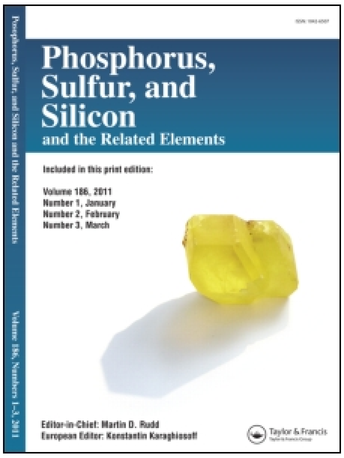

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SYNTHETIC PATHWAYS, STRUCTURAL FEATURES AND BIOCHEMICAL APPLICATIONS AS STERILIZING AGENTS OF SOME DIPHENYLSILICON(IV) CHELATES WITH NSH SYSTEM

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SYNTHETIC PATHWAYS, STRUCTURAL FEATURES AND BIOCHEMICAL APPLICATIONS AS STERILIZING AGENTS OF SOME DIPHENYLSILICON(IV) CHELATES WITH N⌒SH SYSTEM

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The synthesis and structural features of some diphenylsilicon(IV) complexes with biologically active organic moieties derived by the condensation of heterocyclic ketones with thiosemicarbazide have been described. The newly resulting products of the types $Ph_2Si(N⌒S)Cl$ and $Ph_2Si(N⌒S)_2$ were obtained by the 1:1 and 1:2 stoichiometric interactions of diphenyldichlorosilane with the Na-salts of sulfur donor ligands (N⌒SH) in anhydrous methanol. The penta- and hexa- coordinated environment around the silicon(IV) ion have been assigned on the basis of electronic, IR, ^1H NMR and ^{13}C NMR spectral studies as well as physicochemical techniques including molecular weight determinations and conductance measurements. The results of two silicon(IV) complexes along with one ligand as a sterilizing agent on male-mice have also been produced and tried to correlate with the structures of the chelates.

Key words: Organosilicon(IV) complexes; thio-imines; sterilizing agents; ^1H NMR and ^{13}C NMR spectra.

INTRODUCTION

An intensive scrutiny of the literature discloses that there is an impact scope for undertaking systematic studies on N and O/S donor systems on account of their biochemical significance[1–4] in different aspects of human environment. These ligands depending on the reaction conditions may act as ionic or neutral[5] moieties having interesting stereochemistry as only the β-nitrogen coordinates[6] to the metal atom, while the α-nitrogen atom remains uncoordinated. On the other hand, the remaining oxygen or sulfur has a tendency to form strong covalent bond with metal atom. The medical applications[4–7] and effectiveness of the silatranes in the treatment of wounds and tumours is thought to be related to silicon's role in the growth of epithelial and connective tissues and hair, where its function is to impart strength, elasticity and impermeability. Further, it has also been observed that the bioactivity of sulfur atom is greater as compared to the oxygen atom. So, the present situation prompted us to produce such work with monofunctional bidentate azomethine moieties in which the combined effect of silicon along with plus role of sulfur is applicable.

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RESULTS AND DISCUSSION

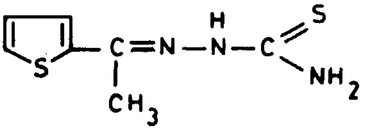
The reaction of diphenyldichlorosilane with the Na-salt of the ligands in 1:1 and 1:2 molar ratios in dry methanol proceed smoothly with precipitation of NaCl, which is removed by filtration.

