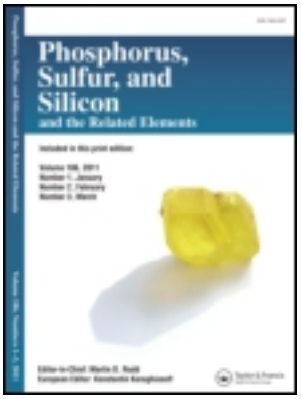


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# Synthesis, Spectroscopic Studies, and Biological Activity of Organosilicon(iv) Complexes of Ligands Derived from 2-Aminobenzothiazole Derivatives and 2-Hydroxy-3-Methoxy Benzaldehyde

Jai Devi [a], Suman Kumari [a] & R. Malhotra [a]
[a] Department of Chemistry, Guru Jambheshwar University of Science and Technology, Hisar, Haryana, India
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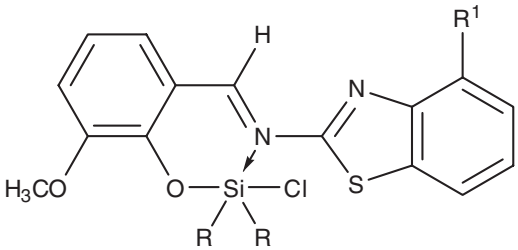
# SYNTHESIS, SPECTROSCOPIC STUDIES, AND BIOLOGICAL ACTIVITY OF ORGANOSILICON(IV) COMPLEXES OF LIGANDS DERIVED FROM 2-AMINOBENZOTHIAZOLE DERIVATIVES AND 2-HYDROXY-3-METHOXY BENZALDEHYDE

**Jai Devi, Suman Kumari, and R. Malhotra**
*Department of Chemistry, Guru Jambheshwar University of Science and Technology, Hisar, Haryana, India*

## GRAPHICAL ABSTRACT




**Abstract** *The Schiff bases derived from the condensation of 2-aminobenzothiazole derivatives and 2-hydroxy-3-methoxybenzaldehyde and their silicon(IV) complexes with the general formula $R_2Si(L)Cl$ (R = Et, Bu, Ph, L = 2-(2-hydroxy-3-methoxy) benzylideneaminobenzothiazole) have been synthesized. These complexes have been characterized by elemental analysis, molar conductance, and spectroscopic studies including IR and NMR ($^1H$, $^{13}C$, and $^{29}Si$) spectroscopy. The analytical data suggest trigonal bipyramidal geometry around the silicon atom in the resulting complexes. The ligands and their organosilicon complexes have also been evaluated for in vitro antimicrobial activity against bacteria (*Staphylococcus aureus*, *Bacillus subtilis*, and *Escherichia coli*) and fungi (*Aspergillus niger *and* Candida albicans*). The complexes were found to be more potent as compared to the ligands.*

*Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.*

**Keywords** Organosilicon complexes; spectroscopic studies; 2-aminobenzothiazole; 2-hydroxy-3-methoxybenzaldehyde

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Address correspondence to Jai Devi, Department of Chemistry, Guru Jambheshwar University of Science and Technology, Hisar 125001, Haryana, India. E-mail: jaidevi_gju@yahoo.com

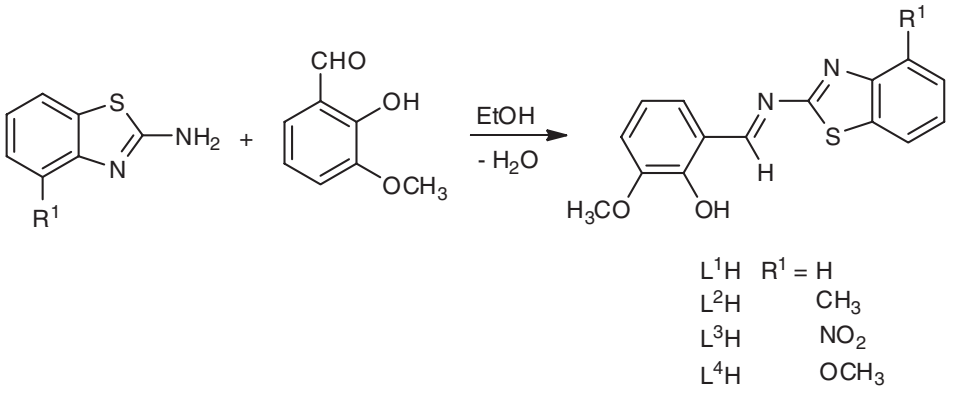
## INTRODUCTION

Organosilicon compounds with sulphur-containing ligands attract much attention due to their wide range of biological activity. The sulphur-containing ligands as well as their organosilicon complexes are known for their tuberculostatic, anticarcinogenic antifungal, antibacterial, insecticidal, and acaricidal activities.[1–6] The biological activities of sulphur-containing ligands are considerably enhanced on complexation.[7,8] The interest in organosilicon(IV) complexes is further motivated by their versatile applicability in pharmaceutical and chemical industries. The medical application and effectiveness of silatranes in the treatment of wounds and tumors are related to the role of silicon in the growth of epithelial and connective tissue and hair, where its function is to impart elasticity, strength, and impermeability to water.[9,10] It has been reported that the 2-aminobenzothiazole is a structural unit in anti-inflammatory drugs, antibiotics, antioxidants, herbicides, and thermoplastic polymers.[11] It acts as flavoring agent and is also present in the luciferine, where it is responsible for the bioluminescence of fire flies.[12]

In the present work, the synthesis of new organosilicon complexes of Schiff bases derived from 2-aminobenzothiazole derivatives and 2-hydroxy-3-methoxy benzaldehyde as well as the results of a screening of these compounds for possible antimicrobial activity is presented.

