

## Synthesis, Characterization, Quantum Mechanical Studies and Antimicrobial Activity of Pentacoordinated Silicon Complexes Derived from Schiff's Bases

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### Abstract

*Some new pentacoordinated organosilicon (IV) derivatives of Schiff's base were synthesized by the 1:1:2 stoichiometric reactions of dichlorodialkylsilane, Schiff's base and triethylamine. The Schiff's bases behaved as tridentate dibasic ligand and reacted with  $R_2SiCl_2$  ( $R=CH_3, C_6H_5$ ) in the presence of triethylamine to yield complexes (1-3). The resulting complexes were characterized by elemental analysis, IR Spectroscopy and ( $^1H, ^{13}C, ^{29}Si$ ) NMR Spectroscopy. Quantum mechanical calculations were carried out using GAUSSIAN 03 Series of program. Due to large size of the complexes, semiempirical methods such as AM1, MNDO, PM3, PM3MM were applied. Total energies, dipole moment and bond lengths were calculated from the geometries optimized with semi-empirical methods. The IR frequencies calculated with computational studies correlated with experimental values and hence suggested the geometry of the synthesized complexes. The complexes (1-3) were also evaluated for in-vitro antibacterial activity against Gram Positive bacteria, Bacillus subtilis, Staphylococcus aureus, Gram negative bacteria, Escherichia Coli and in vitro antifungal activity against Candida albicans and Aspergillus niger.*

**Keywords:** Schiff's base, Pentacoordinate silicon complexes, dichlorodimethylsilane, dichlorodiphenylsilane, semi-empirical methods,

### Introduction

Metal complexes of Schiff's bases have been of considerable interest and they have occupied a central role in the development of inorganic chemistry of chelate systems. For many years there have appeared many publications dealing with metal chelates formed by Schiff's bases<sup>1-6</sup>. The reason for this sustained interests in these compounds are due to their important role as pharmacologically and physiologically active compounds, and their use as biological models<sup>7-9</sup> and for catalyzing oxidations of organic compounds<sup>10</sup>.

In view of the previous importance of Schiff base and in continuation with our earlier work on hypercoordinated silicon complexes of Schiff's base<sup>11-23</sup> we prepared and investigated some novel pentacoordinated organosilicon (IV) derivatives of Schiff's bases. The geometries of the resulting complexes were optimized by semi-empirical method (AM1, MNDO, PM3, PM3MM) to calculate their total energies, bond lengths and dipole moments. The IR frequencies calculated theoretically by computational studies were compared with the experimental values and hence the geometry of synthesized complexes obtained.

The complexes were also studied for their antimicrobial activity. The bacteria and fungi were maintained on dextrose broth and Czapek Dox agar slants respectively. Minimum Inhibitory concentrations (MIC) values were determined by means of two fold serial dilution technique.

## Materials and Methods

All operations were carried out under dry nitrogen atmosphere using an all-glass vacuum line. Solvents were dried and purified according to the standard procedures reported in literature<sup>24</sup>. Triethylamine (Qualigens, India) was stored over KOH pellets for several days and then collected by simple distillation. Dichlorodimethylsilane and dichlorodiphenylsilane were purchased from Aldrich and used as received. Infra Red spectra were routinely obtained as nujol mulls on a Perkin Elmer RX-I FT IR Spectrophotometer. The <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR Spectra were recorded on Jeol FT NMR (300 MHz) spectrometer with TMS as the internal standard. C, H and N analysis of samples were carried out on a Perkin – Elmer model 2400 CHN elemental analyzer while Si contents were estimated gravimetrically. Quantum mechanical calculations were carried out using GAUSSIAN 03 Series of program Geometries were fully optimized by using semi-empirical methods (AM1, MNDO, PM3, PM3MM). Total energy, dipole moment, bond lengths and IR frequencies were calculated

### Procedures and Characterization

#### Synthesis of anthranilic acid – salicylaldehyde schiff base (AASASB), C<sub>14</sub>H<sub>11</sub>NO<sub>3</sub> (Ligand -1)

To a well stirred solution of anthranilic acid (1.37 gm, 10.0 mmoles) dissolved in 30 ml absolute ethanol, salicylaldehyde (1.06 ml, 10.0 mmoles) also dissolved in absolute ethanol was added. The addition was carried out very slowly in 1.0-1.5 hrs. The clear solution was refluxed for 2 hours. An orange coloured solid was obtained which was filtered and washed repeatedly with ethanol. The product was then dried under vacuum. (m.pt. : 205°C).