These reactions can be represented by the following equations:

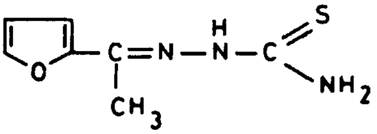
$$\mathrm{Ph_2SiCl_2 + N^\frown S.Na \xrightarrow[1:1]{MeOH} Ph_2Si(N^\frown S)Cl + NaCl}$$

$$\mathrm{Ph_2SiCl_2 + 2\,N^\frown S.Na \xrightarrow[1:2]{MeOH} Ph_2Si(N^\frown S)_2 + 2\,NaCl}$$

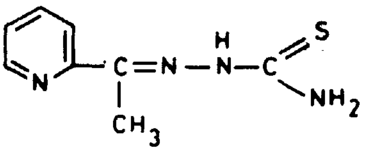
(Where $N^\frown S$ represents the donor set of the ligand molecule $N^\frown SH$). The ligands used are:



(Ac Thiop. TsczH)

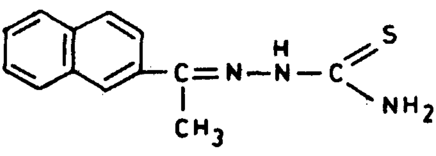


(AcFur.TsczH)



(Ac Pyd.TsczH)

and



(AcNaph.TsczH)

All the newly synthesized complexes have been obtained as coloured solids and are mostly soluble in DMSO, DMF, methanol and chloroform. The molar conductance values of 10^{-3} M solutions (8–12 $\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$) in DMF show them to be nonelectrolyte. The monomeric nature of these complexes has been confirmed by the molecular weight determinations.

SPECTRAL STUDIES

The spectroscopic information of the ligands as well as corresponding silicon complexes is consistant with the formation of proposed structures and some important features may be summarized as follows:

Electronic Spectra

A band due to $>\!C{=}N$ chromophore in the electronic spectra of the ligands at ~380 nm shifts to a shorter wavelength in the complexes and appears at ~360 nm and ~345 nm in 1:1 and 1:2 products, respectively. This clearly indicates the coordination of azomethine nitrogen to the silicon atom. Further, two bands at ~280 nm and ~305 nm remain approximately at the same positions in the spectra of the silicon complexes.

Infra Red Spectra

In the IR spectra of ligands a sharp band in the 1610–1590 cm^{-1} region can be attributed to the characteristic $>$C=N group.[12] This band shifts slightly towards lower frequencies in the silicon complexes indicating thereby the coordination of the azomethine nitrogen to the silicon atom. This is further supported by the presence of a band at 585–560 cm^{-1} due to ν Si $\leftarrow$ N as reported earlier also.[13] The appearance of new bands in the spectra of complexes in the region 765–745 and 540–530 cm^{-1} may be assigned due to ν (Si—C)[14] and ν (Si—S)[15] vibrations, respectively, which were absent in the spectra of ligands. However, in the case of 1:1 products, a band of medium intensity at around 450 cm^{-1} is due to ν (Si—Cl)[16] vibrations. Further, medium to strong intensity bands at ca 1425, 1120, 725 and 700 cm^{-1} are due to ν (Si—C_6H_5)[17] vibrations. The medium intensity bands exhibited in the region 3300–3100 cm^{-1} can be assigned to ν NH of the free ligands, which disappear in the silicon complexes suggesting the possible loss of a proton on the α-nitrogen due to tautomerisation after complexation of the silicon atom to sulfur atom. The bands observed at ~3430 and 3350 cm^{-1} due to symmetric and asymmetric modes of NH_2 group remain at almost on the same position in the spectra of silicon complexes suggesting the noninvolvement of this amino group in chelation.

TABLE I

^{1}H NMR spectral data (δ, ppm) of ligands and their corresponding diphenylsilicon(IV) complexes

