



NITROGEN, OXYGEN BONDED HETROCYCLIC ORGANOSILICON (IV) DERIVATIVES OF A NEW SCHIFF BASE : SYNTHESIS AND SPECTRAL ASPECTS

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ABSTRACT

Some di, tri-organosilicon (IV) metal complexes of a new SNO tridentate heterocyclic Schiff base derived from the reaction of 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-thione with salicylaldehyde have been synthesized and characterized on the basis of elemental analyses, IR, ¹H, ¹³C, ²⁹Si NMR spectra, It has been found that the Schiff base behaves as a neutral tridentate SNO ligand forming chelates with 1 : 2 and 1 : 1 (metal : ligand) stoichiometry.

Key words: Hetrocyclic, Organosilicon, Schiff base.

INTRODUCTION

A considerable amount of work has been carried out on organosilicon (IV) complexes with S, N and O donar ligands¹⁻³ particularly, derived from salicylaldehyde and various amines⁴⁻⁵ from our laboratory. O-hydroxyacetophenone glycine complexes of organosilicon (IV) have already been reported⁶ exhibiting interesting coordination patterns. A very little attention has been paid to the Schiff base derived from salicylaldehyde and 2-amino-5-chlorobenzophenone which is an important metabolite precursor for the synthesis of drugs, known as 1,4-benzodiazepines.⁷ In continuation of our studies on organosilicon (IV) derivatives,⁸ we report Here the synthesis and characterization of some new complexes of organosilicon (IV) with new SNO tridentate heterocyclic Schiff base derived from the reaction of 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-thione with salicylaldehyde

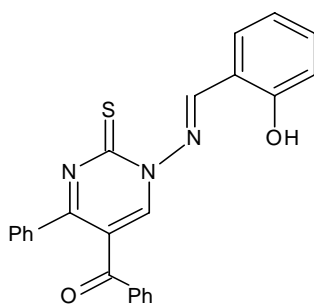


Fig. 1: The ligand

EXPERIMENTAL

Materials and methods

MeOH, EtOH, BuOH, CHCl_3 , DMF, DMSO, toluene, diethyl ether, *n*-heptane, *n*-hexane, and salicylaldehyde were obtained from Fluka or Aldrich. All solvents were dried and purified before use. 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-thione was prepared as described previously¹⁰. Elemental analyses (C, H, N, S) were performed using a Carlo Erba 1106 elemental analyzer. The IR spectra were obtained using KBr discs $4000\text{--}400\text{ cm}^{-1}$ on a Bio-Rad-Win-IR spectrophotometer. The ^1H NMR spectra of the Schiff base and its tin complexes were recorded on a Varian XL-200 NMR instrument.

Preparation of the Schiff base (LH)

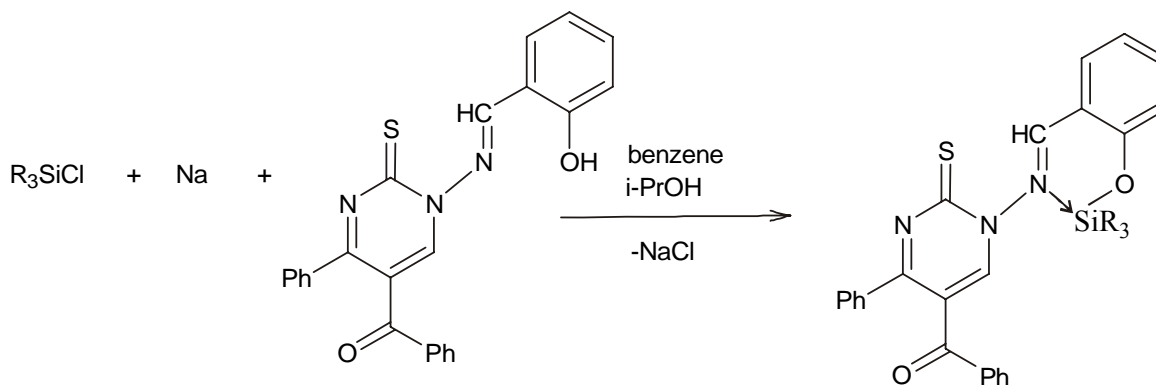
The new Schiff base ligand was prepared by the condensation of 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-thione (0.3070 g, 1 mmol) with salicylaldehyde (0.1220 g, 1 mmol) in *n*-butanol (40 mL) by refluxing for 2 hr. The resulting colored solid was filtered, recrystallized from *n*-BuOH, and dried in a vacuum desiccator, providing LH (0.312 g, 76%) as light-yellow solid, m.p. 205°C . ^1H NMR (ppm): 7.02–7.85 (m, phenyl protons), 10.25 (s, phenolic proton), 9.17 and 8.96 (s, azomethine protons).