**Anal.(%) Calcd. :** C, 69.70; H, 4.56; N, 5.80. **(%) Found:** C,69.54; H,4.42; N,5.64

#### Synthesis of glycine–salicylaldehyde schiff base C<sub>9</sub>H<sub>9</sub>NO<sub>3</sub> (Ligand-2)

To the aqueous solution of glycine (0.75gm,10.0 mmoles), alcoholic solution of salicylaldehyde (1.04gm, 10.0 mmoles) was added dropwise. The addition was carried out in 1.0-1.5 hours. After the completion of addition, the resulting solution was refluxed azeotropically for 2 hours in a round-bottomed flask fitted with Dean-Stark apparatus. The solid product obtained was filtered, washed with absolute ethanol and dried in vacuum. (Yield: 1.22 gm, 80.2%)

**Anal.(%)Calcd. :** C,60.33 ; H,5.02 ;N,7.82. **(%) Found:** C,60.20 ; H,4.92 ; N,7.64

#### Complex (1), C<sub>16</sub>H<sub>15</sub>NO<sub>3</sub>Si

In 25 ml THF, Schiff base ligand -1 (2.04 gm, 8.5 mmoles) and triethylamine (2.37 ml, 17.0 mmoles) were stirred at room temperature when a clear solution was obtained. The temperature was then lowered to 0° C and dichlorodimethylsilane (1.03 ml, 8.5 mmoles) was added dropwise and the resulting mixture was stirred at 0° C for 1 hour. The reaction mixture was allowed to stand overnight in refrigerator and then the precipitated triethylamine hydrochloride was filtered off and washed with THF (3 – 4 times). The solvent was removed from the filtrate under vacuum and the solid product was isolated from dry hexane. (Yield: 18.5 gm, 73.7%).

**Anal. Calc :** C, 64.64; H, 5.05; N, 4.71; Si, 9.42. **Found :** C, 63.95; H, 4.45; N, 4.56; Si, 9.38. **IR (Nujol, cm<sup>-1</sup>) :** 1607 (ν C=N), 1660 (ν COO), 578 (ν Si←N), 890 (ν Si-O), 1111 (ν Si-Me). **δ <sup>1</sup>H NMR (CDCl<sub>3</sub> + 1-2 drops of DMSO-d<sub>6</sub>) :** 8.36 (s,1H, CH=N), 7.0-7.9 (m, aromatic), 1.3 (s, 6H, CH<sub>3</sub>), **δ <sup>13</sup>C NMR (CDCl<sub>3</sub> +1-2 drops DMSO-d<sub>6</sub>) :** 164.1 (C=N), 144.2 (C-O), 170.8 (COO). **δ <sup>29</sup>Si NMR (CDCl<sub>3</sub> +1-2 drops DMSO-d<sub>6</sub>) :** - 94.7.

**Complex (2),  $C_{26}H_{19}NO_3Si$** 

Complex (2) was prepared by the dropwise addition of dichlorodiphenylsilane (1.15 ml, 5.5 mmoles) to a solution of Schiff base ligand-1 (1.32 gm, 5.5 mmoles) and triethylamine (1.5 ml, 11.0 mmoles) in dry THF at 0° C under dry nitrogen atmosphere. Rest of the procedure was analogous to the method given for Complex (1). (Yield: 1.54 gm, 67%).

**Anal. Calc :** C, 74.10; H, 4.51; N, 3.32; Si, 6.65. **Found :** C, 73.32; H, 3.85; N, 2.01; Si, 6.57. **IR (Nujol,  $cm^{-1}$ ) :** 1596 (v C=N), 1668 (v COO), 586 (v Si←N), 884 (v Si-O), 1120 (v Si-Ph).  **$\delta$   $^1H$  NMR ( $CDCl_3$  + 1-2 drops  $DMSO-d_6$ ) :** 8.58 (s, 1H, CH=N), 6.7 – 7.5 (m, aromatic),  **$\delta$   $^{13}C$  NMR ( $CDCl_3$  + 1-2 drops  $DMSO-d_6$ ) :** 166.1 (C=N), 148.2 (C-O), 172.0 (COO).  **$\delta$   $^{29}Si$  NMR ( $CDCl_3$  + 1-2 drops  $DMSO-d_6$ ) :** – 114.0.

**Complex (3),  $C_{11}H_{13}NO_3Si$** 

To a stirred solution of Schiff base ligand-2 (1.52 gm, 8.5 mmoles) and triethylamine (2.37 ml, 17.0 mmoles) in THF, dichlorodimethylsilane (1.03 ml, 8.5 mmoles) was added dropwise. The contents were stirred at 0° C for 1 Hour. The reaction mixture was allowed to stand overnight in refrigerator and then the precipitated solid triethylamine hydrochloride was filtered off and washed with THF. The solid was removed from the filtrate under vacuum and the product was isolated from dry hexane (20 ml). (Yield : 1.08 gm, 54.2%).

