



SYNTHESIS AND CHARACTERIZATION OF ORGANOSILICON (IV) COMPLEXES WITH SOME SCHIFF BASE DERIVATIVES

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ABSTRACT

New Schiff bases derived from 2-hydroxy- or 2-methoxy benzaldehyde and phenyl-3-aminophenyl ketone or 2-amino-3-hydroxy pyridine (L_1 , L_2 , L_3 and L_4 , respectively), have been found to react with the organosilicon (IV) chlorides, R_nSiCl_{4-n} ($R = Me$ or Ph , $n = 1-3$) to yield complexes of the general formulae $[R_nSiCl_{3-n}(L_1-H)]$, $[R_nSiCl_{4-n}(L_2)]$, $n = 1-3$; $[R_nSiCl_{2-n}(L_3-2H)]$, $n = 1,2$; $[Me_2PhSi-(L_3-H)]$ and $[R_nSiCl_{3-n}(L_4-H)]$, $n = 1-3$. These complexes have been characterized physicochemically and spectroscopically. The molecular mechanic techniques were applied to confirm the suggested structures of the complexes by computing the steric energy and the physical properties of each complex.

Key words : Organosilicon (IV), Schiff base.

INTRODUCTION

The rather diffused d-orbitals of silicon atom and their higher energy than s- and p-orbitals of the same level, attracted many chemists to examine the type of coordination of silicon with donor ligands. Hence, a large body of research work on silicon complexes, with coordination numbers higher than four have been reported¹. In view of the importance of organosilicon complexes with Schiff bases as fungicidal, bactericidal, herbicidal, acaricidal, antifeedant ...etc and the limited information on metal complexes of heterocyclic Schiff bases², promoted us to undertake a systematic search in this field. Also, our continuous interest in the field of coordination chemistry of organosilicon³⁻⁶ enhances us to carry out this research work. Therefore, we present here the synthesis and characterization of some new Schiff base derivatives, L_1-L_4 (Fig.1) and their complexes with various organosilicon- (IV) compounds, *i.e.*, R_nSiCl_{4-n} , $R = Me$ or Ph and $n = 1-3$. The study also, includes the molecular calculations of the suggested structures of the complexes in order to obtain the optimized configurations for

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all complexes. A careful survey of the available literature revealed that there is no similar study on organosilicon(IV) complexes with the type of Schiff bases used.

EXPERIMENTAL

Physical measurements

IR spectra were recorded on Unicam SP 2000 Spectrometer at a range ($200 - 4000 \text{ cm}^{-1}$) using Nujol mull and KBr discs. Elemental analyses of the ligands and their complexes were carried out on CHN analyzer, type 1106 (Carlo Erba). Electronic spectra were recorded on a Shimadzu UV/Vis Spectrophotometer UV-160 for 10^{-3} M solutions of the complexes in ethanol at 25°C using 1 cm quartz cell. Conductivity measurements were recorded on a conductivity meter, model 4070 (Jenway), using 10^{-3} M solution of the complexes in ethanol at ambient temperature (25°C). Theoretical computations were applied on the suggested structures of the prepared complexes using MM2 CS ChemOffice version 7.0 by Pentium (IV) computer.

Preparation of compounds

The compounds PhMe_2SiCl , Ph_2SiCl_2 , Me_2SiCl_2 , and MeSiCl_3 were commercial products (Fluka) and used as supplied.

Preparation of ligands

The Schiff base ligands L_1-L_4 (Fig.1) were prepared in our laboratories by refluxing equimolar quantities of phenyl-3-aminophenyl ketone or 2-amino-3-hydroxy pyridine and 2-hydroxybenzaldehyde or 2-methoxybenzaldehyde for *ca.* 1h. The Schiff base formed was filtered off from its cold solution and crystallized from ethanol / ether and dried under vacuum for several hours.

Preparation of complexes

Since all silicon compounds used are hygroscopic, therefore the moisture was excluded by using highly dry apparatus and the solvents were distilled under inert atmosphere. The complexes were prepared according to the general following procedure:

In three-necked round bottom flask fitted with a motor stirrer, condenser and a dropping funnel, a solution of the ligand (0.03 mol) in absolute methanol (100 mL) was stirred. A solution of $\text{R}_n\text{SiCl}_{4-n}$ (PhMe_2SiCl , Ph_2SiCl_2 or MeSiCl_3) (0.03 mol) in absolute methanol (100 mL) was added dropwise with continuous stirring and the mixture was refluxed for 1h. The solid product formed was filtered off and crystallized from ethanol / ether and dried under vacuum for *ca.* 3h.

