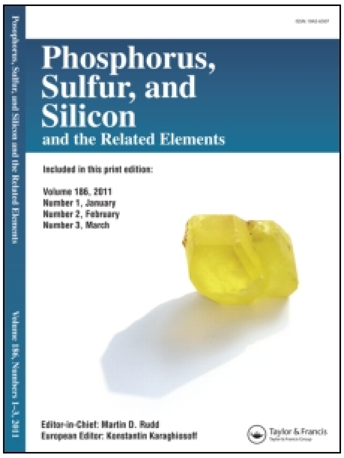

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Synthesis, Characteristic Spectral Studies and in Vitro Antimicrobial Activity of Organosilicon(IV) Complexes of N-(2-Hydroxynaphthalidene)-Amino Acid Schiff Bases

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SYNTHESIS, CHARACTERISTIC SPECTRAL STUDIES AND IN VITRO ANTIMICROBIAL ACTIVITY OF ORGANOSILICON(IV) COMPLEXES OF N-(2-HYDROXYNAPHTHALIDENE)-AMINO ACID SCHIFF BASES

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Fifteen new organosilicon(IV) complexes formulated as $R_3Si[2\text{-}HOC_{10}H_6CH{=}NCH(X)COO]$ *and* $Me_2Si[2\text{-}OC_{10}H_6CH{=}NCH(X)\text{-}COO]$ *(where* $X = H[H_2L^1]$, $-CH_2CH(CH_3)_2[H_2L^2]$, $-CH_2CH_2\text{-}SCH_3[H_2L^3]$, $-CH_3[H_2L^4]$ *and* $-CH(CH_3)_2[H_2L^5]$ *were prepared and characterized by* ^1H *and* ^{13}C *NMR, IR, electronic spectral studies, and elemental analysis. All of the complexes are nonelectrolytes. The spectral studies suggested a distroted trigonal-bipyramidal geometry around the silicon atom. Antimicrobial activity screening for all of the complexes was carried out against various bacteria [* Escherichia coli, Aeromonas formicans, Pseudomonas putida-2252, *and* Staphylococcus aureus-740*] and fungi [*Aureobasidium pullulans-1991, Penicillium chrysogenum-1348, Verticillium dahliae-2063, *and* Aspergillus niger ORS-4*]. The complexes showed good activity.*

Keywords: Amino acids; antimicrobial activity; multinuclear NMR; organosilicon(IV); Schiff bases

INTRODUCTION

Although organotin(IV) and organosilicon(IV) complexes of Schiff bases derived from various amines have received much attention during the last two decades,[1–11] comparatively little attention has been paid to the Schiff base systems derived from amino acids.[12–23] Transition metal complexes of the Schiff bases in which amino groups are provided by amino acids have received considerable attention during the last a few decades due to their possible use as potential N-pyridoxylideneamino

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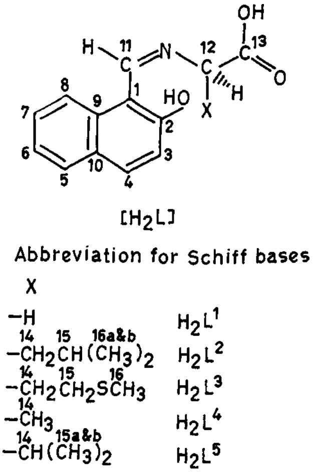


FIGURE 1 General formula of the Schiff bases.

acid systems.[25–31] Pyridoxyl (Vitamin B_6 aldehyde)-amino acid Schiff bases are believed to be intermediates in biologically important amination processes.[32] Furthermore, metal ions catalyse transamination reactions involving vitamin B_6.[33,34] These concurrent results seem to indicate that metal complexes of Schiff bases derived from various amino acids are formed as intermediates in transamination reactions involving vitamin B_6.[35] In view of this, we report the synthesis of organosilicon(IV) derivatives of Schiff bases derived from condensation of 2-hydroxy-1-naphthaldehyde with glycine (H_2L^1), L-leucine (H_2L^2), L-methionine (H_2L^3), DL-α-alanine (H_2L^4), and L-valine (H_2L^5) (Figure 1), and their characterization by elemental analyses and spectroscopic (IR, ^{1}H, and ^{13}C NMR) studies. Their antimicrobial activity screening has been carried out against various bacteria and fungi.

RESULTS AND DISCUSSION

Trimethyl- and triphenyl-silicon(IV) derivatives of Schiff bases (H_2L) derived from condensation of 2-hydroxy-1-naphthaldehyde with different amino acids have been synthesized by the reaction of triorganosilicon(IV) chloride with the monosodium salt of the Schiff bases [NaHL] in ~1:1 molar ratio, whereas the synthesis of dimethylsilicon(IV) derivatives of Schiff bases [H_2L] was carried out by the reaction of dimethylsilicon(IV) dichloride in 1:1 molar ratio with disodium salt of the Schiff bases [Na_2L].

$$H_2NCH(X)\,COOH + NaOMe \rightarrow H_2N\,CH(X)\,COONa + MeOH \qquad (1)$$

$$H_2NCH(X)\,COONa + 2\text{-}HOC_{10}H_6CHO$$
$$\rightarrow 2\text{-}HOC_{10}H_6CH{=}NCH(X)\,COONa[NaHL] \quad (2)$$
$$NaHL + R_3SiCl \rightarrow R_3SiHL + NaCl \quad (3)$$
$$H_2NCH(X)\,COOH + 2\text{-}HOC_{10}H_6CHO$$
$$\rightarrow 2\text{-}HOC_{10}H_6CH{=}NCH(X)\,COOH[H_2L] \quad (4)$$
$$H_2L + 2NaOMe \rightarrow Na_2L + 2MeOH \quad (5)$$
$$Na_2L + Me_2SiCl_2 \rightarrow Me_2SiL + 2NaCl \quad (6)$$

All of the newly synthesized complexes are yellow to dark brown solids which are sparingly soluble in methanol, DMSO, and DMF. The analytical data of the complexes indicated 1:1 stoichiometry between the ligand and the organosilicon(IV) moiety (Table I). All of the complexes were moisture-sensitive and decomposed when exposed to air; therefore, they were stored under a dry nitrogen atmosphere. The molar conductance values of 10^{-3} M solutions in methanol and DMF are in the ranges 58.97–88.57 and 57.52–59.92 $ohm^{-1}cm^2mol^{-1}$, respectively, indicating the partial hydrolysis of the complexes.