**Anal. Calc :** C, 56.17; H, 5.53; N, 5.95; Si, 11.90. **Found :** C, 55.69; H, 5.50; N, 5.57; Si, 11.74. **IR (Nujol,  $cm^{-1}$ ) :** 1617 (v C=N), 1662 (v COO), 575 (v Si←N), 872 (v Si-O), 1110 (v Si-Me).  **$\delta$   $^1H$  NMR ( $CDCl_3$  + 1-2 drops  $DMSO-d_6$ ) :** 8.66 (s, 1H, CH=N), 3.87 (s, 2H, N – CH<sub>2</sub>), 3.87 (s, 2h, N – CH<sub>2</sub>), 0.9 (s, 6H, CH<sub>3</sub>).  **$\delta$   $^{13}C$  NMR ( $CDCl_3$  + 1-2 drops  $DMSO-d_6$ ) :** 158 (C=N), 139 (C-O), 169.1 (COO), 42.3 (NCH<sub>2</sub>).  **$\delta$   $^{29}Si$  NMR ( $CDCl_3$  + 1-2 drops  $DMSO-d_6$ ) :** – 80.

**Results and Discussions**

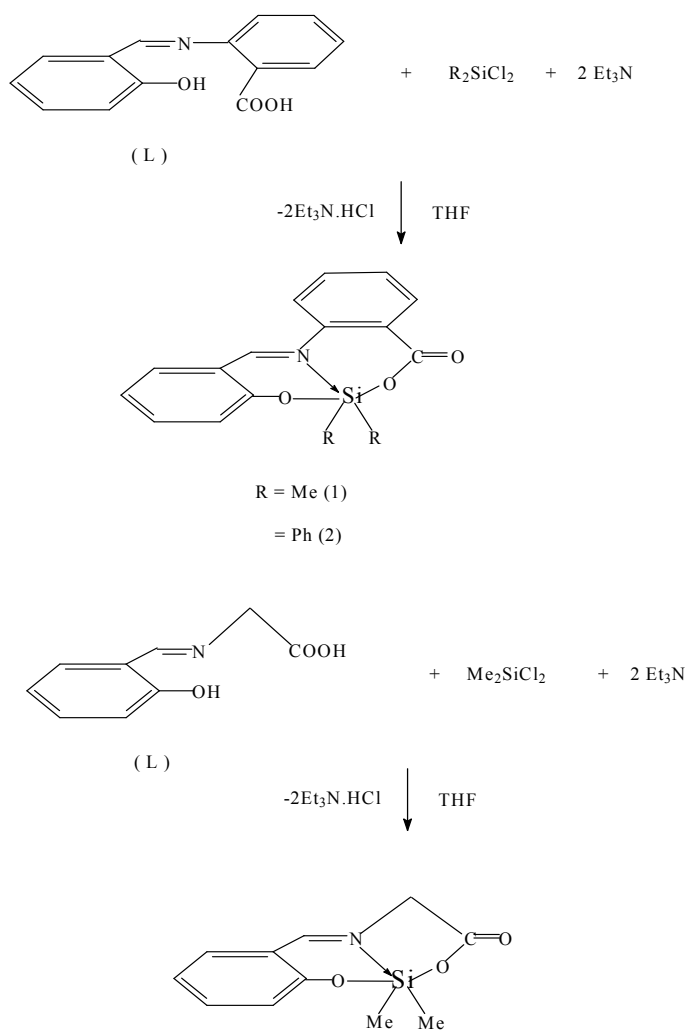
Schiff bases were used as ligands for the preparation of some new pentacoordinated organosilicon (IV) complexes. These were prepared by reacting salicylaldehyde with primary amines such as anthranilic acid and glycine in absolute ethanol. These Schiff bases behaved as tridentate dibasic ligand. The complexes (1-3) were synthesized by the 1:1:2 stoichiometric reactions of Schiff's base (L), dichlorodialkylsilane and triethylamine in dry THF solvent (Scheme – 1). In the resulting complexes, O–N–O was the donor system of ligand molecule. The complexes were hygroscopic solids, soluble in DMF and DMSO but insoluble in common organic solvent. The poor molar conductivity values ( $5-8 \Omega^{-1} cm^2 mol^{-1}$ ), of the complexes indicated that they were non-electrolytes. The complexes were characterized by elemental analysis, IR,  $^1H$ ,  $^{13}C$ ,  $^{29}Si$  NMR spectroscopy. The purity of the complexes were checked by TLC on silica gel – G using anhydrous methanol : benzene (1:1) as the solvent. Each of the compound moved as a single spot and indicated the presence of only one component and hence high purity. The coordination modes in pentacoordinated silicon complexes (1-3) were studied with IR and NMR spectroscopy together with quantum mechanical calculations. The geometries were optimized by semi-empirical methods such as AM1, MNDO, PM3, PM3MM and the experimental spectroscopic data observed for synthesized complexes were compared with the results of quantum mechanical calculations.