Theoretical Calculations

The optimized geometry and the steric energy of the complexes were done using MM2 module in the CS ChemOffice 7.0 Molecular Modeling program package. These calculations were performed using computer Pentium (IV) with processor operating at 2400 MHz.

RESULTS AND DISCUSSION

The physical properties of the new ligands are listed in Table 1 and for the prepared complexes in Table 2 and 3. The elemental analyses of these complexes assigned to 1 : 1 molar ratio of R_nSiCl_{4-n} :Schiff base.

Table 1. Physical properties and elemental analyses of the ligands

L	Colour	M.P. (°C)	Yield (%)	Elemental analyses: Found (Calc.) %		
				% C	% H	% N
L ₁	Yellow	123	74	79.82 (79.73)	4.63 (4.98)	4.93 (4.65)
L ₂	Orange	106	80	80.36 (80.00)	5.52 (5.40)	4.72 (4.44)
L ₃	Yellow	130	71	66.91 (67.29)	4.24 (4.67)	12.81 (13.08)
L ₄	Deep yellow	145	79	68.11 (68.42)	4.93 (5.26)	11.93 (12.28)

Table 2. Physical properties and elemental analyses of the prepared complexes

S. No.	Complex	Colour	M.P. (°C)	Yield (%)	Molar conductivity $cm^2\ ohm^{-1}\ mol^{-1}$	Elemental analyses: Found (Calc.) %		
						% C	% H	% N
1.	[Me ₂ PhSi(L ₁ -H)]	Yellow-green	140-142	70	14	77.43 (77.22)	5.59 (5.75)	3.08 (3.22)
2	[Ph ₂ SiCl(L ₁ -H)]	Orange	60-62*	68	11	74.36 (74.20)	4.82 (4.64)	2.51 (2.71)
3	[Me ₂ SiCl(L ₁ -H)]	Yellow-green	173-175	73	16	66.89 (67.08)	5.30 (5.08)	3.64 (3.56)
4	[MeSiCl ₂ (L ₁ -H)]	Yellow-green	146-148	81	8	60.94 (60.87)	3.92 (4.11)	3.17 (3.38)
5	[Me ₂ PhSiCl(L ₂)]	Yellow	90-92	77	21	71.53 (71.67)	5.84 (5.77)	2.93 (2.88)
6	[Ph ₂ SiCl ₂ (L ₂)]	Yellow	70-72*	78	14	70.06 (69.72)	4.61 (4.75)	2.57 (2.46)
7	[Me ₂ SiCl ₂ (L ₂)]	Yellow-green	148-150	68	13	62.30 (62.16)	5.31 (5.18)	3.29 (3.15)
8	[Me ₂ SiCl ₃ (L ₂)]	Yellow-green	153-155	75	20	57.42 (57.57)	4.66 (4.80)	3.12 (2.92)
9	[Me ₂ PhSi(L ₃ -H)]	Yellow-green	66-68*	74	9	68.88 (68.95)	5.59 (5.75)	7.87 (8.04)
10	[Ph ₂ Si(L ₃ -2H)]	Yellow	156-157	80	12	72.91 (73.08)	4.38 (4.57)	6.93 (7.10)
11	[Me ₂ Si(L ₃ -2H)]	Pale-yellow	166-168	82	17	62.31 (62.20)	5.27 (5.18)	10.52 (10.37)
12	[MeSiCl(L ₃ -2H)]	Pale-yellow	99-101*	73	22	53.60 (53.69)	4.96 (4.82)	9.55 (9.64)
13	[Me ₂ PhSi(L ₄ -H)]	Yellow	174-176	68	18	69.70 (69.59)	6.12 (6.08)	7.81 (7.73)
14	[Ph ₂ SiCl(L ₄ -H)]	Green	169-171	69	16	67.53 (67.48)	4.68 (4.72)	6.38 (6.30)
15	[Me ₂ SiCl(L ₄ -H)]	Yellow	157-160*	74	19	56.19 (56.15)	5.37 (5.30)	8.68 (8.73)
16	[MeSiCl ₂ (L ₄ -H)]	Green	184-186	78	10	49.21 (49.27)	4.06 (4.11)	8.33 (8.21)

* Complexes melt with decomposition.

