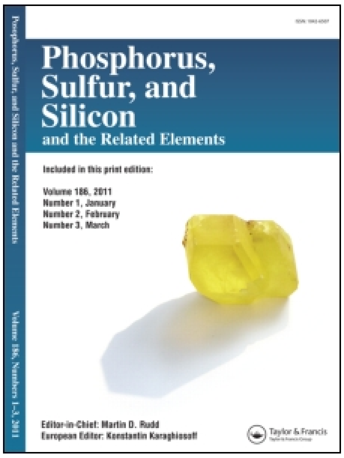

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SOME NEW COORDINATION COMPOUNDS OF ORGANOSILICON(IV) WITH SCHIFF BASES OF SULPHA DRUGS

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New hexa-coordinated complexes of organosilicon(IV) have been synthesized by the diphenyldichlorosilane with the Schiff bases derived from the condensation of heterocyclic ketones and aldehydes with a series of sulpha drugs. Their structures have been inferred on the basis of elemental analysis, UV, IR, and NMR spectral studies. The monomeric and nonelectrolytic nature of these compounds have been confirmed by molecular weight determinations and conductance measurements. The Schiff bases and their silicon complexes also have been screened for their antimicrobial activities against several fungi and bacteria and were found to be quite active in this respect.

Keywords: Antimicrobial studies; heterocyclic aldehydes/ketones; organosilicon (IV) complexes; spectral; sulpha drugs

The heterocyclic compounds with both sulphur and nitrogen atoms in the ring system have been used in the synthesis of biological active complexes.[1,2] The sulphonamides have been known to possess conspicuous biocidal activity.[3,4] It is, however, noteworthy that the biological activity of these Schiff bases are enhanced on undergoing complexation with metal ions.[5,6] Thus metal complexes involving sulphonamide-imines may be of considerable therapeutic importance. It was therefore considered of interest to synthesize Si(IV) derivatives of Schiff bases

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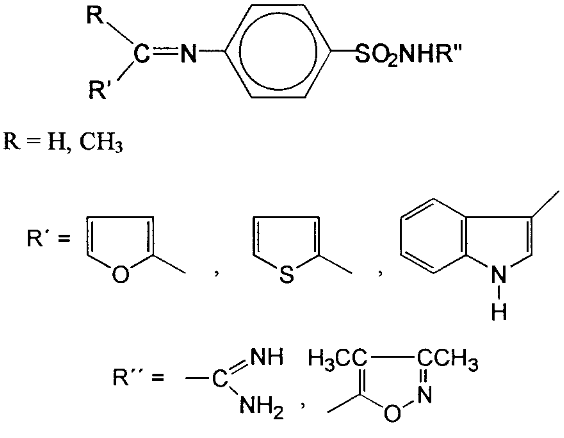


FIGURE 1 Structure of the ligands.

derived by condensation of heterocyclic ketones/aldehydes with some of the well-known sulpha drugs. The structures of the ligands are shown in Figure 1.

EXPERIMENTAL

Chemical and solvents used were dried and purified by standard methods and moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes.

The complexes were analyzed as reported earlier.[7–11] The IR spectra were recorded on a Perkin-Elmer 577 IR spectrophotometer in the region 4000–200 cm^{-1} using KBr optics. The electronic spectra (in methanol) were taken with a Toshniwal spectrophotometer. A Perkin-Elmer Model RB-12 spectrometer was used to obtain the ^1H NMR spectra, DMSO-d_6 was used as the solvent. ^{13}C NMR spectra were recorded on a 90 MHz Jeol NMR spectrometer using dry DMSO as the solvent and TMS as the internal standard. Molar conductance measurements were made in anhydrous dimethylformamide at $36 \pm 1°C$ using a Model-305 Systronics conductivity bridge. Molecular weight determinations were carried out by the Rast camphor method.

Synthesis of Ligands

The ligands were synthesized by the condensation of indole-3-carboxylaldehyde (0.0186 mmol, 2.710 g), thiophene-2-aldehyde

(0.0186 mmol, 2.094 g), 2-acetythiophene (0.0186 mmol, 2.355 g), 2-acetylfuran (0.0186 mmol, 1.646 g) or furfuraldehyde (0.0186 mmol, 1.792 g) with the sulpha drugs (0.0186 mmol, 4.00 g) in 120 mL ethanol. The solution was refluxed on a water bath for 4–5 h and allowed to cool to room temperature. The crystals that separated out were washed with ethanol, recrystallized from the same solvent and dried in vacuo. Their elemental analysis and physical properties are given in Table I.