**Theoretical Studies**

The large size of complexes (1-3) restricted our studies to semi-empirical quantum mechanical computations<sup>25</sup>. The complexes were optimized with semi-empirical methods such as AM1, MNDO,

PM3, PM3MM to calculate the total energies, dipole moment, bond lengths (Table 1, 2, 3) and IR frequencies. The results of theoretical calculations were compared with experimental data. Out of the four methods applied the results calculated by PM3/PM3MM method of calculations correlated best with the experimental values while significant changes were observed for other method namely AM1, MNDO. This may be attributed to the different bonding modes after optimization.

The structures optimized with AM1 and MNDO methods showed tetracoordinated silicon (Figure -1 ) whereas the experimental values of  $^{29}\text{Si}$  NMR Spectra confirmed pentacoordination. For complexes (1) & (2) the molecules in AM1 method has optimized itself in such a manner that the bond between Si and Oxygen atom is absent and in MNDO the nitrogen and Si atom have moved away from each other and therefore bonding between them is not observed. For Complex (3) in AM1 method one methyl group attached to Si atom is not present while in MNDO the phenyl ring along with the oxygen atom had moved away from the silicon atom. (Figure 1). Therefore from both the studies i.e. I.R and NMR data (theoretical as well as experimental) the structures of complexes (1-3) with PM3/PM3MM semi-empirical method was suggested. The optimized geometries of the prepared complexes (1-3) with PM3/PM3MM method are shown in Figure (2).



(Scheme -1)

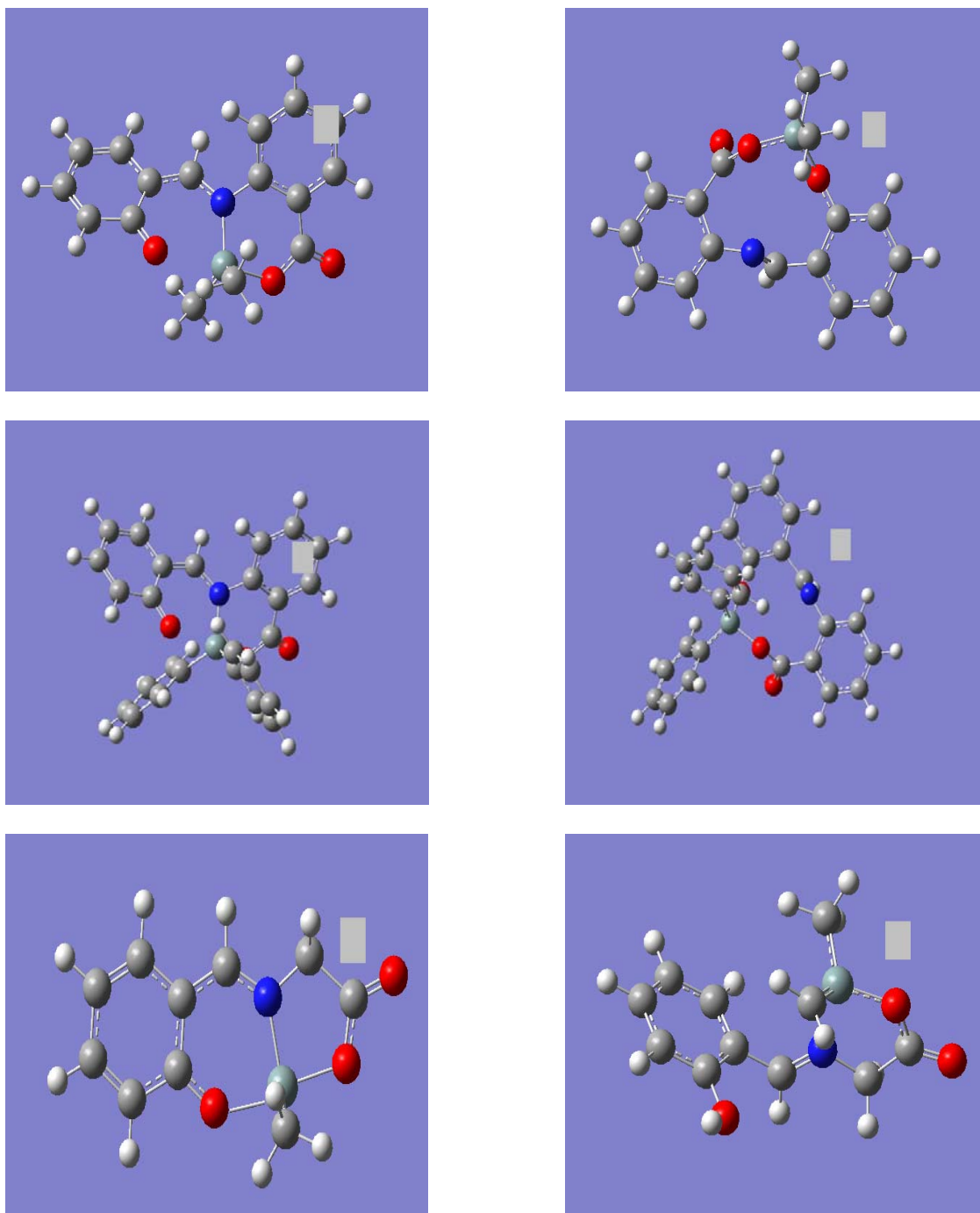
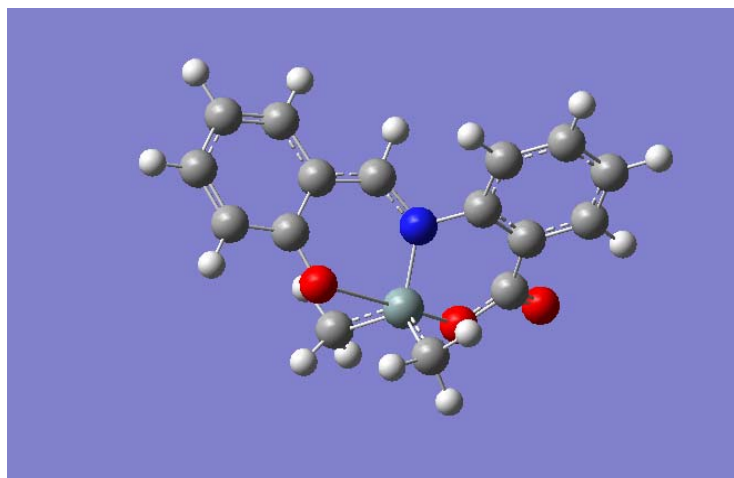
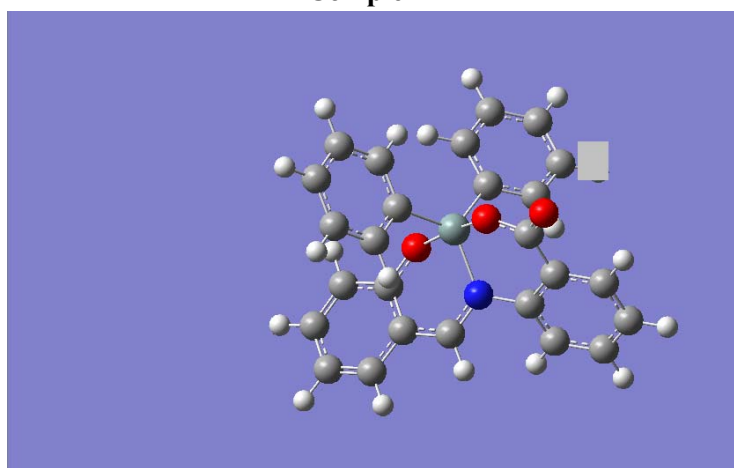