## RESULTS AND DISCUSSION

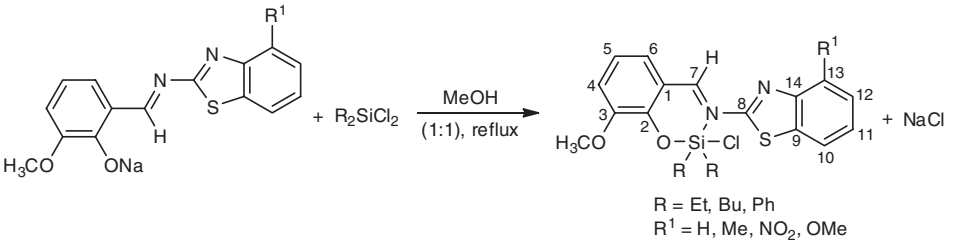
Synthesis of the ligands is given in Scheme 1. The Schiff bases were prepared by condensation of 2-aminobenzothiazole derivatives with 2-hydroxy-3-methoxy benzaldehyde. The purity of the compounds was checked by TLC.




**Scheme 1**

The reactions of diorganodichlorosilanes with the sodium salts of the Schiff bases were carried out in 1:1 molar ratio in dry methanol. They proceed with the precipitation of NaCl, which was removed by filtration. The complexes were isolated after the removal of the solvent by evaporation in vacuo.

The complexes thus prepared were soluble in $CDCl_3$, DMSO, and MeOH. The molar conductance of $10^{-3}$ M solutions of these complexes has the low value




**Scheme 2**



($6^{-20}$ ohm$^{-1}$ cm$^2$ mol$^{-1}$), indicating the nonelectrolytic nature of the complexes. Information about the geometry around the silicon atom in these complexes results from the FT-IR and NMR ($^1$H, $^{13}$C, and $^{29}$Si) spectroscopic data.

## IR Spectra

The IR spectra of the ligands show a broadband at 3450–3200 cm$^{-1}$ due to $\upsilon$(O–H). This band is completely absent in the spectra of the corresponding complexes indicating coordination of the oxygen atom of ligand to the silicon atom (Table 1). A sharp band around 1593 $\pm$ 20 cm$^{-1}$ due to $\upsilon$(C=N) of the free azomethine groups in the Schiff bases is shifted to the lower frequency in the complexes indicating coordination of the azomethine nitrogen atom to the silicon atom. The presence of silicon–oxygen and silicon–nitrogen bonds is further evident from the appearance of new bands for $\upsilon$(Si–O) at 518 $\pm$ 15 cm$^{-1}$, $\upsilon$(Si$-$N) at 426 $\pm$ 10 cm$^{-1}$, and $\upsilon$(Si–Cl) at 442 $\pm$ 15 cm$^{-1}$. The practically unchanged position of $\upsilon$(C=N) at 1623 cm$^{-1}$ and $\upsilon$(C–S–C) at 729 cm$^{-1}$ for the thiazole ring confirms that the thiazole moiety itself does not coordinate to the silicon atom by neither nitrogen nor sulphur atoms.

## NMR Spectra

The $^1$H NMR spectra of the ligands and the corresponding organosilicon(IV) complexes were recorded in $CDCl_3$ using TMS as the internal standard. Chemical shifts are given in Table 2. The NMR spectra of the free ligands show a signal due to the OH proton at $\delta$ = 12.50 ppm, which is absent in the spectra of the complexes, indicating the bonding of the hydroxyl oxygen atom to the silicon atom after the deprotonation of this functional group. The sharp signal at $\delta$ = 9.27 ppm for the azomethine proton in the ligand is shifted downfield in the spectra of the complexes indicating that the nitrogen atom of

**Table 1** Characteristic IR frequencies (in cm$^{-1}$) of Schiff base ligands and their metal complexes

| Ligands/ complexes | $\upsilon$(O$-$H) | $\upsilon$(C=N) Thiazole | $\upsilon$(C=N) Azomethine | $\upsilon$(C$-$S$-$C) Thiazole | $\upsilon$(Si$-$O) | $\upsilon$(Si$-$N) | Si$-$Cl |
|---|---|---|---|---|---|---|---|
| $L_{1-4}H$ | 3450(br) | 1623–1625 | 1596–1599 | 729–731 | — | — | — |
| $Et_2Si(L_{1-4})Cl$ | — | 1622–1625 | 1590–1595 | 728–731 | 518–521 | 426–429 | 442–444 |
| $Bu_2Si(L_{1-4})Cl$ | — | 1623–1625 | 1585–1588 | 729–732 | 520–523 | 428–430 | 443–445 |
| $Ph_2Si(L_{1-4})Cl$ | — | 1623–1626 | 1589–1594 | 728–730 | 525–528 | 438–441 | 448–450 |

