

Some New Coordination Compounds Of Organo Silicon (Iv) With Semicarbazones And Thiosemicarbazones

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Abstract: The reactions of diethoxydimethylsilane have been carried out with semicarbazones and thiosemicarbazones prepared by condensation of aldehydes/ketones with semicarbazide hydrochloride / thiosemicarbazide in absolute alcohol. The mode of bonding of these compounds have been established with the help of different spectral studies (^1H , ^{13}C NMR, infrared and electronic) and elemental analysis. The monomeric nature of these complexes have been confirmed by molecular weight determination. The ligands and their silicon (IV) complexes have also been screened for their fungicidal as well as bactericidal activity and were found to be quite active in this respect.

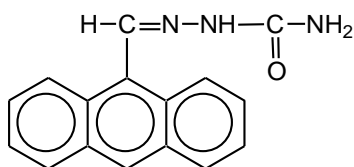
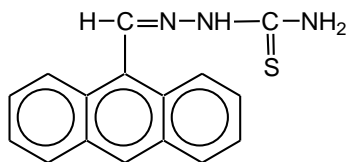
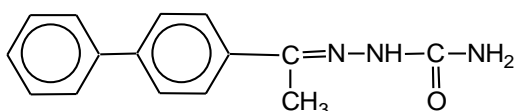
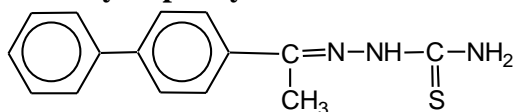
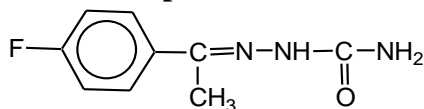
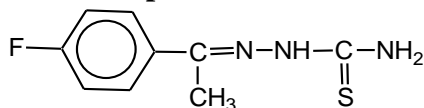
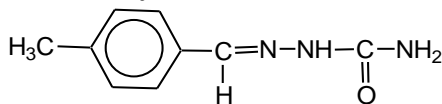
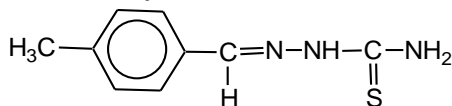
Keywords: Silicon (IV) complexes, diethoxydimethylsilane, spectral studies, semicarbazones and thiosemicarbazones.

INTRODUCTION

Semicarbazones and thiosemicarbazones are the most important nitrogen and oxygen/sulfur donor ligands and have drawn special attention due to their activity against smallpox, viral diseases and certain kinds of tumour¹. The real impetus towards developing the coordination chemistry of these potential ligands was probably provided by the remarkable antitumour, antiviral, antimicrobial, antimalarial and anticonvulsant activities²⁻¹⁰ observed for some of these derivatives which has since been shown to be related to their metal complexing ability¹¹. The stereochemistry of these ligands is also interesting as only the β -nitrogen coordinates to metal atom. Depending on reaction conditions, these compounds may act as ionic or neutral ligands.

Silicon complexes containing Si-O-C, Si-N-C and Si-C bonding play an important role in vital processes and have specific effects on the living organisms. They are also useful in polymer and textile chemistry, space exploration and cosmetics. The interest of organosilicon(IV) compounds is due to their versatile applicability in pharmaceutical and chemical industries. Some work has been reported on the divalent metal complexes of transition metals with bidentate Schiff bases¹².

Extensive studies have been made and a careful survey of literature revealed that there is considerable scope for undertaking systematic studies including the synthesis and biochemical applications of complexes of non transition metals with various semicarbazones and thiosemicarbazones. In the present investigations, several silicon derivatives have been prepared by the reaction of diethoxydimethylsilane with semicarbazones and thiosemicarbazones which are given below:

1. 9-Anthraldehyde semicarbazone**2. 9-Anthraldehyde thiosemicarbazone****3. 4-Acetyl biphenyl semicarbazone****4. 4-Acetyl biphenyl thiosemicarbazone****5. 4-Fluoroacetophenone semicarbazone****6. 4-Fluoroacetophenone thiosemicarbazone****7. p-tolualdehyde semicarbazone****8. p-tolualdehyde thiosemicarbazone****EXPERIMENTAL**

All the glass apparatus fitted with quickfit interchangeable joints were used and all the reactions were carried out under strictly anhydrous conditions. Benzene was first refluxed over sodium wire for several hours and finally distilled azeotropically with ethanol.