Electronic Spectra

The electronic spectra of all the complexes exhibit bands in the regions 202–230, 285–327, and 358–420 nm, which may be due to the π-π^* transition of the benzenoid, or n-π^* (COO), π-π^* transition of the >C=N— chromophore, and n-π^* transition of the >C=N— chromophore coupled with the secondary band of the benzene ring,[18,19] respectively. Further, there was a sharp band observed at 255 ± 6 nm in the spectra of the complexes, which could be assigned as charge transfer band.[18,19]

Infrared Spectra

Important infrared frequencies (in cm^{-1}) and their assignments are given in Table II. It has been reported that Schiff base derived from glycine and 1-(2-hydroxy-4-methylphenyl)-1-ethanone,[30] and potassium salt of Schiff base derived from glycine and 2-hydroxyacetophenone[14] exist predominantly in iminium form as represented in Figures 2a and 2b, on the basis of the appearance of an infrared band around 3400 cm^{-1} due to NH stretching vibrations (may be overlapping with hydrogen bonded O—H stretching vibrations.[14,30] Two bands at 1675 and 1610 cm^{-1} are also assigned[30] to the —COO asymmetric stretch and the C=N/C=C ring stretching vibrations respectively.

TABLE I Analytical and Physical Data of Organosilicon(IV) Complexes of Schiff Bases Derived from Amino Acids

S. no.	Complexes [empirical formula]	m.p. (°C)	Yield (%)	Color Physical state	Analysis (%) found (calcd.) C	H	N	Si	Molar conductance $ohm^{-1}cm^2mol^{-1}$
1	Me_2SiL^1 $[C_{15}H_{15}NO_3Si]$	80–82	22	Dark brown Solid	63.63 (63.13)	5.71 (5.30)	4.54 (4.91)	9.55 (9.84)	88.57[a]
2	Me_2SiL^2 $[C_{19}H_{23}NO_3Si]$	65	76	Light brown Solid	66.33 (66.83)	6.39 (6.79)	3.70 (4.10)	8.31 (8.22)	68.37[a]
3	Me_2SiL^3 $[C_{18}H_{21}NO_3SSi]$	55	36	Dark brown Solid	60.24 (60.14)	5.98 (5.89)	3.55 (3.90)	7.81 (7.81)	59.92[b]
4	Me_2SiL^4 $[C_{16}H_{17}NO_3Si]$	63–65	63	Dark brown Solid	64.25 (64.19)	5.53 (5.72)	4.34 (4.68)	9.58 (9.38)	57.52[b]
5	Me_2SiL^5 $[C_{18}H_{21}NO_3Si]$	67–68	59	Dark brown Solid	65.99 (66.02)	5.92 (6.46)	3.86 (4.28)	8.67 (8.58)	86.57[a]
6	Me_3SiHL^1 $[C_{16}H_{19}NO_3Si]$	70	31	Dark brown Solid	63.54 (63.76)	5.85 (6.35)	4.24 (4.65)	9.21 (9.32)	83.47[a]
7	Me_3SiHL^2 $[C_{20}H_{27}NO_3Si]$	63–65	40	Dark brown Solid	67.00 (67.19)	7.89 (7.61)	3.59 (3.92)	7.48 (7.86)	62.17[a]
8	Me_3SiHL^3 $[C_{19}H_{25}NO_3SSi]$	56	50	Yellow Solid	60.91 (60.77)	6.85 (6.71)	3.25 (3.73)	7.41 (7.48)	73.47[a]
9	Me_3SiHL^4 $[C_{17}H_{21}NO_3Si]$	73	32	Light brown Solid	64.52 (64.73)	6.25 (6.71)	4.52 (4.44)	8.70 (8.90)	63.27[a]
10	Me_3SiHL^5 $[C_{19}H_{25}NO_3Si]$	174–175	59	Yellow Solid	65.92 (66.44)	6.65 (7.34)	4.18 (4.08)	8.52 (8.18)	59.87[a]
11	Ph_3SiHL^1 $[C_{31}H_{25}NO_3Si]$	51–52	92	Dark brown Solid	76.66 (76.36)	5.27 (5.17)	3.35 (2.87)	5.61 (5.76)	82.37[a]
12	Ph_3SiHL^2 $[C_{35}H_{33}NO_3Si]$	110–112	43	Dark brown Solid	77.80 (77.31)	6.15 (6.12)	2.95 (2.58)	5.21 (5.17)	78.87[a]
13	Ph_3SiHL^3 $[C_{34}H_{31}NO_3SSi]$	70	71	Dark brown Solid	72.75 (72.69)	5.59 (5.56)	2.15 (2.49)	5.10 (5.00)	73.07[a]
14	Ph_3SiHL^4 $[C_{32}H_{27}NO_3Si]$	78–80	89	Yellow Solid	76.67 (76.62)	5.39 (5.42)	2.48 (2.79)	5.90 (5.60)	58.97[a]
15	Ph_3SiHL^5 $[C_{34}H_{31}NO_3Si]$	69–70	65	Dark brown Solid	77.25 (77.09)	5.52 (5.90)	2.35 (2.64)	5.70 (5.30)	83.57[a]

[a] In methanol.