**Table 2** $^1$H NMR data of the ligands and their silicon(IV) complexes; $\delta$ (ppm), $J$ (Hz)

| Ligands/ complexes | N=CH | OH | Aromatic-H | $R^1$ | Si−R |
|---|---|---|---|---|---|
| $L_1H$ | 9.30 | 12.48 | 7.99 (d, $J$ = 8.1, 1H, 13-H), 7.86 (d, $J$ = 7.8, 1H, 10-H), 7.53 (t, $J$ = 15.0, 1H, 6-H), 7.41 (t, $J$ = 15.0, 1H, 4-H), 7.16 (dd, $J$ = 7.5, 2H, 11-H, 12-H), 6.97 (t, $J$ = 15.0, 1H, 5-H) | — | — |
| $L_2H$ | 9.27 | 12.50 | 7.67–7.63 (m, 1H, 10-H), 7.28 (t, $J$ = 6.6, 2H, 11-H, 12-H), 7.17 (dd, $J$ = 1.5, 1H, 5-H), 7.07 (d, $J$ = 7.8, 1H, 4-H), 6.96 (t, $J$ = 7.8, 1H, 6-H) | 2.74 (s, 3H) | — |
| $L_3H$ | 9.44 | 11.51 | 8.08 (d, $J$ = 7.8, 1H, 10-H), 7.96 (d, $J$ = 6.0, 1H, 6-H), 7.55 (t, $J$ = 14.1, 1H, 4-H), 7.46 (t, $J$ = 14.7, 2H, 11-H, 12-H), 7.06 (t, $J$ = 17.7, 1H, 5-H) | — | — |
| $L_4H$ | 9.30 | 11.08 | 7.99 (d, $J$ = 7.1, 1H, 10-H), 7.85 (d, $J$ = 7.5, 1H, 6-H), 7.77 (t, $J$ = 6.8, 1H, 4-H), 7.24 (t, $J$ = 7.9, 1H, 5-H), 7.08 (t, $J$ = 6.7, 2H, 11-H, 12-H) | 3.20 (s, 3H) | — |
| $Et_2Si(L_1)Cl$ | 9.99 | — | 7.99 (d, $J$ = 8.1, 1H, 13-H), 7.60 (d, $J$ = 8.1, 1H, 10-H), 7.46 (d, $J$ = 7.0, 1H, 6-H), 7.34–7.26 (m, 2H, 11-H, 12-H), 6.99 (d, $J$ = 7.8, 1H, 4-H), 7.15 (dd, $J$ = 9.3, 1H, 5-H) | — | 1.41 (t, $J$ = 7.2, 4H), 0.89 (q, $J$ = 7.2, 6H) |
| $Bu_2Si(L_1)Cl$ | 9.35 | — | 7.98 (d, $J$ = 8.1, 1H, 13-H), 7.71 (d, $J$ = 6.0, 1H, 10-H), 7.35 (t, $J$ = 12.0, 1H, 6-H), 7.29 (d, $J$ = 5.1, 1H, 4-H), 7.24 (d, $J$ = 9.8, 2H, 11-H, 12-H), 6.93 (t, $J$ = 4.7, 1H, 5-H) | — | 0.73 (t, $J$ = 5.6, 6H), 1.02–0.98 (m, 8H), 0.88 (t, $J$ = 4.5, 4H) |
| $Ph_2Si(L_1)Cl$ | 9.28 | — | 7.96 (d, $J$ = 8.4, 1H, 13-H), 7.84 (dd, $J$ = 7.4, 1H, 10-H), 7.50–7.44 (m, 1H, 11-H), 7.43–7.24 (m, 1H, 12-H), 7.13 (t, $J$ = 6.4, 1H, 6-H), 7.07 (t, $J$ = 6.6, 1H, 5-H), 6.95 (d, $J$ = 7.9, 1H, 4-H) | — | 7.63–7.61 (m, 10H) |
| $Et_2Si(L_2)Cl$ | 9.34 | — | 7.98 (d, $J$ = 7.5, 1H, 10-H), 7.80 ($J$ = 3.3, 1H, 6-H), 7.20 (d, $J$ = 1.7, 1H, 4-H), 6.99 (d, $J$ = 4.5, 1H, 11-H), 6.95 (d, $J$ = 4.9, 1H, 12-H), 6.75 (d, $J$ = 7.0, 1H, 5-H) | 2.74 (s, 3H) | 1.12 (q, $J$ = 4.5, 4H), 0.85 (t, $J$ = 4.5, 6H) |
| $Bu_2Si(L_2)Cl$ | 9.40 | — | 7.23 (d, $J$ = 4.5, 1H, 10-H), 7.16 ($J$ = 7.0, 1H, 6-H), 6.98 (t, $J$ = 6.9, 1H, 11-H), 6.79 (d, $J$ = 6.1, 1H, 12-H), 6.59 (d, $J$ = 8.0, 1H, 4-H), 6.52 (d, $J$ = 7.6, 1H, 5-H) | 2.74 (s, 3H) | 0.76 (t, $J$ = 5.4, 6H), 1.06–0.95 (m, 8H), 0.85 (t, $J$ = 4.5, 4H) |
| $Ph_2Si(L_2)Cl$ | 9.40 | — | 8.34 (d, $J$ = 4.6, 1H, 10-H), 7.99 (d, $J$ = 4.5, 1H, 6-H), 7.79 (t, $J$ = 7.2, 1H, 11-H), 7.65 (d, $J$ = 4.9, 1H, 12-H), 7.56 (d, $J$ = 3.8, 1H, 4-H), 7.52 (d, $J$ = 8.9, d, 1H, 5-H) | 2.75 (s, 3H) | 7.51–7.49 (m, 10H) |