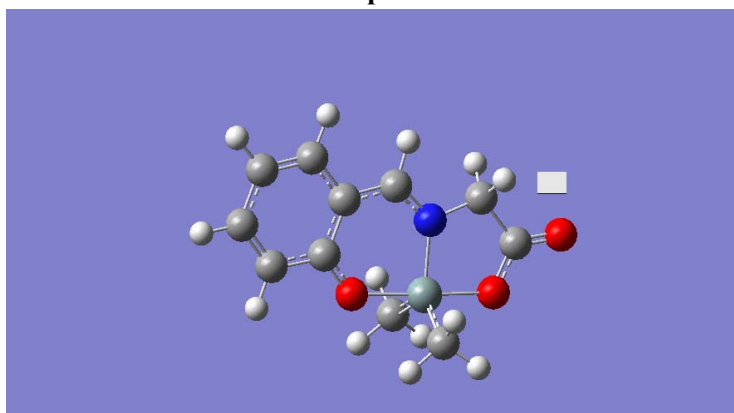
Figure 1



**Complex 1**



**Complex 2**



**Complex 3**

**Figure 2**

**Table 1 : Semi-empirical quantum mechanical computations of Complex (1)**

PARAMETERS	AM1	MNDO	PM3	PM3MM
Total Energy (a.u.)	-0.15714583	-0.21737182	-0.19867582	-0.19867582
Dipole Moment (Debye)	6.4234	2.3557	6.7216	6.7216
Si → N	1.77	-	2.01	2.04
Si – O (1)	1.81	1.67	1.73	1.73
Si – O (2)	-	1.67	1.72	1.72
Si – C (3)	1.79	1.80	1.96	1.96
Si – C (4)	1.79	1.80	1.94	1.94