Synthesis of Si(IV) Complexes

To a weighed amount of diphenylsilicon(IV) dichloride (0.742 g, 2.18 mmol) was added to the calculated amount of the ligand (2.242–2.684 g, 4.36 mmol) in 1:2 molar ratio, in benzene as the reaction medium in an oxygen-free nitrogen atmosphere. On refluxing for about 5 h, the resulting complexes were obtained as colored solids or semi-solids. The excess of solvent was removed under reduced pressure and the compound was dried in vacuo at $35 \pm 5^{\circ}C$ after repeated washing with dry cyclohexane. The compounds were purified by recrystallization from benzene and washing with dry cyclohexane. The compounds were purified by recrystallization from benzene (Table II).

RESULTS AND DISCUSSION

The reaction of diphenylsilicon(IV) dichloride with these ligands have been carrried out in 1:2 molar ratio in benzene solution according to Eq. (1),

$$Ph_2SiCl_2 + 2L \rightarrow Ph_2SiCl_2(L)_2 \qquad (1)$$

where L represents the Schiff bases shown in Figure 1.

On refluxing for about 5 h the resulting complexes are obtained as colored solids or semi-solids. These complexes are susceptible to moisture and aerial oxidation. The low values of molar conductance ($10–15\Omega^{-1}$ cm^2 mol^{-1}) show that these complexes are nonelectrolytes.

Electronic Spectra

The electronic spectra of the ligands was recorded in methanol on a Toshniwal spectrophotometer and exhibit two bands at $= 340$ nm and $= 412$ nm, which are assignable to the π-π^* and n-π^* transitions. Respectively, this band due to the >C-N chromophore[12] of the ligands at 385 ± 2 nm, shifts to shorter wevelength in the complexes and appear

TABLE I Physical Properties and Analytical Data of Ligands

Ligand	Color and state	Yield (%)	m.p.°C	Analysis %				mol. wt. Found (calcd.)
				C found (calcd.)	H found (calcd.)	N found (calcd.)	S found (calcd.)	
Indole-3-carbaldehyde sulfisoxazole (L^1)	Cream solid	86	148	60.72	4.54	14.01	8.03	380
$C_{20}H_{18}N_4O_3S$				(60.91)	(4.60)	(14.21)	(8.12)	(394)
Indole-3-carbaldehyde sulphaguanidine (L^2)	Creamish	88	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)
Thiophene-2-carbaldehyde sulfisoxazole (L^3)	Light brown	92	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)
Thiophene-2-carbaldehyde sulphaguanidine (L^4)	Light brown	92	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)
Furfuraldehyde sulphaguanidine (L^5)	Light brown	84	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)
2-Acetylthiophene sulphaguanidine (L^6)	Creamish	86	108	48.29	4.33	17.35	19.70	302
$C_{13}H_{14}N_4O_2S_2$	white solid			(48.44)	(4.38)	(17.39)	(19.87)	(322)
2-Acetylthiophene sulfisoxazole (L^7)	Brown solid	83	160 (d)	54.43	4.50	11.17	17.00	367
$C_{17}H_{17}O_3N_3S_2$				(54.54)	(4.58)	(11.23)	(17.11)	(374)
2-Acetylfuran sulfisoxazole (L^8)	Cream solid	90	158–160	56.75	4.72	11.51	8.78	350
$C_{17}H_{17}O_4N_3S$				(56.82)	(4.77)	(11.69)	(8.91)	(359)

d = decomposition.