**Table 2** $^1$H NMR data of the ligands and their silicon(IV) complexes; $\delta$ (ppm), $J$ (Hz) *(Continued)*

| Ligands/ complexes | N=CH | OH | Aromatic-H | $R^1$ | Si−R |
|---|---|---|---|---|---|
| $Et_2Si(L_3)Cl$ | 9.47 | — | 7.89 (d, $J = 4.7$, 1H, 10-H), 7.80 (d, $J = 3.2$, 1H, 6-H), 7.74 (t, $J = 8.7$, 1H, 11-H), 7.58 (t, $J = 5.8$, 1H, 12-H), 7.45 (d, $J = 1.7$, 1H, 4-H), 7.34 (t, 11.5, 1H, 5-H) | — | 1.13 (q, $J = 4.7$, 4H), 0.97 (t, $J = 4.7$, 6H) |
| $Bu_2Si(L_3)Cl$ | 9.45 | — | 7.98 (d, $J = 4.8$, 1H, 10-H), 7.85 (d, $J = 7.1$, 1H, 6-H), 7.75 (t, $J = 5.8$, 1H, 11-H), 7.47 (t, $J = 14.3$, 1H, 12-H), 7.21 (d, $J = 4.8$, 1H, 4-H), 7.13 (t, $J = 5.5$, 1H, 5-H) | — | 0.77 (t, $J = 5.1$, 6H), 1.02–0.99 (m, 8H), 0.86 (t, $J = 4.3$, 4H) |
| $Ph_2Si(L_3)Cl$ | 9.48 | — | 8.23 (d, $J = 4.7$, 1H, 10-H), 8.07 (d, $J = 3.1$, 1H, 6-H), 7.99 (t, $J = 5.9$, 1H, 11-H), 7.87 (d, $J = 7.4$, 1H, 12-H), 7.61 (d, $J = 5.8$, 1H, 4-H), 7.21 (t, $J = 11.5$, 1H, 5-H) | — | 7.34–7.31 (m, 10H) |
| $Et_2Si(L_4)Cl$ | 9.35 | — | 8.08 (J = 7.3, d, 1H, $C_{10}$-H), 7.99 (J = 7.9, d, 1H, $C_6$-H), 7.80 (J = 7.8, t, 1H, $C_{11}$-H), 7.56 (J = 9.1, d, 1H, $C_{12}$-H), 7.45(J = 7.1, d, 1H, $C_4$-H), 7.38 (J = 6.9, dd, 1H, $C_5$-H) | 3.20 (s, 3H) | 1.10 (q, $J = 4.9$, 4H), 0.95 (t, $J = 4.9$, 6H) |
| $Bu_2Si(L_4)Cl$ | 9.37 | — | 8.29 (d, $J = 7.8$, 1H, 10-H), 7.95 (d, $J = 6.9$, 1H, 6-H), 7.71 (t, $J = 4.5$, 1H, 11-H), 7.64 (d, $J = 8.1$, 1H, 12-H), 7.37 (d, $J = 6.5$, 1H, 4-H), 7.31 (t, $J = 6.9$, 1H, 5-H) | 3.21 (s, 3H) | 0.79 (t, $J = 5.7$, 6H), 1.02–0.98 (m, 8H), 0.88 (t, $J = 4.9$, 4H) |
| $Ph_2Si(L_4)Cl$ | 9.38 | — | 8.18 (d, $J = 7.8$, 1H, 10-H), 7.97 (d, $J = 7.4$, 1H, 6-H), 7.86 (t, $J = 7.4$, 1H, 11-H), 7.76 (d, $J = 8.1$, 1H, 12-H), 7.58 (d, $J = 5.6$, 1H, 4-H), 7.45 (d, $J = 5.9$, 1H, 5-H) | 3.20 (s, 3H) | 7.74–7.70 (m, 10H) |



the azomethine group is also involved in coordination. The signals for the protons of the benzothiazole ring appear at 8.34–7.50 ppm, while the signals of the protons of the ring of substituted aromatic aldehyde are observed at 7.40–6.50 ppm. The signal for the protons of the methoxy group appears as a sharp singlet at 3.98 ppm in the ligands and its position is not changed on complexation. The signals in the spectra of the complexes at 0.80–1.23, 0.80–1.90, and 7.63–7.61 ppm are caused by the protons of the ethyl, butyl, and phenyl groups attached to the silicon atom. The values of the respective coupling constants are given in Table 2; they are in agreement with literature values.