Preparation of Si (IV) complex [Ph₃(L)]

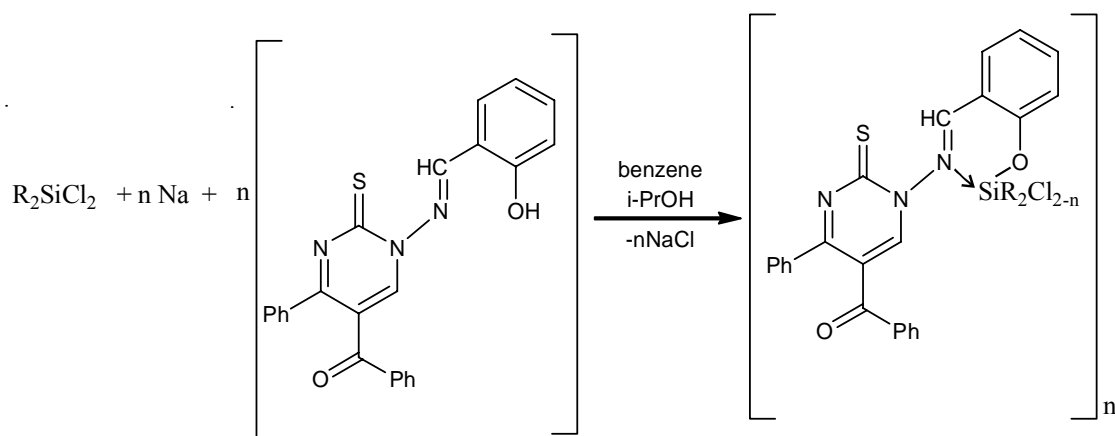
Sodium salt of HL (1.54 g, 1.0 mmol) was dissolved in 30 mL of benzene. Then a solution of tri phenyl silicon chloride (1.05 g, 1.0 mmol) in 15 mL methanol was added drop-wise into the solution over a period of 2 min. After being stirred at 50°C for several hours, the reaction mixture was filtered. The obtained brown product was washed with cold ethanol and diethyl ether and then dried under reduced pressure (2.76g, 70%) as solid having m.p. $233\text{--}235^\circ\text{C}$

RESULTS AND DISCUSSION

The newly synthesized Schiff base ligand and its complexes are very stable at room temperature in the solid state. The ligand is soluble in common organic solvents but its metal complexes are generally soluble in DMF and DMSO. Condensation of salicylaldehyde with 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-thione readily gives rise to the corresponding imine as shown in Fig. 1. LH was easily identified by the IR and ^1H NMR spectra (Table 2). Tridentate complexes were obtained from 1:1 and 1:2 mole ratio reactions with metal ions and the ligand. The ligand (LH) on reaction with Ph_3SiCl , Bu_3SiCl , Bu_2SiCl_2 , Me_3SiCl and Me_2SiCl yields corresponding to the formulas $[\text{Ph}_3\text{Si}(\text{L})]$, $[\text{Bu}_3\text{Si}(\text{L})]$, $[\text{Bu}_2\text{Si}(\text{L})\text{Cl}]$, $[\text{Bu}_2\text{Si}(\text{L})_2]$, $[\text{Me}_3\text{Si}(\text{L})]$, $[\text{Me}_2\text{Si}(\text{L})\text{Cl}]$ and $[\text{Me}_2\text{Si}(\text{L})_2]$. The complexes were prepared by the general reactions shown below.



where R = Ph, (Comp. 1), R = *n*-Bu (Comp. 2)



where R = n-Bu, n=1 (Comp. 3); R=n-Bu, n=2 (Comp. 4); R= Me, n=1 (Comp. 5); R=Me, n=2 (Comp. 6).