TABLE II Physical Properties and Analytical Data of Si(IV) Complexes

Reactants		Molar ratio	Compounds color & state	Yield (%)	m.p.°C	Analysis, % found (calcd.)						mol wt. Found (calcd.)
Silica	Ligand					C	H	N	S	Cl	Si	
Ph_2SiCl_2	L^1	1:2	$Ph_2SiCl_2(L^1)_2$	88	208 (d)	59.81	4.40	10.62	6.01	6.71	2.52	1032.6
			Brown solid			(59.66)	(4.45)	(10.76)	(6.15)	(6.82)	(2.69)	(1041.2)
Ph_2SiCl_2	L^2	1:2	$Ph_2SiCl_2(L^2)_2$	86	210	56.34	4.28	14.86	6.78	7.49	2.91	926.80
			Yellow solid			(56.46)	(4.31)	(14.97)	(6.84)	(7.59)	(3.00)	(935.21)
Ph_2SiCl_2	L^3	1:2	$Ph_2SiCl_2(L^3)_2$	90	—	54.07	4.06	8.51	13.01	7.17	2.78	961.61
			Greenish brown semi solid			(54.14)	(4.13)	(8.61)	(13.12)	(7.28)	(2.88)	(975.21)
Ph_2SiCl_2	L^4	1:2	$Ph_2SiCl_2(L^4)_2$	92	226	49.59	3.87	12.77	14.62	8.02	3.15	859.60
			Greenish brown solid			(49.70)	(3.94)	(12.89)	(14.73)	(8.17)	(3.23)	(869.21)
Ph_2SiCl_2	L^5	1:2	$Ph_2SiCl_2(L^5)_2$	92	—	51.27	4.01	13.21	7.54	8.36	3.26	826.26
			Blackish brown semi solid			(51.39)	(4.09)	(13.38)	(7.64)	(8.48)	(3.35)	(837.21)
Ph_2SiCl_2	L^6	1:2	$Ph_2SiCl_2(L^6)_2$	84	186	50.72	4.12	12.34	14.19	7.81	3.08	887.14
			Creamish white solid			(50.80)	(4.27)	(12.48)	(14.26)	(7.91)	(3.13)	(897.57)
Ph_2SiCl_2	L^7	1:2	$Ph_2SiCl_2(L^7)_2$	86	260 (d)	54.81	4.34	8.31	12.70	7.01	2.68	998.01
			Brown solid			(54.94)	(4.41)	(8.36)	(12.74)	(7.07)	(2.79)	(1004.71)
Ph_2SiCl_2	L^8	1:2	$Ph_2SiCl_2(L^8)_2$	88	198 (d)	56.02	4.51	8.58	6.49	7.20	2.72	961.02
			Cream solid			(56.19)	(4.56)	(8.64)	(6.58)	(7.30)	(2.89)	(972.05)

at 380 nm. This indicates the coordination of the azomethine nitrogen to the silicon atom.

Infrared Spectra

The ligands exhibit a broad and strong band in the region 3400–3150 cm^{-1} due to the υ(NH). In the spectra of complexes this bands remains approximately at the same position, which clearly indicates the noninvolvement of NH group in complexation. A sharp and strong band at $= 1620 \pm 5$ cm^{-1} assignable to υ(C=N)[13,14], is shifted to lower wave numbers 1600 ± 5 cm^{-1} in the spectra of the silicon complexes, indicating coordination through the azomethine nitrogen to the silicon atom. New bands observed in the complexes at 570, 540, and 510 cm^{-1} are due to υ(Si—N)[15], υ(Si—C)[16], and υ(Si—Cl)[17] modes, respectively, which are not observed ion the spectra of the Schiff bases.

^{1}H NMR Spectra

To further confirm the bonding pattern in these complexes, ^{1}H NMR spectra of the ligands and their silicon derivatives were recorded in DMSO-d_6 using TMS as internal reference. The ^{1}H NMR spectra of ligands show NH proton signal at δ 10.09 ± 0.10 ppm. These signals remains unchanged in the complexes showing its noninvolvement in the coordination. A signal at δ 8.10 ± 0.12 ppm is observed in the complexes due to the azomethine protons, which moves down field in comparison to its original position in the free ligand, thereby indicating the coordination through the azomethine nitrogen to the silicon atom.

^{13}C NMR Spectra

The ^{13}C NMR spectra of indole-3-carboxyladehyde sulphaguanidine and furfuraldehyde sulphaguanidine and their corresponding silicon also have been recorded in Table III. The signals due to the carbon atoms attached to the azomethine groups in the ligands appear at δ 165.8 and δ 171.1 ppm. However, in the spectra of the corresponding silicon complexes these signals appears at δ 158.2 and δ 161.1 ppm. The considerable shifts in the carbon atoms attached to nitrogen indicate the involvement of nitrogen atom in coordination with the silicon atom.