**Table 2 : Semi-empirical quantum mechanical computations of Complex (2)**

PARAMETERS	AM1	MNDO	PM3	PM3MM
Total Energy (a.u.)	-0.05201176	-0.12793707	-0.08599420	-0.08599420
Dipole Moment (Debye)	5.9597	2.2551	7.1491	7.1491
Si → N	1.77	-	1.91	1.91
Si – O (1)	1.82	1.07	1.78	1.78
Si – O (2)	-	1.07	1.74	1.74
Si – C (3)	1.75	1.79	1.92	1.92
Si – C (4)	1.75	1.79	1.90	1.90

**Table 3 : Semi-empirical quantum mechanical computations of Complex (3)**

PARAMETERS	AM1	MNDO	PM3	PM3MM
Total Energy (a.u.)	-0.21734353	-0.15693501	-0.17433251	-0.17433254
Dipole Moment (Debye)	7.1788	8.460	5.9630	5.9630
Si → N	1.84	2.08	1.89	1.89
Si – O (1)	1.98	1.69	1.73	1.73
Si – O (2)	1.88	-	3.52	3.52
Si – C (3)	1.80	1.80	1.88	1.88
Si – C (4)	-	1.62	1.67	1.67

### IR Spectra

A broad and strong absorption band in the range 3220 – 3475  $\text{cm}^{-1}$  which is due to  $\nu(\text{O-H})$  and is present in the spectra of Schiff's base was absent in the spectra of complexes (1–3) and thereby suggested the involvement of this functional group in coordination after the deprotonation. The  $\nu(\text{C=N})$  absorption band in Schiff's bases was seen at 1632  $\text{cm}^{-1}$  but in the complexes (1 – 3) it appeared at 1607, 1596 and 1617  $\text{cm}^{-1}$  respectively. The lowering of  $\nu(\text{C=N})$  by  $\sim 15\text{-}35 \text{ cm}^{-1}$  indicated coordination of Schiff base to central silicon atom through azomethine nitrogen. Other modes such as  $\nu(\text{Si} \leftarrow \text{N})$ ,  $\nu(\text{Si} - \text{O})$ ,  $\nu(\text{Si} - \text{Me})$ ,  $\nu(\text{COO})$ ,  $\nu(\text{Si} - \text{Ph})$  occurred at usual frequencies and are given in experimental section. The experimentally obtained values were compared with the values calculated by theoretical studies (semi-empirical quantum mechanical computations viz. AM1, MNDO, PM3, PM3MM). This comparison showed that the experimental values correlated well with the values computed from PM3 / PM3MM method of calculation. (Table-2). Therefore the optimized geometries of complexes (1–3) were as given in Figure 2.

Table : 4 Major infrared absorptions ( $\text{cm}^{-1}$ ) of complexes (1-3) obtained by semi-empirical quantum mechanical studies and experimental data.

	COMPLEX -1	COMPLEX -2	COMPLEX – 3
AM1	1645, 1587, 1157, 875, 589	1691, 1588, 1154, 891, 569	1607, 1570, 1160, 1075, 871, 577
MNDO	1686,1159,789,508	1698,1572,1157,880, 581	1677,1598,1113,852,560
PM3	1661,1599,1116,893, 571	1664,1594,1119,887, 589	1659,1616,1106,874,570
PM3MM	1661,1599,1116,893, 571	1664,1594,1119,887, 589	1659,1616,1106,874,570
EXPERIMENTAL DATA	1660,1607,1111,890, 578	1668,1596,1120,884, 586	1662,1617,1110,872,575

### ***H NMR Spectra***

The Proton magnetic resonance spectral data of ligand and its silicon complexes were recorded in  $\text{CDCl}_3 + \text{DMSO}-d_6$ . The  $^1\text{H}$  NMR Spectrum of ligands (Schiff's base) showed a signal at  $\delta$  8.13 ppm due to proton of azomethine moiety ( $-\text{CH}=\text{N}-$ ). This signal was shifted in the complexes (1-3)  $\delta$  (8.36 – 8.66 ppm). This was attributed to the donation of lone pair of electrons by the azomethine nitrogen to silicon atom. The broad signal due to OH protons at  $\delta$  12.22 ppm observed in the spectra of Schiff's base disappeared in the spectra of silicon complexes and showed involvement of this group in bonding. Other signals due to aromatic protons, methyl protons and methylene protons appeared at their required values and are given in the experimental section.

### ***C NMR Spectra***

The  $^{13}\text{C}$  NMR Spectra data for ligands and its metal complexes in  $\text{CDCl}_3 + \text{DMSO} - d_6$  supported coordination of ligand through azomethine nitrogen and phenolic oxygen. Shifts in the positions of carbon atoms adjacent to atoms involved in complex formation indicated bonding pattern in the complexes.