[b] In DMF.

TABLE II Infrared Frequencies (in cm^{-1}) of Organosilicon(IV) Complexes of Schiff Bases Derived from Amino Acids

S. no.	ν(C=N)/ ν(C=C)	ν_{as}(COO) ν_s(COO)	$\Delta\nu$	ν_{as}(Si—O) ν_s(Si—O)	ν(Si←N)	ν_{as}(Si—C)	δ_{as}(Si—C) δ_s(Si—C)
1	[b]	1626 s 1399 s	227	821 s 675 s	550 s	749 m	1475 w —
2	1591 sh	1634 s 1399 m	235	816 s 675 m	566 s	766 m	1466 w 1249 m
3	[b]	1631 vs 1408 m	223	800 w —	550 m	749 m	1470 w 1233 s
4	[b]	1616 s 1391 s	225	800 m 674 m	583 m	741 m	1458 w 1250 w
5	1581 m	1625 s 1398 m	227	849 s 645 w	581 m	746 s	— 1200 w
6	1604 vs	1666 sh 1392 s	274	829 w 666 m	541 m	758 w	1460 sh 1245 m
7	[b]	1624 vs 1370 m	254	818 m 600 w	548 m	748 s	1468 m 1233 w
8	1572 w	1628 m 1406 s	222	834 w 640 sh	548 m	774 m	1466 w 1238 w
9	1588 sh	1634 vs 1406 m	228	860 w 662 w	541 m	750 s	1465 m 1257 w
10	[b]	1632 vs 1400 m	232	844 s 666 m	550 m	774 s	1479 w 1232 w
11	1583 w	1633 s 1400 s	233	856 m 633 w	512 vs 583 w	705 vs, 750 sh, 1111 s, 1483 w	— —
12	[b]	1627 s 1396 w	231	853 s 633 sh	511 vs 583 w	705 vs, 750 sh, 1118 m, 1480 w	—
13	1571 w	1624 s 1397 m	227	849 s 641 s	511 vs 550 sh	706, 750 sh, 1115 m, 1483 w	—
14	[b]	1634 s, br, 1403 m	231	836 s 630 w	511 vs	705 vs, 750 sh, 1118 m, 1483 w	—
15	1589 w	1626 vs 1395 vs	231	843 vs 600 w	509 vs	706 s, 743 w, 1118 s, 1453 m	—

[a] S. no. are those as represented in Table I.

[b] Azomethine ν(C=N) band merges with ν_{as}(COO); m, medium; vs, very strong; sh, shoulder; br, broad; s, strong; w, weak.

The Schiff bases (H_2L) derived from 2-hydroxy-1-naphthaldehyde and various amino acids exhibit intramolecular hydrogen bonded structures (Figure 3), but structure corresponds to Figure 3a is more stable, and it is also consistent with the previously reported structure of similar Schiff bases.

The infrared spectra of the dimethylsilicon(IV) complexes of the type, Me_2SiL do not exhibit a strong band in the 3500–3200 cm^{-1} region, due to νOH/NH, indicating the deprotonation of the phenolic and

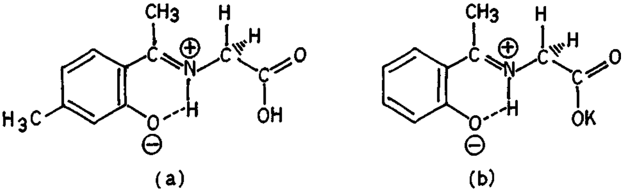


FIGURE 2 (a) Structure of Schiff base derived from glycine and 1-(2-hydroxy-4-methyl-phenyl)-1-ethanone; (b) derived from glycine and 2-hydroxyacetophenone.

carboxylic oxygen of the Schiff bases upon complexation with silicon as expected.[18,19,22,23] Whereas the infrared spectra of triorganosilicon(IV) derivatives of monosodium salts of Schiff bases derived from 2-hydroxy-1-naphthaldehyde and sodium salts of the amino acides exhibit a band in the 3300–3200 cm^{-1} region, which could be due to phenolic —OH stretching vibrations. This suggests that the phenolic oxygen in R_3SiHL complexes is not involved in coordination.

Two sharp bands in the regions 1572–1634 and 509–583 cm^{-1} are observed and assigned to the ν(C=N) azomethine[18,19] and ν(Si ← N)[22,23] frequencies, respectively, indicating the coordination of the ligand to the central silicon atom through the azomethine nitrogen. In the spectra of the complexes two sharp bands are observed at 1629 ± 5 and 1389 ± 19 cm^{-1} and are assigned to ν_{as}(COO) and ν_s(COO) respectively. In some complexes, either a single sharp band at 1624 ± 8 cm^{-1} or the band at ~1620 ± 15 cm^{-1} is somewhat broad and shouldered, which may be attributed to the combination of C=N/C=C ring stretching vibrations and —COO asymmetric stretching vibrations. It is clear from Table II that the range of ν_{as}(COO) values shown by the complexes is substantially lower than for ionic normal ester like trimethylsilylacetate (1725 cm^{-1}),[36] but higher than for the bridged trimethyltin acetate

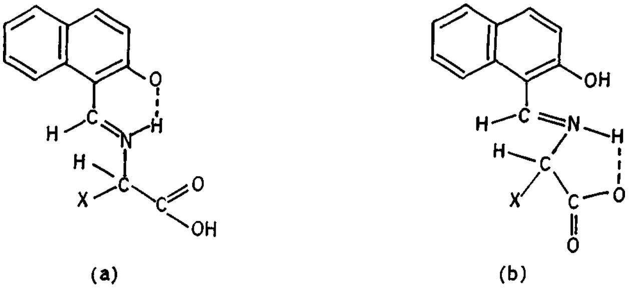


FIGURE 3 Intramolecularly hydrogen bonded possible structures of $2\text{-}HOC_{10}H_6CH{=}NCH(X)COOH$.