Analytical method and physical measurements

Nitrogen and sulfur were estimated by Kjeldahl's method and Messenger's method, respectively^{13,14}. The IR spectra were recorded on FTIR spectrophotometer using a model A-8400 S, Shimadzu in KBr pellets. ¹H and ¹³C NMR spectra were recorded on JEOL AL-300 spectrometer in d₆ DMSO or CDCl₃ using TMS as internal standard at 90MHz. Molecular weight determinations were carried out by the Rast Camphor Method. Molar conductance measurements were made in anhydrous dimethyl formamide at 36±1°C using a model 305 systronics conductivity bridge. The purity of the compounds were checked by thin layer chromatography.

Synthesis of ligands

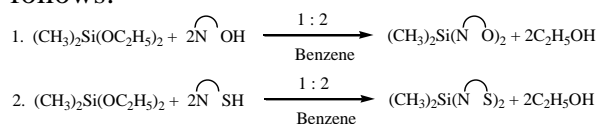
All the ligands were synthesized by the condensation of aldehydes / ketones viz. 9-anthraldehyde, 4-acetylbiphenyl, 4-fluoroacetophenone and p-tolualdehyde with semicarbazide/thiosemicarbazide in 1:1 molar ratio using absolute alcohol as the reaction medium. The mixture was heated on a water bath for about half an hour and then allowed to cool at room temperature. The crystals that separated out were recrystallized from the same solvent. Their physical properties and analysis have been recorded in Table 1.

Synthesis of silicon (IV) complexes

Silicon (IV) complexes were synthesized by the reaction of diethoxydimethylsilane with semicarbazones and thiosemicarbazones in 1: 2 molar ratio in dry benzene as reaction medium. The mixture was refluxed on refluxing column for about 3-4 hours. The product was rendered free from the solvent under reduced pressure and dried in vacuo at 40-50°C. The physical properties and analysis have been recorded in Table 2.

RESULTS AND DISCUSSION

The reactions of diethoxydimethylsilane with above mentioned ligands are given as follows:



(Where $\overset{\curvearrowright}{\text{N}}\text{OH}$ and $\overset{\curvearrowright}{\text{N}}\text{SH}$ represent the donor sets of ligands).

All the values of molar conductance ($10\text{-}15 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in dry DMF at room temperature indicate their non electrolytic nature.

Electronic spectra

The electronic spectra of ligands and its silicon derivatives have been recorded. Two medium intensity bands at $\sim 380 \text{ nm}$ and $\sim 410 \text{ nm}$ are observed. The band at $\sim 380 \text{ nm}$ due to $\pi\text{-}\pi^*$ transition in the ligands remain as such in the spectrum of the silicon complex. The band around $\sim 410 \text{ nm}$ is due to $n\text{-}\pi^*$ transition of the azomethine group which shifts in the spectra of the complexes. This may be due to coordination of azomethine nitrogen to metal atom.

IR spectra

In the infrared spectra of the ligands, medium intensity bands appearing in the region $3100\text{-}2850 \text{ cm}^{-1}$ may be assigned to νNH vibrations. In the solution spectra of ligands, νNH does not appear and νSH is

deserved at $\sim 2550 \text{ cm}^{-1}$ due to tautomerization. In the complexes, νNH or νSH bands do not appear due to formation of silicon-oxygen, silicon-sulfur and silicon-nitrogen bands.

The $\nu\text{C=N}$ frequency of the free azomethine is observed in the region $1588\text{-}1608 \text{ cm}^{-1}$ and it is shifted to lower frequency by $\sim 15 \text{ cm}^{-1}$ in the case of complexes, indicating the coordination of azomethine nitrogen to silicon atom.

In the literature, a shift of this frequency to the higher as well as lower wave number side has been reported and in some cases even no change has been noted. In the complexes, several new bands in the region $580\text{-}570 \text{ cm}^{-1}$, 540 cm^{-1} and $600\text{-}610 \text{ cm}^{-1}$ are due to $\nu\text{Si}\leftarrow\text{N}^{15}$, $\nu\text{Si}\text{-S}^{16}$ and $\nu\text{Si}\text{-O}$, respectively and which are absent in the spectra of the ligands. The infrared spectral data of the ligands and their complexes are given in Table 3.