### ***Si NMR Spectra***

The  $^{29}\text{Si}$  NMR Spectra of the complexes (1–3) were recorded in  $\text{CDCl}_3 + \text{DMSO} - d_6$ . Sharp signals at  $\delta$  – 94.7, – 114 and – 80.0 ppm were assigned to 1, 2, 3 complexes respectively which indicated pentacoordinated environment around silicon atom.

### **Antimicrobial Activity**

Minimum Inhibitory Concentration (MIC) : The lowest concentration of a compound that resulted in complete inhibition of the visible microbial growth after incubation. MIC Values of complexes (1 – 3) were determined by using two fold serial dilution technique. In this technique, stock solutions of the complexes were prepared in dry DMSO. The incubation period for all the test bacteria was 24 Hrs. at  $37 \pm 1^\circ \text{C}$ . Initially the stock solution having a concentration of 1.00 mg/ml was prepared. This solution, 0.1 ml was added to 1.8 ml of sterile nutrient broth to form the first dilution (50  $\mu\text{g}/\text{ml}$ ). 1 ml of the solution from first dilution was diluted further with 1 ml of sterile nutrient broth to form the second solution. A set of tubes containing only the sterile nutrient broth was kept as control. The tubes were



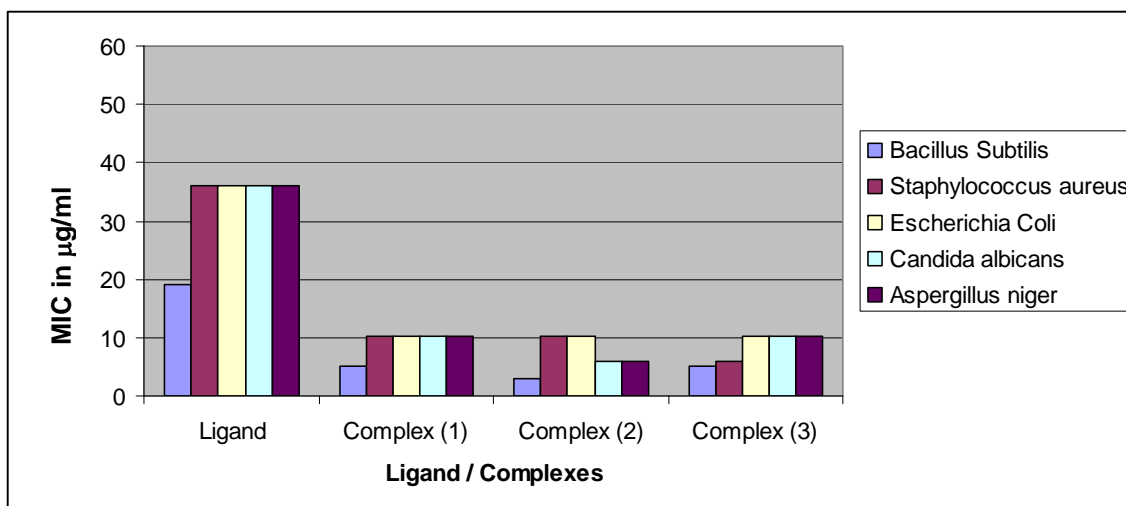
then inoculated with 100  $\mu$ L of suspension of the test bacteria. The inoculated tubes were incubated at  $37 \pm 1^{\circ}$  C for 24Hrs and MIC values were determined. The antifungal activity of the complexes (1-3) against *Candida albicans* and *Aspergillus niger* was also determined by the same technique. The incubation period of *Candida albicans* was 36 hrs at  $37 \pm 1^{\circ}$  C and for *A. niger* was 7 days at  $25 \pm 1^{\circ}$  C. MIC data against bacteria *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and fungi *Candida albicans* and *Aspergillus niger* is summarized in Table 5.

**Table 5 : The in vitro antimicrobial activity of ligand and its complexes (1 - 3)  
(MIC values in  $\mu$ g / ml)\***

	BACTERIA			FUNGI	
	Bacillus Subtilis	Staphylococcus aureus	Escherichia Coli	Candida albicans	Aspergillus niger
Schiff base (L-1 / L-2)	19.0	36.0	36.0	36.0	36.0
Complex-1	5.15	10.3	10.3	10.3	10.3
Complex-2	3.00	10.3	10.3	6.0	6.0
Complex-3	5.15	6.0	10.3	10.3	10.3

\* The MIC Values of standard drugs for antibacterial activity (Tetracycline, Chloramphenicol, Kanamycin, Cefazoline, Sodium Cefotaxime) and antifungal activity (Cycloheximide, Carbendazim, Flucozonazole) were found to be  $< 3.12 \mu$ g / ml.