The $^{13}$C NMR spectra of the ligands and the corresponding organosilicon(IV) complexes were recorded in $CDCl_3$. Chemical shifts are given relative to the TMS and are compiled in Table 3. In the $^{13}$C NMR spectra of the free ligands, the signal of the azomethine carbon atom appears at $\delta = 163.0$–$165.6$ ppm and is shifted by 10 ppm on complexation to the diorganosilicon(IV) dichloride, confirming the involment of azomethine nitrogen in coordination. The signals of the $CH_3$ and $CH_2$ carbon atoms of the ethyl group attached to silicon are found at 8.2–8.4 and 20.1–19.3 ppm, respectively, while the $^{13}$C NMR signals of the *n*-butyl group attached to silicon are observed at 8.6, 18.3, 19.9, and 27.3 ppm.

**Table 3** $^{13}C$ NMR data of the ligands and their silicon(IV) complexes; $\delta$ (ppm)

| Ligands/ complexes | C=N | $OCH_3$ | Aromatic | R | Si−R |
|---|---|---|---|---|---|
| $L_1H$ | 163.0 | 55.8 | 117.2 (C-1), 145.4 (C-2), 133.2 (C-3), 115.7 (C-5), 113.7 (C-4), 128.1 (C-6), 190.1 (C-8), 153.9 (C-9), 125.3 (C-10), 130.0 (C-11), 132.8 (C-12), 135.7 (C-13), 155.9 (C-14) | — | — |
| $L_2H$ | 165.6 | 56.0 | 118.3 (C-1), 146.1 (C-2), 130.4 (C-3), 110.2 (C-4), 114.1 (C-5), 124.6 (C-6), 191.1 (C-8), 150.7 (C-9), 122.0 (C-10), 126.8 (C-11), 128.6 (C-12), 130.8 (C-13), 152.0 (C-14) | 18.4 | — |
| $L_3H$ | 164.6 | 55.1 | 118.9 (C-1), 133.9 (C-2), 128.9 (C-3), 112.0 (C-4), 117.1 (C-5), 122.9 (C-6), 192.0 (C-8), 135.2 (C-9), 121.9 (C-10), 127.1 (C-11), 128.9 (C-12), 132.9 (C-13), 140.0 (C-14) | — | — |
| $L_4H$ | 163.8 | 56.8 | 117.9 (C-1), 144.9 (C-2), 132.8 (C-3), 113.7 (C-4), 115.1 (C-5), 125.0 (C-6), 192.1 (C-8), 152.0 (C-9), 123.1 (C-10), 126.4 (C-11), 130.8 (C-12), 133.7 (C-13), 154.4 (C-14) | 43.5 | — |
| $Et_2Si(L_1)Cl$ | 163.9 | 57.0 | 118.1 (C-1), 143.9 (C-2), 134.0 (C-3), 116.3 (C-4), 112.6 (C-5), 128.9 (C-6), 191.4 (C-8), 152.9 (C-9), 126.1 (C-10), 132.1 (C-11), 132.9 (C-12), 136.9 (C-13), 154.7 (C-14) | — | 8.7, 17.4 |
| $Bu_2Si(L_1)Cl$ | 162.9 | 55.5 | 118.9 (C-1), 145.9 (C-2), 133.8 (C-3), 114.7 (C-4), 116.3 (C-5), 128.9 (C-6), 193.0 (C-8), 153.1 (C-9), 126.1 (C-10), 135.1 (C-11), 136.0 (C-12), 138.7(C-13), 154.1 (C-14) | — | 8.4, 17.9, 18.1, 26.9 |
| $Ph_2Si(L_1)Cl$ | 162.3 | 56.4 | 117.6 (C-1), 144.1 (C-2), 132.9 (C-3), 115.9 (C-4), 113.1 (C-5), 129.0 (C-6), 192.4 (C-8), 153.0 (C-9), 126.9 (C-10), 134.0 (C-11), 135.1 (C-12), 137.2 (C-13), 153.9 (C-14) | — | 136.3, 133.6, 131.9, 128.1 |
| $Et_2Si(L_2)Cl$ | 166.1 | 56.2 | 119.1 (C-1), 145.6 (C-2), 131.2 (C-3), 111.9 (C-4), 114.8 (C-5), 123.9 (C-6), 192.0 (C-8), 150.9 (C-9), 123.1 (C-10), 127.7 (C-11), 128.9 (C-12), 132.1 (C-13), 152.9 (C-14) | 19.8 | 8.2, 17.3 |
| $Bu_2Si(L_2)Cl$ | 165.9 | 55.6 | 117.9 (C-1), 146.0 (C-2), 130.4 (C-3), 113.4 (C-4), 116.2 (C-5), 123.9 (C-6), 193.1 (C-8), 152.0 (C-9), 125.9 (C-10), 127.5 (C-11), 129.4 (C-12), 132.6 (C-13), 153.2 (C-14) | 19.9 | 8.3, 17.3, 18.6, 26.9 |
| $Ph_2Si(L_2)Cl$ | 167.7 | 56.7 | 118.9 (C-1), 145.9 (C-2), 132.1 (C-3), 112.5 (C-4), 114.2 (C-5), 123.1 (C-6), 193.0 (C-8), 150.1 (C-9), 124.4 (C-10), 126.9 (C-11), 128.4 (C-12), 131.5 (C-13), 154.2 (C-14) | 19.3 | 135.9, 133.6, 129.9, 127.5 |
| $Et_2Si(L_3)Cl$ | 168.7 | 55.8 | 119.2 (C-1), 134.0 (C-2), 129.2 (C-3), 114.6 (C-4), 117.6 (C-5), 123.6 (C-6), 196.2 (C-8), 135.4 (C-9), 121.4 (C-10), 126.7 (C-11), 127.0 (C-12), 135.4 (C-13), 140.3 (C-14) | — | 8.2, 20.7 |
| $Bu_2Si(L_3)Cl$ | 165.8 | 56.2 | 119.3 (C-1), 135.1 (C-2), 128.0 (C-3), 118.1 (C-4), 119.1 (C-5), 125.1 (C-6), 192.0 (C-8), 134.4 (C-9), 121.6 (C-10), 126.5 (C-11), 130.8 (C-12), 134.9 (C-13), 150.4 (C-14) | — | 8.6, 18.3, 19.8, 27.3 |
| $Ph_2Si(L_3)Cl$ | 168.3 | 56.4 | 119.8 (C-1), 135.9 (C-2), 128.9 (C-3), 115.7 (C-4), 121.0 (C-5), 125.8 (C-6), 193.1 (C-8), 135.9 (C-9), 122.9 (C-10), 127.8 (C-11), 130.5 (C-12), 134.4 (C-13), 143.0 (C-14) | — | 136.9, 132.4, 131.9, 129.8 |