(1576 cm^{-1}).[37] Furthermore, the separation between the ν_{as}(COO) and ν_s(COO) is about 248 ± 26 cm^{-1}, indicating the covalent nature of the metal-oxygen bond.[18,19,22] Ionic bonding, bridging, or chelation can therefore be excluded, and it must be assumed that the carboxyl groups bind silicon unidentately.[18,19,22] The sharp bands at 830 ± 30 and 635 ± 35 cm^{-1} in the spectra of the complexes have been assigned to ν_{as}(Si—O) and ν_s(Si—O) respectively.[7–9,22,23]

Five-coordinate complexes of the type $R_3Si(NO)$ (where NO = coordinating site of the monoanions of H_2L^1 to H_2L^5) may assume either of the three trigonal-bipyramidal arrangements (A), (B), and (C) of C_s, C_{3v} and C_s symmetry respectively (Figure 4). The IR spectra of trimethylsilicon(IV) derivatives show two bands around 1470 ± 10 cm^{-1} and 1245 ± 13 cm^{-1}, which have been assigned to the asymmetric and symmetric deformation modes of CH_3—Si respectively.[22,23,38] A strong band at 761 ± 13 cm^{-1} may be due to ν(Si—C) modes.[22,23,38] Whereas the IR spectra of triphenylsilicon(IV) derivatives depict four medium to strong intensity bands at 705, 747 ± 4, 1115 ± 4 and 1468 ± 15 cm^{-1}, which have been assigned to the ν(Si—C_6H_5) modes.[22,23] Due to the steric properties of the bidentate ligands the structure (B) was ruled out, and it was concluded that the three organic (Me or Ph) groups are not in equatorial positions and the two donor atoms viz., oxygen and nitrogen of the ligands, are not in axial positions.[22,23] Thus, the trimethyl- and triphenyl-silicon(IV) derivatives of bidentate monoanions of the Schiff bases derived from the condensation of 2-hydroxy-1-naphthaldehyde and various amino acids have been tentatively proposed to have either the structure (A) or (C) in a distorted trigonal-bipyramidal geometry around silicon. A structure similar to C but with an apical nitrogen can not be excluded. The structure (C) has also been proposed[19] for the corresponding complexes of Ph_3Sn(IV) moiety of the type Ph_3SnHL.

Five-coordinate complexes of the type $Me_2Si(ONO)$ [where ONO = coordinating site of dianions of H_2L^1 to H_2L^5] may assume either of three trigonal-bipyramidal arrangements (D), (E) and (F) of C_{2v}, C_s and C_{2v} symmetry respectively (Figure 5). It is apparent from an examination of the available data for five- and six-coordinate diorganotin(IV) complexes that the preferred geometries are, respectively, trigonal-bipyramidal with *cis* (equatorial) organic groups and octahedral with a *trans* arrangement of organic groups, seemingly independent of any charge carried by the complex.[18,19,36] The IR spectra of Me_2SiL^1 to Me_2SiL^5 (where L^1 to L^5 are tridentate dianions of Schiff bases H_2L^1 to H_2L^5) show two bands around 1467 ± 9 and 1225 ± 25 cm^{-1}, which have been assigned to the asymmetric and symmetric deformation modes of CH_3—Si respectively.[22,23,38] A strong band around 754 ± 13 cm^{-1} may

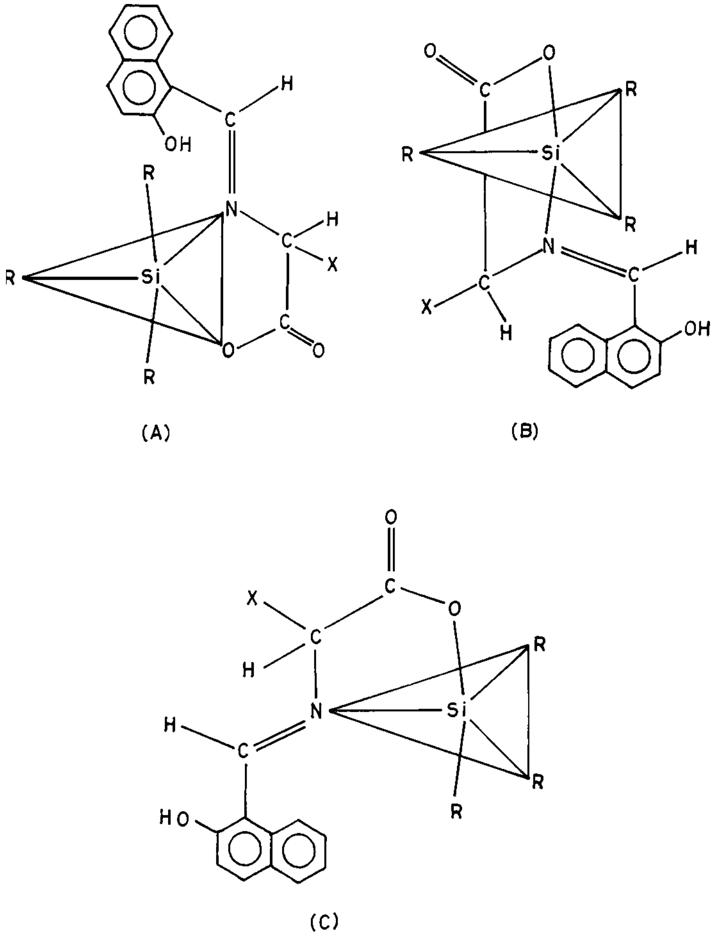


FIGURE 4 Possible geometries for R_3SiHL (Where HL = $2\text{-}HOC_{10}H_6CH{=}NCH(X)COO$).