The values shown in the table indicated lower MIC values of the complexes as compared to the ligand against all the test bacteria and fungi, thereby signified the greater activity of the complexes. The greater activity of the complexes as compared to the ligand was due to the introduction of a lipophilic substituent either alkyl or aryl which conferred toxicity due to the enhanced permeation of the complex through the lipid layer of the cell membrane of the microorganism. Further complexes of dichlorodiphenylsilane were found to be more potent as compared to dichlorodimethylsilane. Complex (2) showed activity close to that by conventional bactericide & fungicide.



Graphical representation of MIC values for in vitro antimicrobial activity vs Ligand/Complexes.

## Conclusions

Silicon complexes of Schiff's base ligands were synthesized by the 1:1:2 stoichiometric reactions of dichlorodialkylsilane, Schiff's base and triethylamine under completely anhydrous conditions. They were shown to have penta-coordinated centers through spectroscopic studies and quantum mechanical calculations. The antimicrobial activity of the complexes revealed that the activity increased on complexation.

## References

- [1] H.S. Maslen, T.N. Water, *Coord. Chem. Rev.*, 1975, 17, 137
- [2] A.A.A. El. Gaber, A.M.A. Hassan, M. Shabasy, A.M. Roudi, *Synth. React. Inorg. Met. Org. Chem.* 1991,21,1265.
- [3] M. Tumer, H. Koksall, S. Serin, *Synth. React. Inorg. Met. – Org. Chem.* 1997, 27(5), 775-786
- [4] M. Deveci, B. Mecimek, *Synth. React. Inorg. Met. – Org. Chem.* 1998, 28(3), 331-338
- [5] A. Syamal, B.K. Gupta, *Ind. J. Chem.* 1982, 21 A, 83
- [6] R.C. Maurya, D.D. Mishra, N.S. Rao, *Polyhedron.* 1992, 11(222), 2837-2840
- [7] S. Singh, R. Malhotra, A. Hooda, K.S. Dhindsa, *Bull. Soc. Chim. Belg.* 1996, 105, 451 – 456
- [8] P. Viswanathamurthi, N. Dharmaraj, K. Natarajan, *Synth. React. Inorg. Met. –Org. Chem.* 2000, 30(7), 1273-1285
- [9] A.P. Mishra, *J. Indian Chem. Soc.* 1999, 76, 135-137
- [10] S. Forster, A. Rieker, K. Maruyama, K. Murata, A. Nishinaga, *J. Org. Chem.* 1996, 61, 9635
- [11] J.K. Puri, G. Singh, P. Duggal, *Main Group Met. Chem.*, 2007, 30, 3
- [12] J.K. Puri, G. Singh, P. Duggal, *Phosphorus, Sulphur, Silicon Relat. Elem.* 2008, 183, 1853.
- [13] J.K. Puri, R. Singh, V.K. Chahal, G.J.P. Singh, R.P. Sharma, *Main Group Metal Chemistry*, 2009, 322, 79-83
- [14] J.K. Puri, R. Singh, V.K. Chahal, R.P. Sharma, *ARKIVOC*, 2009, XI, 247-256.
- [15] S.P. Narula, M. Puri, N. Garg, J.K. Puri, R.K. Chadha, *Phosphorus, Sulphur, Silicon, Relat. Elem.* 2007, 182, 569.
- [16] S.P. Narula, M. Puri, N. Garg, J.K. Puri, R.K. Chadha, *Main Group Met. Chem.* 2005, 25, 11.
- [17] S.P. Narula, R. Shankar, M. Kumar, Meenu. *Inorg. Chem.* 1994, 33, 2176.
- [18] S.P. Narula, R. Shankar, Meenu; R.D. Anand, *Polyhedron.* 1999, 18, 2055
- [19] J.K. Puri, R. Singh, V.K. Chahal, R.P. Sharma, P. Venugopalan, *J.O.C*, 2010, 695, 183
- [20] J.K. Puri, R. Singh, V.K. Chahal, R.P. Sharma, A.K. Malik, V. Ferretti, *Journal of Molecular Structure*, 2011, 982, 107
- [21] J.K. Puri, R. Singh, V.K. Chahal, *Chem.Soc.Rev.*, 2011, 40, 1791
- [22] J.K. Puri, R. Singh, V.K. Chahal, R.P. Sharma, J. Wagler, E. Kroke, *J. Organometallic Chemistry*, 2011, 696, 1341
- [23] S.P. Narula, Meenu, R.D. Anand, J.K. Puri, R. Shankar, *Main Group Met. Chem.*, 2000, 8, 23
- [24] W.L.F. Armarego, D.D. Perrin *Purification of Laboratory Chemicals* ( Butterworth- Heinemann, Oxford, 1999), 4<sup>th</sup> ed.,chap. 3, pp. 63-360
- [25] J. Wagler, M. Schley, D. Gerlach, U. Bohme, B. Brendler, G.Z. Roewer, *Naturforsch*, 2005, 60b, 1054.