Table 1: Elemental analysis and physical properties of semicarbazones and thiosemicarbazones.

S. No.	Ligands	Colour & State	Melting point (°C)	Analysis: Found (Calcd.) (%)				Molecular weight: Found (Calcd.)
				C	H	N	S	
1.	C ₁₆ H ₁₃ N ₃ O (L ¹ H) 9-Anthraldehyde semicarbazone	Orange powder solid	220° (d)	72.64 (72.99)	4.67 (4.97)	15.70 (15.96)	-	258.37 (263.26)
2.	C ₁₆ H ₁₃ N ₃ S (L ² H) 9-Anthraldehyde thiosemicarbazone	Yellowish Orange solid	190°	68.34 (68.79)	4.61 (4.68)	14.84 (15.04)	11.26 (11.47)	274.44 (279.33)
3.	C ₁₅ H ₁₅ N ₃ O (L ³ H) 4-Acetylbiphenyl semicarbazone	Yellow powder solid	240°(d)	70.08 (71.13)	5.62 (5.96)	16.48 (16.59)	-	243.37 (253.26)
4.	C ₁₅ H ₁₅ N ₃ S (L ⁴ H) 4-Acetylbiphenyl thiosemicarbazone	White powder solid	180°	66.53 (66.88)	5.59 (5.60)	15.49 (15.60)	11.69 (11.90)	257.44 (269.33)
5.	C ₉ H ₁₀ N ₃ OF (L ⁵ H) 4-Fluoroacetophenone semicarbazone	Shiny white solid	190°	54.75 (55.00)	4.98 (5.00)	21.80 (22.00)	-	190.28 (195.17)
6.	C ₉ H ₁₀ N ₃ SF (L ⁶ H) 4-Fluoroacetophenone thiosemicarbazone	Shiny cream solid	140°	50.65 (51.00)	4.97 (5.00)	19.89 (20.00)	14.79 (15.00)	201.35 (211.24)
7.	C ₉ H ₁₁ N ₃ O (L ⁷ H) p-tolualdehyde semicarbazone	Shiny cream solid	190°	60.64 (61.00)	5.96 (6.00)	23.88 (24.0)	-	167.32 (177.21)
8.	C ₉ H ₁₁ N ₃ S (L ⁸ H) p-tolualdehyde thiosemicarbazone	Shiny white solid	145°	55.79 (56.00)	5.95 (6.00)	21.80 (22.00)	16.77 (17.00)	183.36 (193.27)

Table 2: Reactions of diethoxydimethylsilane with semicarbazones and thiosemicarbazones.

S. No.	Silicon compound	Ligands	Molar ratio	Product and colour & state	Melting point (°C)	Analysis: Found (Calcd.) %			Molecular weight Found (Calcd.)
						Si	N	S	
1.	(CH ₃) ₂ Si(OC ₂ H ₅) ₂	C ₁₆ H ₁₃ N ₃ O	1 :2	SiC ₃₄ H ₃₀ N ₆ O ₂ Orange solid	283°	4.75 (4.81)	14.16 (14.42)	-	582.61 (582.73)
2.	(CH ₃) ₂ Si(OC ₂ H ₅) ₂	C ₁₆ H ₁₃ N ₃ S	1 :2	SiC ₃₄ H ₃₀ N ₆ S ₂ Orange solid	215°	4.43 (4.56)	13.49 (13.66)	10.35 (10.42)	614.72 (614.85)
3.	(CH ₃) ₂ Si(OC ₂ H ₅) ₂	C ₁₅ H ₁₅ N ₃ O	1 :2	SiC ₃₂ H ₃₄ N ₆ O ₂ Yellow solid	280°	4.88 (4.99)	14.83 (14.93)	-	562.68 (562.74)
4.	(CH ₃) ₂ Si(OC ₂ H ₅) ₂	C ₁₅ H ₁₅ N ₃ S	1 :2	SiC ₃₂ H ₃₄ N ₆ S ₂ Cream solid	115°	4.67 (4.72)	13.72 (14.12)	10.76 (10.77)	594.77 (594.86)
5.	(CH ₃) ₂ Si(OC ₂ H ₅) ₂	C ₉ H ₁₀ N ₃ OF	1 :2	SiC ₂₀ H ₂₄ N ₆ O ₂ F ₂ Yellowish cream solid	285°	6.04 (6.28)	18.52 (18.82)	-	446.42 (446.53)
6.	(CH ₃) ₂ Si(OC ₂ H ₅) ₂	C ₉ H ₁₀ N ₃ SF	1 :2	SiC ₂₀ H ₂₄ N ₆ S ₂ F ₂ Very light brown solid	125°	5.74 (5.86)	17.21 (17.55)	13.08 (13.39)	477.55 (478.65)
7.	(CH ₃) ₂ Si(OC ₂ H ₅) ₂	C ₉ H ₁₁ N ₃ O	1 :2	SiC ₂₀ H ₂₆ N ₆ O ₂ Yellowish cream solid	210°	6.75 (6.84)	20.13 (20.47)	-	410.31 (410.55)
8.	(CH ₃) ₂ Si(OC ₂ H ₅) ₂	C ₉ H ₁₁ N ₃ S	1 :2	SiC ₂₀ H ₂₆ N ₆ S ₂ Cream solid	175°	6.22 (6.34)	18.81 (18.98)	14.40 (14.48)	441.43 (442.67)

