20 (17.00)	-	5.75 (5.45)	488.59 (471.41)
14	Reddish yellow	78	262	65.09 (65.31)	4.97 (5.20)	10.35 (10.13)	8.73 (8.51)	6.92 (6.69)	405.97 (388.29)
15	Yellow	73	225	68.79 (69.02)	5.41 (5.67)	15.04 (14.79)	-	5.03 (4.78)	558.72 (539.83)

a thought that the silicon complexes are more biocidal than the ligand and on lowering the concentration these activities decrease considerably.

EXPERIMENTAL

All the chemicals used were dried and distilled before use. Moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes.

Preparation of Ligands
The semicarbazones of corresponding heterocyclic aldehydes viz., 3-indolecarbaldehyde, 2-thiophenecarbaldehyde, 2-pyridinecarbaldehyde, 2-furaldehyde and cinnamaldehyde were prepared by the reported method.[17]

Preparation of Complexes
To a weighed amount of diphenyldichlorosilane in ~30 ml of dry methanol in a 100 ml R.B. flask was added the requisite amount of Na-salts of the ligands in 1:1 and 1:2 stoichiometric proportions. The contents were refluxed for 10–12 hours and the precipitate of sodium chloride so formed was filtered off. The excess of the solvent was removed under pressure and the products were purified from a methanol-cyclohexane (1:1) solution and the resulting pure derivatives so obtained were dried under vacuum for 2–3 hours.

The analytical data of the complexes for silicon, carbon, hydrogen, nitrogen and chlorine agreed with the theoretical values within the limits of experimental errors (Table VI).

Analytical Methods and Physical Measurements
Carbon and hydrogen analysis were performed at the microanalytical laboratory of the department. Nitrogen and sulphur were estimated by the Kjeldahl's and Messenger's methods, respectively. Silicon was estimated gravimetrically as SiO_2. The conductivity was measured with a conductivity bridge 304 (direct reading type) Systronics model and the molecular weights were determined by the Rast-Camphor method. I.R. spectra were recorded on a Perkin Elmer 577 grating spectrophotometer in KBr pellets. The electronic spectra were obtained on a Pye Unicam SP-8-100 spectrophotometer in dry methanol. ^1H and ^{13}C NMR spectra were recorded on a Jeol FX 90Q spectrometer at 89.5 and 22.49 MHz, respectively.

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