**Table 3** $^{13}$C NMR data of the ligands and their silicon(IV) complexes; $\delta$ (ppm) *(Continued)*

| Ligands/ complexes | C=N | $OCH_3$ | Aromatic | R | Si−R |
|---|---|---|---|---|---|
| $Et_2Si(L_4)Cl$ | 164.4 | 57.3 | 118.4 (C-1), 145.0 (C-2), 131.6 (C-3), 115.4 (C-4), 117.9 (C-5), 126.2 (C-6), 193.7 (C-8), 153.9 (C-9), 124.1 (C-10), 128.4 (C-11), 132.5 (C-12), 135.1 (C-13), 153.7 (C-14) | 44.5 | 8.5, 20.1 |
| $Bu_2Si(L_4)Cl$ | 164.3 | 58.6 | 120.4 (C-1), 145.3 (C-2), 133.2 (C-3), 112.9 (C-4), 122.5 (C-5), 126.3 (C-6), 193.2 (C-8), 154.0 (C-9), 124.7 (C-10), 131.8 (C-11), 133.5 (C-12), 137.0 (C-13), 158.4 (C-14) | 45.4 | 8.4, 17.7, 18.1, 24.9 |
| $Ph_2Si(L_4)Cl$ | 165.1 | 56.9 | 118.9 (C-1), 144.6 (C-2), 132.5 (C-3), 113.1 (C-4), 120.6 (C-5), 127.3 (C-6), 194.1 (C-8), 153.9 (C-9), 125.4 (C-10), 130.8 (C-11), 131.6 (C-12), 135.6 (C-13), 155.7 (C-14) | 45.9 | 137.4, 134.9, 128.3, 126.6 |

Signals due to the carbon atoms of the phenyl group appear in the range of 126.6–137.4 ppm. The $^{13}$C NMR signals of the carbon atoms of substituted aromatic aldehyde ring are observed in the range of 117.2–129.0 ppm and those of the benzothiazole moiety at 193.1–121.4 ppm.

In the $^{29}$Si NMR spectra of the complexes, a sharp signal appears in the range of −96.2 to −98.9 ppm[13] with respect to TMS indicating a pentacordinated environment around the silicon atom with the nitrogen atom occupying equatorial position and the most electronegative atom occupying axial position[14,15]. On the basis of the spectroscopic studies, the pentacordinated structure of the complexes shown in Figure 1 has been proposed.

## Antimicrobial Activity

The ligands and their complexes were tested for antimicrobial activities using a twofold serial dilution technique. The stock solution was prepared by dissolving the compounds in dry DMSO to give a concentration of 100 $\mu$g/mL. For *in vitro* antimicrobial activity, these compounds were screened against gram-positive bacteria [*Staphylococcus*