be due to ν(Si—C) modes,[22,23,38] which suggests the presence of two *cis* methyl groups in the equatorial positions of the trigonal-bipyramidal structure (as shown in Figure 5d) with two axial oxygen and one equatorial nitrogen atoms of the ligand. Similar structure has also been reported[18,19] for R_2SnL complexes (where L = dianion of the Schiff bases derived from 2-hydroxy-1-naphthaldehyde/acetylacetone and various amino acids) on the basis of ^{119}Sn Mössbauer spectral studies. The single crystal X-ray diffraction study of $Bu_2Sn[OC_6H_4CH{=}NCH(CH(CH_3)_2)COO]$ also indicated[16] that the tin atom has a distorted

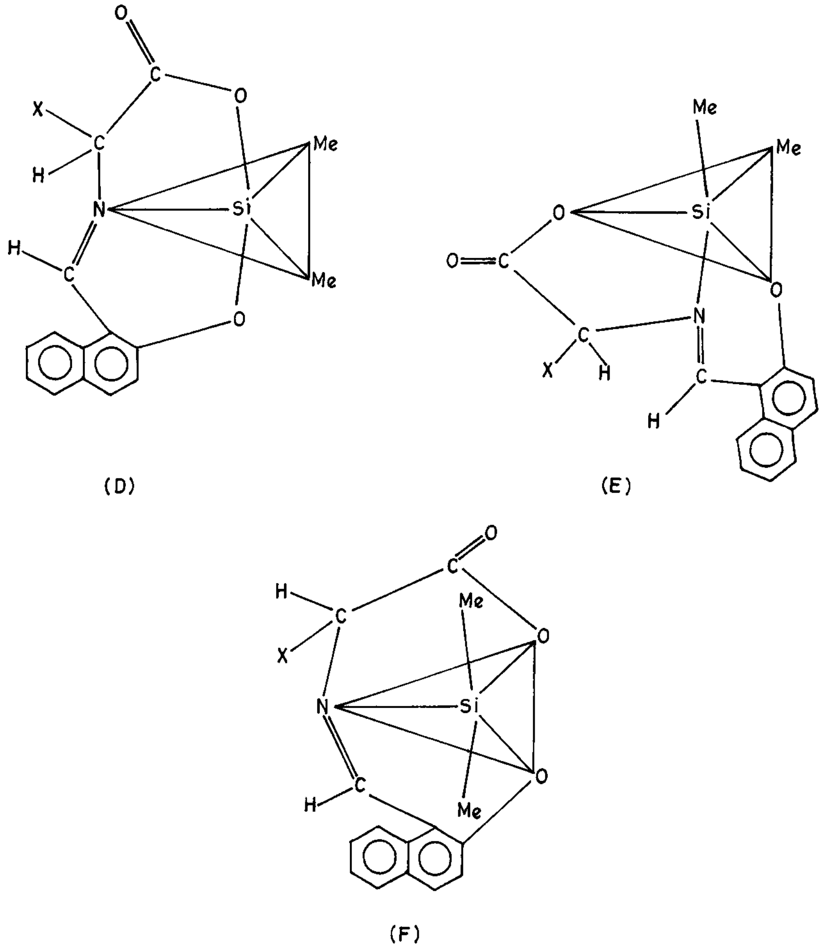


FIGURE 5 Possible geometries for Me_2SiL (Where L = 2-$OC_{10}H_6CH$=NCH(X)COO).

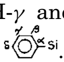
trigonal-bipyramidal coordination with two axial Sn—O bonds of 2.078 (10) and 2.151 (8) Å and the equatorial Sn—N bond of 2.158 (8) Å, and with no short internuclear contacts.

^{1}H NMR Spectra

The structural pattern discussed above receives further support from ^{1}H NMR spectra of some complexes (Table III). A sharp singlet at δ 8.50 ppm and a signal at $\delta \sim 13.0$ ppm in the spectrum of

TABLE III ^{1}H NMR Chemical Shifts (in δ ppm) of Organosilicon(IV) Derivatives of Schiff Bases Derived from Amino Acids