Table 3: Important IR spectral data of ligands and their silicon (IV) complexes.

S.No.	Compounds	$\nu\text{NH}/\nu\text{OH}$ (cm^{-1})	$>\text{C}=\text{N}$ (cm^{-1})	$\nu\text{Si}\leftarrow\text{N}$ (cm^{-1})	$\nu\text{Si}-\text{S}$ (cm^{-1})	$\nu\text{Si}-\text{O}$ (cm^{-1})
1.	L^1H	3100-2850	1600	-	-	-
2.	$\text{Si}.2\text{L}^1\text{H}$	-	1590	580	-	600
3.	L^2H	3000-2850	1600	-	-	-
4.	$\text{Si}.2\text{L}^2\text{H}$	-	1590	572	540	-
5.	L^3H	3050-2850	1608	-	-	-
6.	$\text{Si}.2\text{L}^3\text{H}$	-	1588	570	-	610

¹H NMR spectra

The proton magnetic resonance spectra of ligands and their corresponding complexes have been recorded in d₆-DMSO or CDCl₃ using TMS as the internal standard.

The broad signals due to NH protons at δ 10.15 ppm in the ligands disappear in the case of silicon complexes showing ligation of silicon with nitrogen, oxygen and sulfur.

The azomethine proton signal

$\left(\begin{array}{c} \text{---C=NH} \\ | \\ \text{H} \end{array} \right)$ appearing at δ 8.00 in the

ligand undergoes deshielding in complex which indicates coordination of the

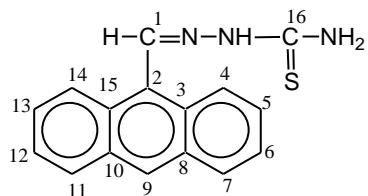
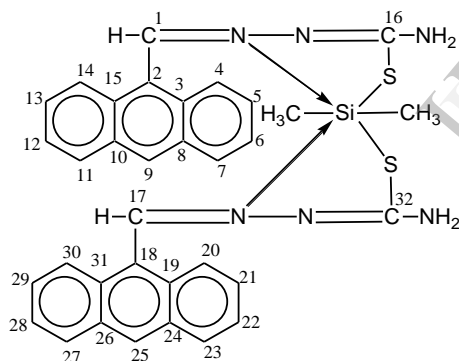
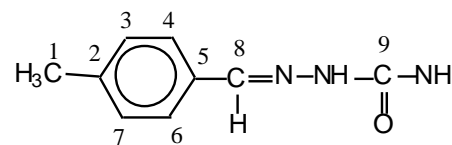
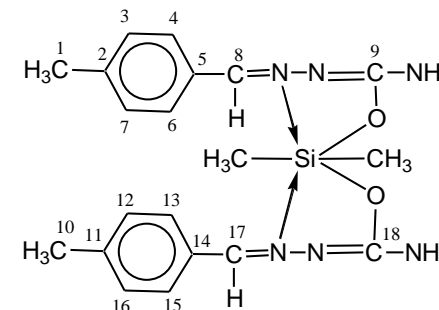
azomethine nitrogen to silicon atom. The new proton signals at δ 1.52 and δ 1.45 ppm in the compounds are due to the methyl protons of the (CH₃)₂ Si group.