Table 1 : Physical and elemental analyses

Compound	MP °C	Yield %	Analysis (%) Found &(Cal.)					
			C	H	Si	N	S	Cl
C ₄₂ H ₃₁ N ₃ O ₂ SSi	240	70	75.31 (75.31)	4.66 (4.66)	4.19 (4.19)	6.27 (6.27)	4.79 (4.79)	
C ₃₃ H ₃₇ ClN ₃ O ₂ SSi	270	75	65.70 (65.70)	6.18 (6.18)	4.66 (4.66)	6.97 (6.97)	5.32 (5.32)	5.88 (5.88)
C ₃₂ H ₃₄ ClN ₃ O ₂ SSi	282	78	65.34 (65.34)	5.83 (5.83)	4.77 (4.77)	7.14 (7.14)	5.45 (5.45)	6.03 (6.03)
C ₅₆ H ₅₀ N ₆ O ₄ S ₂ Si	279	80	69.83 (69.83)	5.23 (5.23)	2.92 (2.92)	8.72 (8.72)	6.66 (6.66)	
C ₂₆ H ₂₂ ClN ₃ O ₂ SSi	275	74	61.95 (61.95)	4.40 (4.40)	5.57 (5.57)	8.34 (8.34)	6.36 (6.36)	7.03 (7.03)
C ₅₀ H ₃₈ N ₆ O ₄ S ₂ Si	280	77	68.31 (68.31)	4.36 (4.36)	3.19 (3.19)	9.56 (9.56)	7.30 (7.30)	

Table 2: Characteristic IR and electronic absorption spectral data of the ligand and its metal complexes

Compound	C=S	C=N	C-O	Si-N	Si-O	Si-S
LH	1,050 m	1,640 m	1,28 s	-	-	-
C ₄₂ H ₃₁ N ₃ O ₂ SSi	1,020 m	1,600 m	1,266 m	550 w	1075 w	495 w
C ₃₃ H ₃₇ ClN ₃ O ₂ SSi	1,028 m	1,610 m	1,260 m	560 w	1060 w	475 w
C ₃₂ H ₃₄ ClN ₃ O ₂ SSi	1,030 w	1,610 m	1,272 s	540 w	1070 w	506 w
C ₅₆ H ₅₀ N ₆ O ₄ S ₂ Si	1,035 m	1,598 m	1,270 m	545 w	1065 w	490 w
C ₂₆ H ₂₂ ClN ₃ O ₂ SSi	1,035 m	1,590 m	1,272 m	545 w	1080 w	515 w
C ₅₀ H ₃₈ N ₆ O ₄ S ₂ Si	1,030 m	1,610 m	1,273 m	550 w	1070 w	520 w

Table 3: ^1H , ^{13}C and ^{29}Si NMR spectral data of organosilicon (iv) derivatives of the new heterocyclic ligand

Sl. No.	Compound	Chemical Shift (δ) ppm		
		^1H	^{29}Si	^{13}C
1	$\text{C}_{42}\text{H}_{31}\text{N}_3\text{O}_2\text{SSi}$	6.80-8.65 (m, 33H, Ph)	-57.60	126.4-139.8 (Ph), 188.2 (C=O), 160.3 (C=N)
2	$\text{C}_{33}\text{H}_{37}\text{ClN}_3\text{O}_2\text{SSi}$	6.75-7.82 (m, 43H, Ph); 0.4-1.5 (m, 32H, n-Bu); 0.5-1.1 (t, 9H, terminal CH_3 of butyl group).	-45.46	127.2-140.7 (Ph), 189.0 (C=O), 158.4 (C=N) 8.64, 11.44, 18.34 (Si-Bu)
3	$\text{C}_{32}\text{H}_{34}\text{ClN}_3\text{O}_2\text{SSi}$	6.35-8.2 (m, 28H, Ph); 0.5-1.4 (m, 27H, n-Bu); 0.4-1.0 (t, 9H, terminal CH_3 of butyl group)	-146.14	125.8-141.2 (Ph), 188.6 (C=O), 159.0 (C=N), 9.21, 12.32, 18.68 (Si-Bu)
4	$\text{C}_{56}\text{H}_{50}\text{N}_6\text{O}_4\text{S}_2\text{Si}$	6.9-8.3 (m, 28H, Ph); 0.6-1.5 (m, 18H, n-Bu); 0.5-1.1 (t, 6H, terminal CH_3 of butyl group.)	-326.23	126.6-140.2 (Ph) 190.2 (C=O), 160.1 (C=N), 9.63, 12.81, 19.93 (Si-Bu)
5	$\text{C}_{26}\text{H}_{22}\text{ClN}_3\text{O}_2\text{SSi}$	6.80-8.40 (m, 28H, Ph); 1.2 (s, 6H, CH_3).	-159.50	125.7-140.68 (ph), 189.7 (C=O) 157.6 (C=N), 7.41 (Si-Me)
6	$\text{C}_{50}\text{H}_{38}\text{N}_6\text{O}_4\text{S}_2\text{Si}$	6.62-8.41 (m, 28H, Ph); 1.0 (s, 6H, CH_3).	189.63	126.9-141.2 (Ph), 188.3 (C=O), 158.7 (C=N), 7.86 (Si-Me)