Compound	Aromatic (m)	-NH (bs)	$-NH_2$ (bs)	$-CH_3$	Si-C_6H_5
AcThiop.TsczH	8.68 - 7.16	10.68	2.81	1.68	-
Ph_2Si(AcThiop.Tscz)Cl	8.98 - 7.23	-	2.84	2.11	6.11
Ph_2Si(AcThiop.Tscz)$_2$	9.12 - 7.28	-	2.85	2.13	6.23
AcFur.TsczH	7.80 - 6.60	9.90	2.83	1.80	-
Ph_2Si(AcFur.Tscz)Cl	8.23 - 6.81	-	2.85	1.98	5.89
Ph_2Si(AcFur.Tscz)$_2$	8.35 - 6.88	-	2.86	2.10	6.13
AcPyd.TsczH	8.92 - 7.48	10.64	2.84	1.80	-
Ph_2Si(AcPyd.Tscz)Cl	9.38 - 7.59	-	2.86	2.12	6.18
Ph_2Si(AcPyd.Tscz)$_2$	9.41 - 7.62	-	2.88	2.19	6.23
AcNaph.TsczH	8.93 - 7.55	10.65	2.90	1.91	-
Ph_2Si(AcNaph.Tscz)Cl	9.21 - 7.63	-	2.91	2.11	6.00
Ph_2Si(AcNaph.Tscz)$_2$	9.37 - 7.75	-	2.91	2.13	6.17

Proton Magnetic Resonance Spectra

The bonding pattern discussed above gets further support by the nuclear magnetic resonance spectral studies of ligands and their silicon (IV) complexes (Table I). However, for the sake of convenience the ^{1}H NMR spectra of 2-acetylpyridine thiosemicarbazone and its silicon complexes will be discussed in detail and the main points of which are:

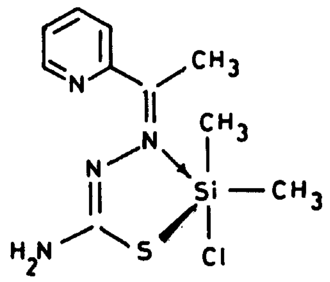
(i) The broad signal exhibited by the ligand due to NH proton at δ 10.64 ppm disappears in the diphenylsilicon(IV) complexes indicating the coordination of nitrogen as well as sulfur to silicon atom.

(ii) In the spectra of complexes, the down field shifting in the position of $-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}{=}\mathrm{N}-$ protons also indicates the coordination of azomethine nitrogen to the silicon atom.

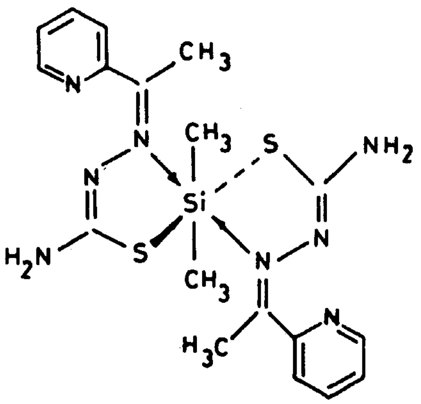
(iii) The appearance of signals due to NH_2 protons at the same positions in the ligand and its complexes, confirms the noninvolvement of this group in coordination. Further, new signals at δ 6.18 ppm and δ 6.23 ppm in 1:1 and 1:2 complexes, respectively, are due to the phenyl proton of Ph_2Si group.

^{13}C NMR Spectra

The ^{13}C NMR spectra of 2-acetylpyridine thiosemicarbazone and its silicon complexes have also been recorded (Table II). A considerable shift in the positions of carbons attached to different participating groups clearly indicates the bonding of azomethine nitrogen and thiolic sulfur to the silicon atom. Thus, on the basis of above discussions it is clear that the ligands by coordinating to silicon atom through the thiolic sulfur and azomethine nitrogen behave as monobasic bidentate ligands. Secondly, all the newly synthesized complexes are monomers and non-electrolytes. Therefore, the following structures, based on the above observations, may be proposed for the silicon complexes and in which the silicon atom seems to be in penta-(1:1 complex) and hexa-coordinated (1:2 complex) states.[16] The ligand shown in these structures is AcPyd. TsczH.