Complex (solvent used)	δ (ppm)
Me_3SiHL^2 ($CDCl_3$)	13.17, s, 1H (OH phenolic); 7.14, d (9), 1H (H-3); 7.98, d (9), 1H (H-4); 7.80, d (8), 1H (H-5); 7.44, dd (7,8), 1H (H-6); 7.62, dd (7,8), 1H (H-7); 8.34, d (8), 1H (H-8); 9.55, s, 1H (H-11); 3.81, d (14), 1H (H-12); 2.13, dd (8,8), 2H (H-14); 1.80, m, 1H (H-15); 1.04, d (6), 3H (H-16a); 0.95, d (6), 3H (H-16b); 0.85, s, 3H (CH_3 of Si); 0.73, s, 6H [$(CH_3)_2$ of Si]
Me_3SiHL^3 ($CDCl_3$)	13.17, s, 1H (OH phenolic); 7.15, d (9), 1H (H-3); 7.99, d (9), 1H (H-4); 7.81, d (8), 1H (H-5); 7.45, dd (8,8), 1H (H-6); 7.63, dd (8,8), 1H (H-7); 8.36, d (8), 1H (H-8); 9.83, s, 1H (H-11); 4.42, d (6), 1H (H-12); 2.53, qu (8,8,6,8), 2H (H-14); 2.68, dd (8,8), 2H (H-15); 2.11, s, 3H (H-16); 1.85, s, 3H (CH_3 of Si); 1.26, s, 6H [$(CH_3)_2$ of Si]
Ph_3SiHL^3 ($CDCl_3$)	13.20, s, 1H (OH phenolic); 6.63, d (9), 1H (H-3); 7.90, d (9), 1H (H-4); 7.73, d (8), 1H (H-5); 7.34, m, 10H (H-6 + H-γ and H-δ of $(C_6H_5)_3$ Si); 7.49, dd (7,8), 1H (H-7); 8.25, d (8), 1H (H-8); 7.60, d (7), 6H (H-β of $(C_6H_5)_3$ Si); 9.69, s, 1H (H-11); 4.08, d (7), 1H (H-12); 2.15, br m, 4H (H-14 and H-15); 1.73, s, 3H (H-16)
Ph_3SiHL^5 (DMSO-d_6)	13.35, s, 1H (OH phenolic); 6.68, d (8), 1H (H-3); 7.96; d (8), 1H (H-4); 7.79, d (8), 1H (H-5); 7.36, m, 11H (H-6, H-7 + H-γ and H-δ of $(C_6H_5)_3$ Si); 8.30, d (9), 1H (H-8); 9.80, s, 1H (H-11); 7.63, d (6), 6H (H-β of $(C_6H_5)_2$ Si); 3.61, d (7), 1H (H-12); 2.16, m, 1H (H-14); 0.87, d (7), 3H (H-15a); 0.69, d (7), 3H (H-15b)
Me_2SiL^5 ($CDCl_3$)	6.73, d (9), 1H (H-3); 7.95, d (9), 1H (H-4); 7.77, d (8), 1H (H-5); 7.39, dd (8,8), 1H (H-6); 7.59, dd (8,8), 1H (H-7); 8.31, d (8), 1H (H-8); 9.78, s, 1H (H-11); 3.80, d (8), 1H (H-12); 3.67, m, 1H (H-14); 1.26, d, 3H (H-15a); 1.01, d, 3H (H-15b); 0.78, s, 6H[$(CH_3)_2$ Si]

s, singlet; d, doublet; m, multiplet; q, quartet; qu, quintet; br, broad; Ph_3SiCl, 7.59, d (6), 6H [H-β of $(C_6H_5)_3Si$]; 7.39, m, 9H (H-γ and H-δ of $(C_6H_5)_3$ Si) in DMSO-d_6 at Bruker WM-400 MHz FTNMR instrument; 

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$2\text{-}HOC_{10}H_6CH{=}NCH_2COOEt$ have been assigned[15] to the azomethine proton and phenolic proton respectively. The absence of a signal due to the OH proton of the carboxylic acid group (in dimethyl- and triorganosilicon complexes) and the hydrogen bonded phenolic proton (in case of dimethylsilicon(IV) complex) at δ 12.00–13.00 ppm suggests the deprotonation of the carboxylic or phenolic oxygen atom of the ligands on complexation.[18,19,22,23] But in ^{1}H NMR spectra of the triorganosilicon(IV) complexes of the type R_3SiHL, a strong sharp singlet at δ 13.15 ± 10 ppm is observed due to the (—OH) phenolic proton which is not involved in coordination, and it is also not intramolecularly, hydrogen bonded in the complexes, otherwise it becomes broadened.[15] A very sharp singlet at δ 9.70 ± 0.15 ppm has been assigned to the azomethine

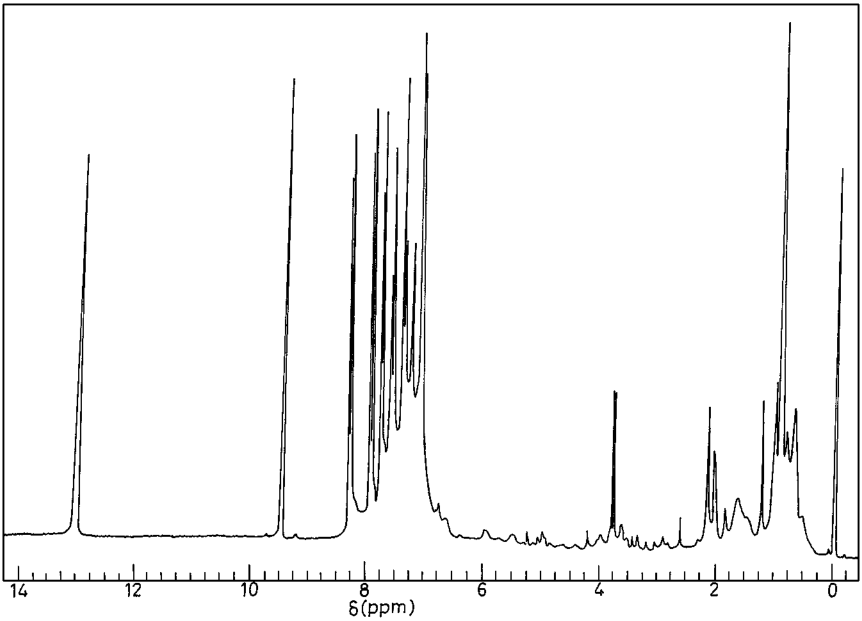


FIGURE 6 ^{1}H NMR spectrum of Me_3SiHL^2.