¹³C NMR spectra

The ¹³C NMR spectra of ligands and their corresponding silicon (IV) complexes have been recorded in Table 4. The signals due to carbon atoms attached to azomethine groups and sulfur atoms show considerable shifts which indicate the involvement of nitrogen in coordination with the silicon atom.

Table 4: ^{13}C NMR spectral data (δ ppm) of ligands and their corresponding silicon (IV) complexes.

Compounds	Chemical shifts in δ ppm															
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆
L ² H	178.0	128.9	132.3	128.1	125.3	125.3	128.1	131.9	128.5	131.9	128.1	125.3	125.3	128.1	132.3	186.0
Si.2L ² H	165.3	126.0	132.0	128.0	125.0	125.0	128.0	132.0	126.0	132.0	128.0	125.0	125.0	128.0	132.0	163.0
L ⁷ H	20.9	140.0	129.3	128.9	128.2	128.9	129.3	179.0	161.0	-	-	-	-	-	-	-
Si.2L ⁷ H	20.9	138.0	129.0	128.0	126.0	128.0	129.0	166.3	163.0	20.9	138.0	129.0	128.0	126.0	128.0	129.0

**Fig. 1: L²H****Fig. 2: Si.2L²H****Fig. 3: L⁷H****Fig. 4: Si.2L⁷H**

BIOLOGICAL ACTIVITY

The antimicrobial activity of ligands and their metal complexes with silicon are tested using paper disc diffusion method^{17,18}. The ligands and their corresponding complexes are screened against *F.oxysporum*, *A. flavus* and *R. phaseoli*. All of the complexes are found to be most active against these fungi at all concentrations (10, 50, 100 and 200 ppm). Potato dextrose agar medium is prepared in the flasks and sterilized. For antifungal activity, radial growth method is used. Some representative complexes are also tested against gram positive bacteria (*S.aureus*) and gram negative bacteria (*E.coli*).The bacteria are cultured for 24 hours at 37°C in an incubator.

The fungicidal as well as bactericidal activity of the ligands and their metal complexes increase with increase in concentration of the compounds. The results are recorded in the form of inhibition zone (diameter in mm) and activity index. The results show that the silicon complexes are more potent in their inhibition properties than the free ligands.The data are presented in Table 5.

ACKNOWLEDGEMENT

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Table 5 : Antimicrobial activity of the ligands and their silicon (IV) complexes.

Microorganisms		$C_{16}H_{13}N_3S$		$SiC_{34}H_{30}N_6S_2$		$C_{15}H_{15}N_3O$		$SiC_{32}H_{34}N_6O_2$	
		100 ppm	200 ppm	100 ppm	200 ppm	100 ppm	200 ppm	100 ppm	200 ppm
<i>F. oxysporum</i>	IZ (AI)	24 (1.09)	38 (2.37)	30 (1.36)	42 (2.62)	12 (0.54)	20 (1.25)	18 (0.81)	28 (1.75)
<i>R. phaseoli</i>	IZ (AI)	22 (1.00)	34 (1.54)	24 (1.09)	36 (1.63)	22 (1.00)	34 (1.54)	24 (1.09)	36 (1.63)
<i>A. flavus</i>	IZ (AI)	26 (1.00)	38 (1.90)	38 (1.46)	53 (2.65)	26 (1.00)	40 (2.00)	38 (1.46)	55 (2.75)
<i>S. aureus</i>	IZ (AI)	16 (0.88)	38 (1.11)	20 (1.11)	42 (1.23)	10 (0.55)	22 (0.64)	14 (0.77)	26 (0.76)
<i>E. coli</i>	IZ (AI)	20 (1.00)	38 (1.00)	24 (1.20)	42 (1.10)	12 (0.60)	20 (0.52)	16 (0.80)	24 (0.63)

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

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