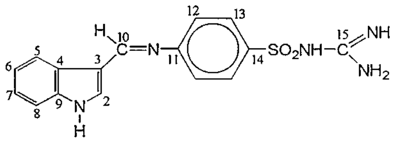
^{29}Si NMR Spectra

In the ^{29}Si NMR Spectra of the silicon complexes give a sharp signal around at δ-124.98 ± 2 ppm, which is indicative of hexa-coordination around the silicon atom and is in agreement with the previously

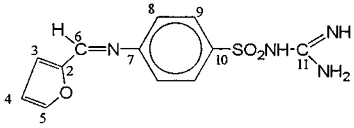
TABLE III ^{13}C NMR Spectral Data (δ ppm) of Ligands and their Organosilicon(IV) Complexes

	Chemical shift in δ ppm													
Compounds	2	3	4	5	6	7	8	9	10	11	12	13	14	15
L^2	137.1	135.4	123.5	122.8	120.4	119.2	110.7	167.7	165.8	121.3	115.2	115.1	162.8	161.7
$Ph_2SiCl_2(L^2)^2$	136.7	136.5	124.7	123.6	121.3	119.9	118.1	165.2	158.2	125.4	122.0	115.0	161.2	161.3
L^5	150.6	134.6	114.7	146.2	170.1	126.6	122.2	119.3	116.9	164.5	—	—	—	—
$Ph_2SiCl_2(L^5)^2$	151.3	133.0	112.5	146.0	161.7	126.0	122.4	119.0	117.1	164.2	—	—	—	—

L^2



L^5



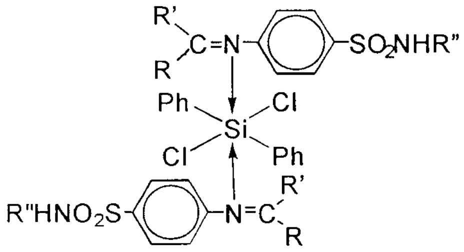


FIGURE 2 Suggested structures of the Si(IV) complexes.

reported values[17] in the range of −120 to −130 ppm. On the basis of the spectral evidence, the following tentative structure with octahedral geometry can be proposed (Figure 2).

Antimicrobial Activity

The antimicrobial activity of a few ligands and their corresponding complexes were tested by paper disc method[18] for their antimicrobial activities at a concerntration of 1 mg/disc. Streptomycin and Micostatin were used as the reference compounds for antibacterical and antifungal activities, respectively. The data are presented in Table IV. They

TABLE IV Antimicrobial Activity of the Ligands and Their Silicon(IV) Complexes

		Compounds					
Microorganism		L^2	$Ph_2SiCl_2(L^2)_2$	L^3	$Ph_2SiCl_2(L^3)_2$	L^4	$Ph_2SiCl_2(L^4)_2$
B. thurengiensis	IZ	8.8	9.8	7.6	9	10.6	11.8
	(AI)	(0.62)	(0.70)	(0.54)	(0.64)	(0.75)	(0.84)
S. aureus	IZ	9.1	11.6	8.1	10.2	9.2	10.9
	(AI)	(0.82)	(1.05)	(0.73)	(0.93)	(0.83)	(0.99)
K. pheumeniae	IZ	6.2	10.2	6.2	8.2	8.2	9.7
	(AI)	(0.47)	(0.78)	(0.47)	(0.63)	(0.63)	(0.74)
E. coli	IZ	9.2	11.6	8.6	10.8	10.1	11.6
	(AI)	(0.76)	(0.96)	(0.71)	(0.9)	(0.84)	(0.96)
A. niger	IZ	6.2	9.9	6.2	9.0	6.8	10.2
	(AI)	(0.80)	(1.38)	(0.69)	(1.23)	(0.82)	(1.43)
A. flavus	IZ	6.2	6.9	6.0	7.3	5.2	6.8
	(AI)	(0.77)	(0.86)	(0.75)	(0.91)	(0.65)	(0.85)
R. phaseoli	IZ	6.0	6.9	4.6	6.9	7.2	8.7
	(AI)	(0.75)	(0.86)	(0.57)	(0.86)	(0.91)	(1.08)
P. crysogenous	IZ	6.2	9.1	4.5	7.9	6	8
	(AI)	(0.88)	(1.3)	(0.64)	(1.12)	(0.88)	(1.27)

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

were tested against *S. aureus, E. coli, B. thurengiensis, K. pneumeniae* (bacteria) and *A. niger, A. flavus, R. phaseoli, P. crysogenous* (fungi).The results have been recorded in the form of inhibition zones (diameter in mm) and activity index.

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

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