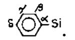
proton.[18,19,22,23] However, spin-spin coupling between the azomethine proton and the silicon nucleus $^{3}J(Si{-}N{=}CH)$ has also been detected in all the complexes because of the presence of satellite signals on each side of singlet of the azomethine proton (Figure 6). The $^{3}J(Si{-}N{=}CH)$ in the complexes are in the range 81–94 Hz. This type of spin-spin coupling $^{3}J(Sn{-}N{=}CH)$ has been previously reported[15] in the corresponding organotin(IV) complexes and other organotin(IV) complexes of Schiff bases where the tin nuclei are located *trans* position to the azomethine proton. It thus confirms the presence of nitrogen-silicon coordination in the complexes. Two singlets due to $-SiMe_3$ protons have been assigned at δ 1.85–0.85 and δ 1.26–0.73 ppm in trimethylsilicon(IV) complexes, indicating the presence of methyl groups in two different environments. Whereas in Me_2SiL^5 only one singlet at δ 0.78 ppm is observed due to two methyl groups in the equatorial positions of a trigonal-bipyramidal geometry around silicon in dimethylsilicon(IV) complexes (Figure 5d). In Ph_3SiHL^2 and Ph_3SiHL^3, a multiplet at δ 7.35 ± 0.01 ppm is observed due to the aromatic protons attached to the ligand (H-6 and/or H-7 of naphthalene ring) and *meta* (H-γ) and *para* (H-δ) protons of the phenyl ring attached to silicon, whereas a sharp doublet at δ 7.62 ± 0.02 ppm is due to the *ortho* (H-β) protons of the phenyl ring attached to silicon. The signals for the other aromatic protons of the ligands are observed in the range δ 8.36–6.63 ppm in the complexes. The signals due to $-CH_2$,$-CH$ and $-CH_3$ of the ligands have also been assigned and are given in Table III.[18,19,22,23] The number of protons of the various groups calculated from the integration curves and those calculated for the expected molecular formula agree with each other.

^{13}C NMR Spectra

The number of signals in the ^{13}C NMR spectra of Me_3SiHL^1, Me_3SiHL^4, Ph_3SiHL^2, Ph_3SiHL^3, and Me_2SiL^3 corresponds to the number of magnetically nonequivalent carbon atoms in the complexes (Table IV). This fact, together with the analysis of the ^{13}C NMR spectra, confirms the identity of the compounds. The shift in ^{13}C chemical resonances in the spectra of the complexes compared to those of the free amino acids[39] and aldehyde[40] shows the coordination of the azomethine nitrogen as well as bonding with the $-COO$ group to the silicon atom.

TABLE IV ^{13}C NMR Chemical Shifts (δ in ppm) of Organosilicon(IV) Derivatives of Schiff Bases Derived from Amino Acids

Complex (solvent used)	δ (ppm)
Me_3SiHL^1 (DMSO-d_6)	C-1, 118.8; C-2, 163.6; C-3, 124.8; C-4, 134.7; C-5, 132.6; C-6, 123.3; C-7, 130.9; C-8, 119.1; C-9, 133.8; C-10, 127.3; C-11, 166.2; C-12, 54.7; C-13, 172.5; C-α (of$(CH_3)_3$ Si), 7.3
Me_3SiHL^4 (DMSO-d_6)	C-1, 106.7; C-2, 159.4; C-3, 124.3; C-4, 138.7; C-5, 129.7; C-6, 122.7; C-7, 128.0; C-8, 118.7; C-9, 134.2; C-10, 126.0; C-11, 164.6; C-12, 48.4; C-13, 176.4; C-14, 16.2; C-α (of$(CH_3)_3$ Si), 6.8
Ph_3SiHL^2 (DMSO-d_6)	C-1, 105.7; C-2, 173.8; C-3, 126.8; C-4, 137.5; C-5, 129.3; C-6, 122.2; C-7, 128.2; C-8, 118.7; C-9, 135.2; C-10, 129.7; C-11, 157.3; C-12, 64.2; C-13, 179.1; C-14, 43.4; C-15, 25.0; C-16a, 23.5; C-16b, 22.2; C-α, 137.1; C-β, 135.0; C-γ, 125.3; C-δ, 130.1 (of $(C_6C_5)_3$ Si)
Ph_3SiHL^3 (DMSO-d_6)	C-1, 106.0; C-2, 173.2; C-3, 122.5; C-4, 137.9; C-5, 128.2; C-6, 125.4; C-7, 130.1; C-8, 118.7; C-9, 137.0; C-10, 126.8; C-11, 157.3; C-12, 64.6; C-13, 179.4; C-14, 30.0; C-15, 34.2; C-16, 15.1; C-α, 135.8; C-β, 135.0; C-γ, 128.4; C-δ, 129.3 (of $(C_6H_5)_3$ Si)
Me_2SiL^3 (DMSO-d_6)	C-1, 106.9; C-2, 172.3; C-3, 124.5; C-4, 138.6; C-5, 129.4; C-6, 123.3; C-7, 128.5; C-8, 119.4; C-9, 134.3; C-10, 127.9; C-11, 164.8; C-12, 51.5; C-13, 175.5; C-14, 30.0; C-15, 32.8; C-16, 15.0; C-α (of $(CH_3)_3$ Si), 7.5



Antimicrobial Activity

The antimicrobial activity of Ph_3SiCl, Me_3SiCl, and Me_2SiCl_2 and their complexes with Schiff bases derived from 2-hydroxy-1-naphthaldehyde and various amino acids have been screened against bacterial and fungal strains and the data are compiled in Table V. Most of the complexes show lower minimum inhibitory concentration (MIC) values in comparison to the parent compounds, Me_3SiCl, Ph_3SiCl, and Ph_2SiCl_2 against all the bacteria and fungi used, signifying the greater activity of the complexes. It is also observed that the complexes exhibit better bactericidal activity than fungicidal activity, and the order of their activity against the bacterial strains (1 to 4) is: Ph_3Si complexes $<Me_2Si$ complexes $\approx Me_3Si$ complexes. All of the complexes are inactive against *E. coli* except Me_2SiL^1 and Me_3SiHL^3, and are also inactive against *Aspergillus niger*. There is no definite correlation between the antimicrobial data and the substituents present in the Schiff bases.