Table 3. Selected IR frequencies and electronic transitions for the complexes

No.	Selected IR data* (cm ⁻¹)						UV/Vis λ_{\max} (nm)
	ν (C=N)	ν (Si-N)	ν (Si-O)	ν (Si-CH ₃)	ν (Si-Ph)	ν (Si-Cl)	
1	1632 m	532 w	682 m	743 m	421 m	–	235, 340, 270, 310
2	1643 w	512 m	697 w	–	512 w	621 w	225, 280, 315, 270
3	1630 w	545 m	715 w	741 m	472 w	632 s	270, 315, 262, 300
4	1651 s	562 m	743 w	745 s	455 m	640 s	230, 275, 310, 365
5	1644 w	533 w	722 w	752 w	519 w	–	245, 284, 324, 370
6	1662 w	506 w	688 w	–	433 m	652 s	238, 270, 325, 340
7	1639 w	542 s	711 m	749 w	410 w	636 w	241, 275, 330, 250
8	1672 m	526 w	742 m	740 s	492 s	619 s	225, 268, 280, 320
9	1631 m	550 w	735 m	747 w	–	–	228, 260, 290, 340
10	1648 m	513 s	679 s	–	–	650 w	234, 270, 320, 255
11	1659 m	517 s	709 s	738 m	–	655 w	240, 265, 285, 365
12	1655 m	561 m	750 s	748 s	–	643 w	245, 285, 325, 270
13	1656 m	557 m	720 s	752 m	–	–	233, 280, 270, 320
14	1673 m	537 w	744 s	–	–	621 s	239, 275, 340, 370
15	1666 m	503 w	710 w	750 m	–	633 s	240, 281, 347, 370
16	1637 m	497 s	707 w	745 m	–	657 m	242, 280, 290, 335

For IR data, s, strong; m, medium and w, weak.

The chelated silicon forms with these ligands are of interest as the silicon attains its highest coordination number of five or six. The present study concerns with the structures and the type of bonding between the functional groups of the ligands with silicon.

The IR spectra of complexes showed bands in the region 497–562 cm⁻¹ and 738–752 cm⁻¹ which is assigned to ν (N-Si) and ν (Me-Si), respectively^{7,8}. The absorption band appeared in the region 679–750 cm⁻¹ is attributed to the stretching frequency of Si-O. In the ligand spectra, the absorption bands at 1625, 1632, 1615 and 1622 cm⁻¹ are assigned to the stretching frequency of C=N in L₁, L₂, L₃, and L₄, respectively, while in all prepared complexes, the C=N stretching frequency was shifted to a higher frequency value, *i.e.*, in the region 1630–1673 cm⁻¹. The IR spectra of the complexes, also, showed bands in the regions 410–519 cm⁻¹ and 619–657 cm⁻¹, which attributed to ν (Si-Ph) and ν (Si-Cl), respectively. The (C=N)_{py} value is

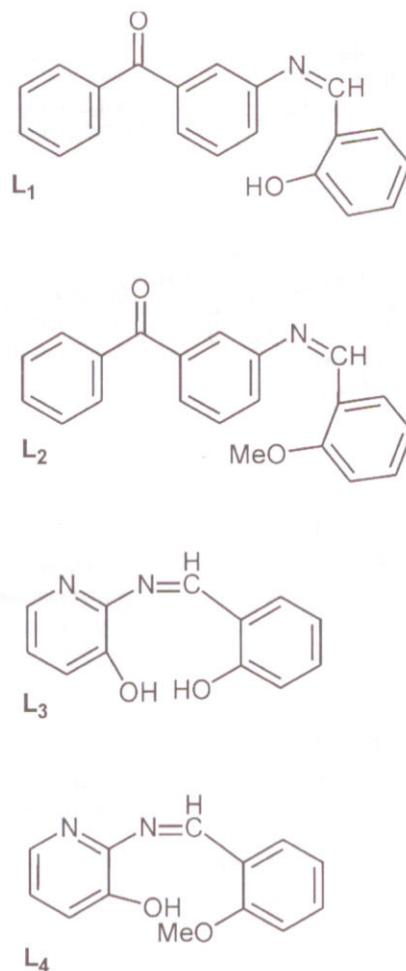


Fig.1. The suggested structures of the free Schiff bases

slightly affected upon coordination and this is well known for the coordination of such ligands with various metal acceptors⁹⁻¹¹.