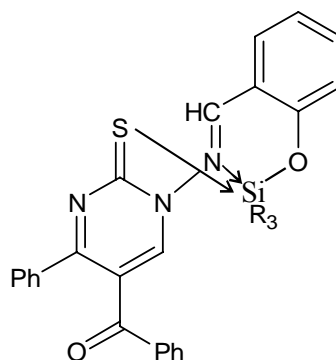
IR Spectral data

The infrared spectra of these organosilicon (IV) complexes have been recorded in the form of KBr pellets in the range $4000\text{--}400\text{ cm}^{-1}$. Tentative assignments have been made on the basis of earlier publications^{4,5}. The spectrum of the ligand shows bands in the regions 1050 , $3260\text{--}3380$, 1620 cm^{-1} , which have been assigned to $\nu(\text{C}=\text{S})$, $\nu(\text{OH})$, $\nu(\text{C}=\text{N})$ respectively⁹. The disappearance of 3260 cm^{-1} indicates the deprotonation of the O-H and consequent coordination of phenolic oxygen atom to silicon metal, which is further substantiated by the appearance of bands in the region $570\text{--}440\text{ cm}^{-1}$, that may be due to Si-C and Si-O stretching vibrations¹⁰⁻¹¹. The bands present at 1615 , 1050 cm^{-1} due to $\nu\text{ C}=\text{N}$, $\nu\text{ C}=\text{S}$ in the ligand is found to be shifted for about $20\text{--}25\text{ cm}^{-1}$ to lower wave number in the complexes suggesting coordination of the azomethine nitrogen and sulphur to the central metal atom¹³.

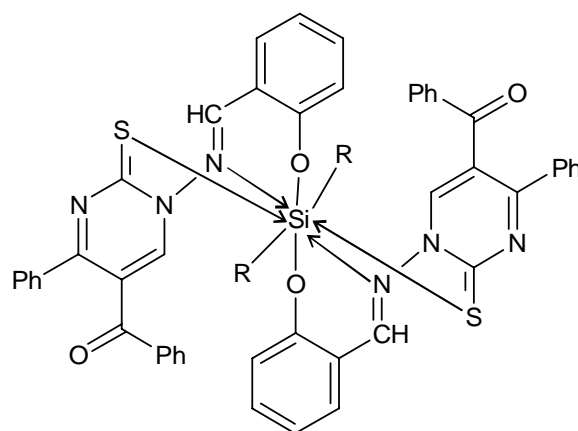
NMR Spectral data

The NMR spectra of ligand is characterised by appearance of a signal at 12.40 ppm for phenolic -OH group, at 10.60 ppm for azomethine group and a multiplet at $6.84\text{--}7.86\text{ ppm}$ attributable to protons of phenyl moiety. The resonance at 12.40 ppm is present in the spectra of the complexes, integration of protons along with appearance of Si-O stretching band in IR and ^{29}Si NMR suggesting the deprotonation of the phenolic -OH and its subsequent involvement in coordination. The coordination through azomethine and sulphur is supported by the high field shift of the free ligand signal at 10.60 ppm to 11.60 ppm in the complexes.¹⁴ The resonance due to the phenyl moiety remains unaffected. The PMR spectra of complexes exhibit phenylene proton resonances are overlapping with the phenylene proton resonances of the ligand to give a complex pattern at $6.76\text{--}8.25\text{ ppm}$. The resonances due to the butyl protons are observed in the region $0.60\text{--}1.86\text{ ppm}$, with a well defined triplet at 0.85 ppm ($J = 8\text{ Hz}$) which is due to methyl protons of butyl group. The methyl protons of the dimethylsilicon (IV) derivatives appear as a sharp singlet at 0.44 ppm .

The²⁹ Si chemical shifts of all the derivatives have been observed in the range at -86.85 to -433.27 ppm. Thus based on above spectral studies the following structures may be tentatively proposed for triorganosilicon (IV) and diorganosilicon (IV) derivatives of the ligand, respectively.



(a)



(b)

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