(1:1 Complex)



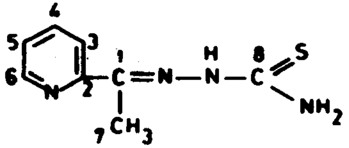
(1:2 Complex)

TABLE II

^{13}C NMR spectral data (δ, ppm) of ligands and its corresponding diphenylsilicon(IV) complexes

COMPOUND	1	2	3	4	5	6	7	8	Si-C
AcPyd.TsczH*	156.20	147.52	123.04	119.89	135.50	146.88	11.33	179.19	-
$Ph_2Si(AcPyd.Tscz)Cl$	148.71	145.41	122.67	118.54	135.01	146.50	13.48	168.91	15.10
$Ph_2Si(AcPyd.Tscz)_2$	149.53	146.13	122.87	119.14	135.23	146.63	13.79	169.73	17.20

*



A penta-coordinated geometry in case of 1:1 complexes is supported by the fact that these complexes also undergo 1:1 addition reactions with pyridine and as a result of which the central silicon atom acquires a stable hexa-coordinated state.

BIOACTIVITY

The study on the antifertility activity of the ligand, 2-acetylthiophene thiosemicarbazone and its silicon complexes as a sterilizing agent in male-mice have been undertaken. Twenty adult male mice (body weight = 40–50 gms) were divided into four groups of five animals each. The animals were kept in plastic cages (dimensions, 10″ × 8″ × 8″) and only three animals were housed in each case. The animals were fed the mice feed pellets and tap water was provided for ad-libitum. Out of four groups, one was used as a control group and the animals of this group received 0.2 ml olive oil/animal/day; orally. The ligand and its complexes were suspended in olive oil separately and given to animals at a dose level of 20 mg/kg body weight/day; orally by gavage tube for 20 days. After 24 hours of the last administration of the compound, the animals were autopsied and the reproduction tract was dissected out. The motility and the count of sperm were measured. It has been observed that the motility and count of sperm decreased after the administration of the ligand and its silicon complexes. A significant decrease ($P < 0.01$) in motility from 81.3 ± 4.6 to 31.7 ± 6.0% was observed in the animals treated with ligand and the sperm count also decreased ($P < 0.05$) from 23.4 ± 2.1 to 10.3 ± 3.3 million/milliliter. A highly significant ($P < 0.001$) decline in the motility of sperms was observed in the case of silicon complexes. The sperm count was also found to decrease significantly in the treated animals. The data recorded in (Table III) indicate that the ligand and its complexes affect the motility as well as count of sperms in male mice. Further, it is also observed that the ligand itself is able to inhibit fertility but due to the added synergistic effects of silicon complexes its activity gets enhanced. Thus, it can be postulated that further intensive studies

TABLE III

Antifertility activity of ligand and its diphenylsilicon(IV) complexes

Compound	Sperm Motility (%)	Sperm Count In Cauda epididymis (mi / ml)
Vehicle Alone (Olive Oil)	81.3 ± 4.6	23.4 ± 2.1
AcThiop.TsczH	31.7 ± 6.0b	10.3 ± 3.3[d]
$Ph_2Si(AcThiop.Tscz)Cl$	16.3 ± 2.3[a]	4.0 ± 1.0[a]
$Ph_2Si(AcThiop.Tscz)_2$	14.5 ± 1.5[a]	3.5 ± 1.5[a]

Values are expressed as mean ± S.E. (Standard Error).
[a] $P < 0.01$, [b]$P < 0.01$, and [d] $P < 0.05$.