It seems likely that there are three types of coordination modes of the silicon central atom and the reactive sites in the ligands, depending on the ligand's nature. In complexes (5-8), the silicon atom linked with the Schiff bases in a monodentate fashion via N-imine (as the most active site in the ligand), but in the complexes (1-4), (9), and (13-16) the silicon atom linked with the ligands in a bidentate fashion via the N-imine and the oxygen of the hydroxy group forming five or six member rings¹², while in the complexes (10-12), the silicon atom linked with the Schiff bases in a tridentate fashion via N-imine and with two oxygen atoms of the hydroxy groups forming two rings within the complex (five and six member rings)¹³ (Fig. 2).

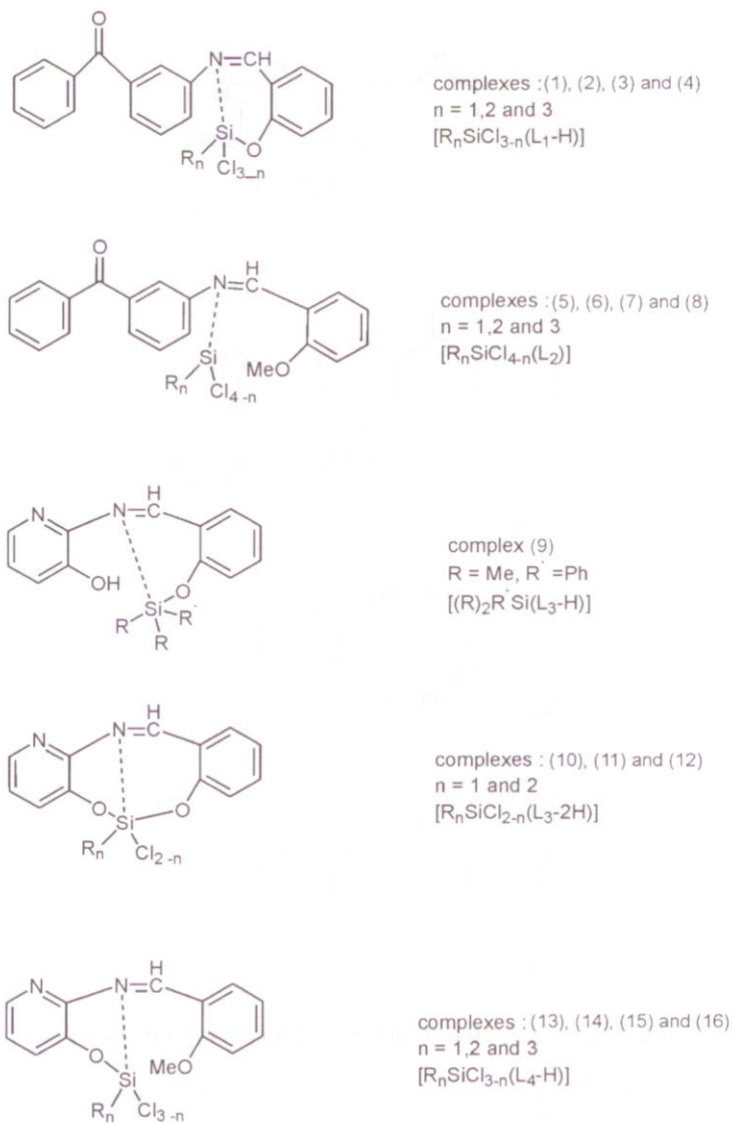


Fig.2. The suggested structures of the prepared complexes

UV/Vis spectra data of complexes showed absorption band attributed to the Schiff bases in its complexes¹⁴. The absorption band appearing in the region 225 – 245 nm was attributed to $\pi \rightarrow \pi^*$ electronic transitions in the aryl ring. The band appearing in the region 260–290 nm was attributed to $\pi \rightarrow \pi^*$ electronic transitions in the C=N group, and the band appearing in the region 325–370 nm is assigned to $n \rightarrow \pi^*$ electronic transition in the C=N group too. The bands due to d–d transitions in the d-orbitals of silicon atom were very weak to be observed^{15,16}.

The molar conductivity of 10^{-3} M solutions of all prepared complexes in ethanol at room temperature (25°C) indicated that they are non-electrolytes.

Theoretical calculations^{17,18} have paid a considerable attention to the characterization and inferences of geometrical optimization of the prepared complexes. Therefore, we could obtain the optimized geometry for each complex by computing the minimum steric energy and the theoretical physical parameters, such as bond lengths and bond angles for each complex using MM2 CS ChemOffice version 7.0 molecular modeling program. The steric energies of the prepared complexes are listed in Table 4. The configuration of complex (1) and (16) (Fig.3 and 4, respectively) were drawn here, as an example, with some selected bond lengths (Table 5 and 7, respectively) and some selected angles (Table 6 and 8).