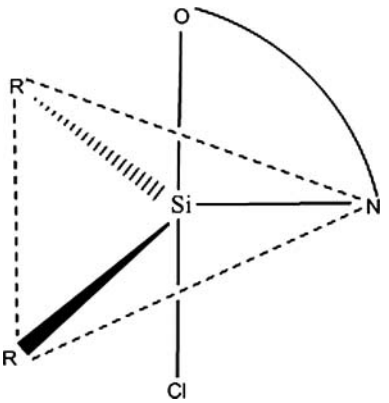



**Figure 1** Proposed structure of the silicon(IV) complexes.

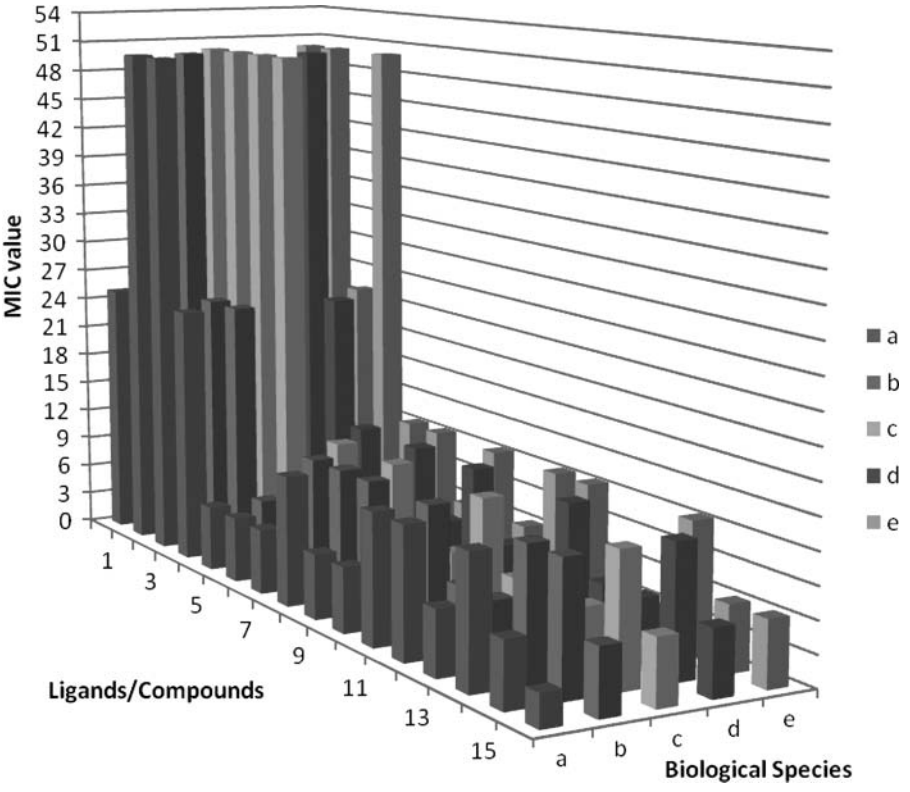



**Figure 2** Biological activity of the silicon(IV) complexes.

*aureus*(a) and *Bacillus subtilis*(b)] and gram-negative bacteria [*Escherichia coli*(c)] and against fungi [*Aspergillus niger*(d) and *Candida albicans*(e)]. The incubation period of *Aspergillus niger* and *Candida albicans* was 7 days at 25 °C ± 1 °C and 36 h at 37 °C ± 1 °C, respectively, whereas for bacteria it was 24 h at 37 °C ± 1 °C. The conventional bactericides tetracycline and chloramphenicol and fungicide fluconazole were used as standards for comparing the activity of the compounds (MIC values are given in Figure 2).

From the data of the antimicrobial activity it may be concluded:

(i) *In vitro* biocidal studies indicate that the organosilicon(IV) complexes of type $R_2Si(L)Cl$ were more potent than their parent ligands against the same microorganisms under identical experimental conditions, but due to their poor water solubility *in vivo* studies remain untouched. The increased antimicrobial activity may be explained on the basis of chelation theory,[16,17] according to which the polarity of the metal ion is reduced when the positive charge of the metal ion is shared with a donor group. The increased lipophilicity enhances the penetration of the metal complexes into the lipid layer of cell membrane resulting in interference with normal cell process.

(ii) Among the complexes, $Ph_2Si(L_{1-4})Cl$ was found to be more active than $Bu_2Si(L_{1-4})Cl$ and $Et_2Si(L_{1-4})Cl$. This may be due to the fact that the bulkiness of substituent R increases the lipophilicity coupled with the polarity of Si–C bond, which increases the bioactivity of these complexes in the order Ph > Bu > Et.