TABLE IV

Physical properties and analytical data of organosilicon(IV) complexes

product Formed and Colour	Yield (%)	M. P. (°C)	Elemental Analysis (%)						Mol. Wt
			C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	S Found (Calcd.)	Cl Found (Calcd.)	Si Found (Calcd.)	Found (Calcd.)
$Ph_2Si(AcThiop.Tscz)Cl$ (Yellow)	69	110	54.35 (54.85)	4.11 (4.36)	9.89 (10.10)	14.78 (14.41)	8.76 (8.52)	6.91 (6.75)	403.00 (416.05)
$Ph_2Si(AcThiop.Tscz)_2$ (Brown)	71	135	53.48 (53.95)	4.21 (4.53)	14.31 (14.52)	22.39 (22.16)	- -	4.96 (4.85)	561.00 (578.88)
$Ph_2Si(AcFur.Tscz)Cl$ (Light Brown)	78	200	56.78 (57.06)	4.26 (4.54)	10.29 (10.51)	8.31 (8.02)	9.13 (8.86)	7.23 (7.02)	373.00 (399.98)
$Ph_2Si(AcFur.Tscz)_2$ (Dark Brown)	64	182	56.76 (57.12)	4.48 (4.79)	15.12 (15.37)	11.96 (11.73)	- -	5.31 (5.14)	569.00 (546.75)
$Ph_2Si(AcPyd.Tscz)Cl$ (Yellow)	73	255	58.13 (58.45)	4.38 (4.66)	13.41 (13.63)	8.07 (7.80)	(8.89 (8.63)	7.01 (6.83)	427.00 (411.01)
$Ph_2Si(AcPyd.Tscz)_2$ (Brown)	75	300	58.81 (59.13)	4.63 (4.96)	19.49 (19.70)	11.56 (11.27)	- -	5.17 (4.94)	548.00 (568.81)
$Ph_2Si(AcNaph.Tscz)Cl$ (Yellow)	65	260	65.01 (65.27)	4.58 (4.82)	8.89 (9.13)	7.24 (6.97)	7.94 (7.71)	6.32 (6.11)	473.00 (460.08)
$Ph_2Si(AcNaph.Tscz)_2$ (Cream)	68	230	68.18 (68.43)	4.88 (5.14)	12.39 (12.60)	9.93 (9.62)	- -	4.43 (4.21)	648.00 (666.95)

in this direction might lead to the development of safer and easily acceptable male oral contraceptive.

EXPERIMENTAL

Apparatus fitted with quickfit interchangeable joints was used to carry out the reactions under completely anhydrous conditions. All the chemicals were dried and distilled before use and the reactions were carried out with a ratio head fitted with condenser and protected with calcium chloride drying tubes.

Preparation of ligands. The ligands were prepared by the condensation of 2-acetylthiophene, 2-acetylpyridine, 2-acetylnaphthalene and 2-acetylfuran with thiosemicarbazide in equimolar ratio in absolute alcohol. These were further purified by recrystallization in the same solvent. Their physicochemical properties have been reported in our earlier publication.[18]

Synthesis of diphenylsilicon (IV) complexes. For the preparation of the complexes, diphenyldichlorosilane and the sodium salt of the ligands were mixed in 1:1 and 1:2 stoichiometric proportions in presence of dry methanol in a 100 ml round bottom flask. The reaction mixture was refluxed for a period of 8–14 hours. The precipitated sodium chloride after the completion of the reaction was filtered off and the solvent was removed from the filtrate. The resulting products were then dried under vacuum for 3–4 hours. The compounds were recrystallised from a mixture of methanol and normal hexane and their purity was further checked by T. L. C. using silica gel-G. The analytical data and physical properties have been reported in (Table IV).

Analytical methods and physical measurements. Carbon and hydrogen analyses were performed at the microanalytical laboratory of the department. Nitrogen and sulfur were estimated by kjeldahl's and Messenger's methods, respectively. Silicon was determined gravimetrically as SiO_2. The conductance was measured at 32 ± 1°C with a conductivity bridge type 304 systronics model and the molecular weights were determined by the Rast-Camphor method. IR spectra were recorded on a perkin-Elmer 577 grating spectrophotometer as Nujol mulls using KBr optics. The electronic spectra of ligand and of the resulting complexes were obtained on a pye unicam SP 8–100 spectrophotometer in dry methanol. The ^1H NMR and ^{13}C NMR spectra were recorded on a Jeol FX 90Q spectrometer in DMSO-d_6 using TMS as the internal standard at 89.55 and 22.49 MH_z respectively.

ACKNOWLEDGEMENT

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