Table 4. Computational steric energies of the ligands and their complexes (KCal / mol)

No.	Steric energy	No.	Steric energy
L ₁	10.782	7	56.531
L ₂	19.457	8	70.477
L ₃	5.702	9	41.474
L ₄	21.533	10	45.491
1	46.536	11	44.520
2	40.948	12	46.949
3	45.322	13	56.306
4	49.128	14	48.633
5	44.843	15	55.722
6	44.781	16	58.349

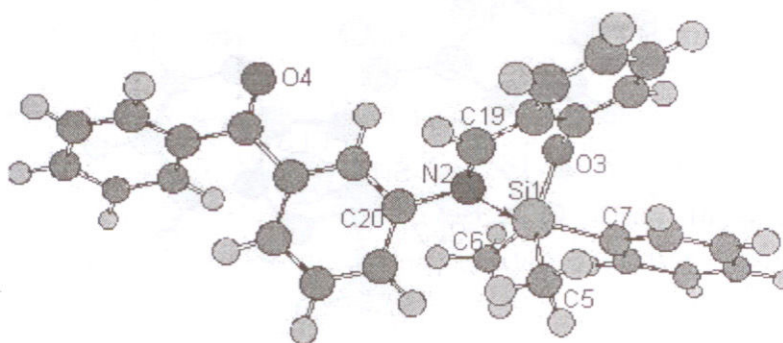


Fig.3. Configuration of complex (1), [Me₂PhSi(L₁-H)] optimized by MM2 CS ChemOffice molecular modeling program package

Table 5. Some selected calculated parameters of the complex (1), [Me₂PhSi(L₁-H)]

	Selected calculated parameters	Value
Bond lengths (Å)	Si(1) — O (3)	1.665
	Si(1) — C (5)	1.920
	Si(1) — C (6)	1.908
	Si(1) — C (7)	1.949
	Si(1) — N (2)	1.866
Angles (°)	O (3) — Si(1) — C (5)	134.976
	O (3) — Si(1) — C (6)	120.290
	O (3) — Si(1) — C (7)	83.118
	C (5) — Si(1) — C (6)	104.593
	C (6) — Si(1) — C (7)	88.556
	C (3) — Si(1) — C (7)	96.832
	O (3) — Si(1) — N (2)	88.271
	C (6) — Si(1) — N (2)	96.286
	C (5) — Si(1) — N (2)	90.385
	C (7) — Si(1) — N (2)	166.677

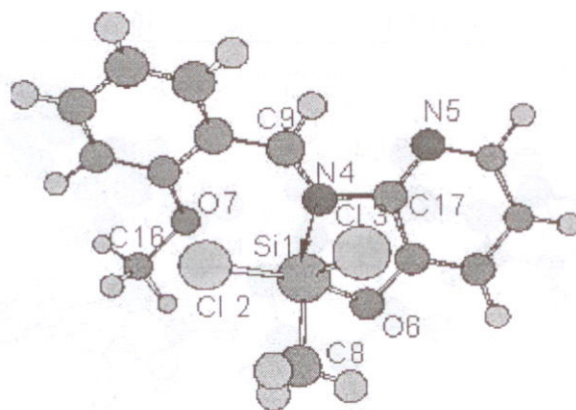
**Fig.4.** Configuration of the complex (16), [MeSiCl₂(L₄-H)] optimized by MM2 CS Chem Office molecular modeling program package

Table 6. Some selected calculated parameters of the complex (16), [MeSiCl₂(L₄-H)]

	Selected calculated parameters	Value
Bond lengths (Å)	Si(1) — Cl(2)	2.136
	Si(1) — Cl(3)	2.147
	Si(1) — O(6)	1.668
	Si(1) — C(8)	1.954
	Si(1) — N(4)	1.871
Angles (°)	Cl(2) — Si(1) — Cl(3)	97.872
	Cl(2) — Si(1) — O(6)	160.560
	Cl(2) — Si(1) — C(8)	87.521
	Cl(3) — Si(1) — O(6)	100.122
	Cl(3) — Si(1) — C(8)	89.123
	O(6) — Si(1) — C(8)	85.470
	Cl(2) — Si(1) — N(4)	96.865
	Cl(3) — Si(1) — N(4)	90.441
	O(6) — Si(1) — N(4)	90.308
C(8) — Si(1) — N(4)	175.603	

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