**Table 4** Elemental analysis of the ligands and their silicon complexes[a]

| Ligand/complexes | Molecular formula | C Found (calcd.) | H Found (calcd.) | Cl Found (calcd.) | N Found (calcd.) | S Found (calcd.) | Si Found (calcd.) |
|---|---|---|---|---|---|---|---|
| $L_1H$ | $C_{15}H_{12}N_2O_2S$ | 63.31 (63.36) | 4.23 (4.25) | — | 9.82 (9.85) | 11.21 (11.25) | — |
| $L_2H$ | $C_{16}H_{14}N_2O_2S$ | 64.39 (64.41) | 4.71 (4.73) | — | 9.90 (9.93) | 10.73 (10.75) | — |
| $L_3H$ | $C_{15}H_{11}N_3O_4S$ | 61.10 (61.13) | 4.37 (4.49) | — | 8.89 (8.91) | 10.67 (10.70) | — |
| $L_4H$ | $C_{16}H_{14}N_2O_3S$ | 54.68 (54.70) | 3.34 (3.37) | — | 12.73 (12.76) | 9.70 (9.74) | — |
| $Et_2Si(L_1)Cl$ | $C_{19}H_{21}N_2O_2SSiCl$ | 56.21 (56.22) | 5.15 (5.17) | 8.73 (8.75) | 6.88 (6.90) | 7.86 (7.89) | 7.13 (7.15) |
| $Bu_2Si(L_1)Cl$ | $C_{23}H_{29}N_2O_2SSiCl$ | 59.77 (59.80) | 6.26 (6.28) | 7.65 (7.69) | 6.04 (6.06) | 6.91 (6.93) | 6.27 (6.29) |
| $Ph_2Si(L_1)Cl$ | $C_{27}H_{21}N_2O_2SSiCl$ | 64.58 (64.60) | 4.16 (4.19) | 7.05 (7.08) | 5.55 (5.58) | 6.36 (6.38) | 5.76 (5.78) |
| $Et_2Si\ (L_2)Cl$ | $C_{20}H_{23}N_2O_2SSiCl$ | 57.18 (57.21) | 5.36 (5.48) | 8.43 (8.46) | 6.64 (6.67) | 7.60 (7.63) | 6.89 (6.91) |
| $Bu_2Si(L_2)Cl$ | $C_{24}H_{31}N_2O_2SSiCl$ | 60.55 (60.58) | 6.49 (6.52) | 7.44 (7.46) | 5.87 (5.89) | 6.70 (6.73) | 6.06 (6.09) |
| $Ph_2Si(L_2)Cl$ | $C_{28}H_{23}N_2O_2SSiCl$ | 65.17 (65.18) | 4.43 (4.46) | 6.85 (6.88) | 5.41 (5.43) | 6.17 (6.20) | 5.60 (5.62) |
| $Et_2Si(L_3)Cl$ | $C_{20}H_{23}N_2O_3SSiCl$ | 55.08 (55.11) | 5.25 (5.28) | 7.84 (7.88) | 6.40 (6.43) | 7.32 (7.34) | 6.63 (6.66) |
| $Bu_2Si(L_3)Cl$ | $C_{24}H_{31}N_2O_3SSiCl$ | 58.57 (58.60) | 6.28 (6.30) | 7.00 (7.01) | 5.68 (5.70) | 6.49 (6.51) | 5.87 (5.90) |
| $Ph_2Si(L_3)Cl$ | $C_{28}H_{23}N_2O_3SSiCl$ | 63.18 (63.21) | 4.29 (4.32) | 6.46 (6.49) | 5.53 (5.26) | 6.00 (6.02) | 5.43 (5.45) |
| $Et_2Si(L_4)Cl$ | $C_{19}H_{20}N_3O_4SSiCl$ | 50.56 (50.61) | 4.42 (4.44) | 8.12 (8.15) | 9.30 (9.32) | 7.09 (7.10) | 6.42 (6.44) |
| $Bu_2Si(L_4)Cl$ | $C_{23}H_{28}N_3O_4SSiCl$ | 54.47 (54.50) | 5.50 (5.53) | 7.20 (7.22) | 8.26 (8.29) | 6.30 (6.32) | 5.68 (5.72) |
| $Ph_2Si(L_4)Cl$ | $C_{27}H_{20}N_3O_4SSiCl$ | 59.23 (59.29) | 3.63 (3.65) | 6.84 (6.86) | 7.65 (7.68) | 5.83 (5.86) | 5.28 (5.30) |

[a]All complexes undergo decomposition at temperatures between 250 °C–300 °C.

(iii) The conventional fungicide and bactericide show the inhibition at the concentration less than 3.12 ppm. None of the compounds shows a better inhibition than the conventional fungicide and bactericide used. Some of the compounds have toxicity similar to that of the conventional fungicide against *Bacillus subtilis* and fungi *Aspergillus niger* and *Candida albicans*.

## EXPERIMENTAL

All the experimental work was carried out under dry nitrogen using vacuum line. All chemicals used in this work were purchased from Aldrich and used without further purification. Solvents were purified according to the standard procedures. IR spectra were obtained using a Spectrum BX Series FT-IR spectrophotometer as KBr pellets. $^{1}$H NMR and $^{13}$C NMR spectra were recorded with a Bruker Avance II 400 MHz NMR spectrometer and all chemical shifts are reported in ppm relative to TMS as an internal standard in $CDCl_3$. Elemental analyses were carried out on Perkin Elmer 2400 instrument. Molar conductances were measured with a conductivity bridge type Model-306 Systronics in DMSO as solvent. The content of silicon and chlorine were determined gravimetrically.

### Synthesis of the Ligands

The Schiff bases were prepared by condensation of equimolar quantities of the respective 2-aminobenzothiazole derivative (0.001 mol) and 2-hydroxy-3-methoxy benzaldehyde (0.001 mol) in dry ethanol as solvent. The reaction mixture was stirred at room temperature and then refluxed for 3 h. The resulting yellowish solid thus obtained was filtered and recrystallized from ethanol. The purity of the compounds was checked by TLC.

### Synthesis of the Organosilicon(IV) Complexes

The complexes were prepared in inert atmosphere using dry nitrogen. First, the sodium salts of the Schiff bases were prepared by allowing an equimolar ratio of the ligand and sodium metal to react in dry methanol (15 mL). An equimolar amount of the diorganosilicon(IV) dichloride was then slowly added to the sodium salt of the respective ligand and the reaction mixture was stirred for about half an hour and then refluxed for two hours. Solid sodium chloride formed during the reaction was removed by filtration. The excess of solvent was removed under reduced pressure to give the crude product. The compound was repeatedly washed with dry hexane and the solid was recrystallized using a mixture of dry methanol and dry hexane and finally dried in vaccuo. All the other organosilicon(IV) derivatives of Schiff base ligands were synthesized by applying this procedure. The elemental analyses of the complexes are given in Table 4.

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