TABLE V Biological Activity of Organosilicon (IV) Complexes of Schiff Bases Derived from Amino Acids[a]

	Minimum inhibitory concentration (MIC) in (μg/ml) against							
	Bacteria				Fungi			
Complexes	1	2	3	4	5	6	7	8
Me_3SiCl	<100	<50	<50	<100	<50	<25	<100	>100
Me_2SiCl_2	<100	<50	<50	>100	<50	<100	<100	>100
Ph_3SiCl	<100	<50	<50	<100	<100	<50	<50	>100
Me_2SiL^1	<6.25	<12.5	<50	<6.25	<50	<50	<12.5	<12.5
Me_2SiL^3	<100	<12.5	<25	<25	<50	<12.5	<50	<50
Me_2SiL^4	<50	<50	<12.5	<6.25	<50	<50	<12.5	<12.5
Me_2SiL^5	<50	<6.25	<6.25	<25	<50	<50	<50	<50
Me_3SiHL^1	<25	<12.5	<6.25	<6.25	<50	<50	<50	<50
Me_3SiHL^2	<50	<12.5	<50	<12.5	<50	<50	<50	<50
Me_3SiHL^3	<6.25	<50	<50	<6.25	<50	<6.25	<6.25	<50
Me_3SiHL^4	<50	<100	<25	<50	<50	<12.5	<50	<25
Me_3SiHL^5	<100	<50	<6.25	<6.25	<50	<100	<50	<50
Ph_3SiHL^1	<100	<50	<25	<50	<50	<12.5	<100	<6.25
Ph_3SiHL^2	<100	<25	<25	<50	<50	<50	<6.25	<50
Ph_3SiHL^3	<50	<25	<25	<50	<50	<50	<100	<50
Ph_3SiHL^4	<100	<50	<6.25	<25	<50	<50	<6.25	<50
Ph_3SiHL^5	<50	<25	<6.25	<12.5	<50	<6.25	<100	<50

[a] Me_2SiL^2, could not be screened due to its insufficient solubility in DMSO; 1, *Escherichia coli*; 2, *Pseudomonas putida*; 3, *Aeromonas formicans*; 4, *Staphylococcus aureus*; 5, *Aspergillus niger*; 6, *Auerobasidium pullulans*; 7, *Verticillium dahliae*; 8, *Penicillium chrysogenum*; >100, *Inactive.*

EXPERIMENTAL

All reagents viz., trimethylchlorosilane (Merck), triphenylchlorosilane (Merck), dimethyldichlorosilane (Merck), 2-hydroxy-1-naphthaldehyde (Fluka), glycine (Richie Renolds Chemicals, Inc.), L-methionine (Sisco Research Laboratory, India), L-leucine(Sigma), DL-α-alanine and L-valine (B.D.H.) were used as received. Strictly anhydrous conditions were maintained during the preparation of the complexes, since the chlorosilanes and the product complexes are moisture-sensitive.

Silicon was determined gravimetrically as silicon dioxide and nitrogen by Kjeldahl's method as reported earlier.[22,23] Melting points were determined on a Toshniwal capillary melting point apparatus and are uncorrected. Molar conductances of 10^{-3} M solution of the complexes in DMF were measured at 25 ± 1°C with an Elico CM 180 conductivity meter. The electronic spectra were recorded on a Beckman DU-6 spectrophotometer in methanol/DMF. The infrared spectra (4000–400 cm^{-1} in KBr discs) were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a DRX-300 MHz spectrometer at CDRI, Lucknow using DMSO-d6/$CDCl_3$ as solvent and tetramethylsilane as the internal standard. Antimicorbial activities of the complexes were carried out using a two fold serial dilution technique as reported earlier.[22,23]

Synthesis of Mono Sodium Salts of Schiff Bases [NaHL]

The sodium methoxide was prepared by dissolving sodium (0.13 g, 5.50 mmol) in absolute methanol (10 mL) under dry nitrogen. To this was added the amino acid (5.0 mmol) in absolute methanol (25 mL) with constant stirring. The solution was refluxed on a water bath for 1 hr. A methanolic solution (10 mL) of 2-hydroxy-1-naphthaldehyde (0.86 g, 5.0 mmol) was added to the sodium salt of amino acid and refluxed for 2–3 h. Excess of solvent was distilled off under reduced pressure. Several attempts to solidify the monosodium salts of the Schiff bases by using various solvents failed. The viscous oily mass thus obtained was dried over P_4O_{10} under vacuum for several hrs. Therefore, they were used in situ for the synthesis of the complexes.

Synthesis of Trimethyl- and Triphenyl-Silicon(IV) Complexes (R_3SiHL) of Schiff Bases

Trimethylsilicon(IV) chloride (0.54 g, 5.0 mmol) or triphenylsilicon(IV) chloride (1.47 g, 5.0 mmol) was dissolved in absolute methanol (10 mL) and added to the preformed solution of the monosodium salt of the

Schiff bases [NaHL] (5.0 mmol) in 1:1 molar ratio. An immediate reaction took place, the mixture was refluxed with constant stirring for 4–5 h; filtered to remove sodium chloride, and the excess of solvent was removed under reduced pressure. The complexes thus obtained were purified by repeated washing with dry n-hexane (60–80°C) and recrystallized from a mixture of (3:2 v/v, 10 mL) of methanol and n-hexane (60–80°C). The complexes were dried in vacuo and stored under dry nitrogen atmosphere.

Synthesis of Disodium Salts of Schiff Bases [Na_2L]

The Schiff bases were prepared by the condensation of 2-hydroxy-1-naphthaldehyde (0.86 g, 5.0 mmol) and the various amino acids (5.0 mmol) in absolute methanol (25 mL). The solution was stirred at room temperature (25 ± 1°C) for half an hour and then refluxed on a water bath for 3–4 h. Excess of solvent was distilled off under reduced pressure. Several efforts to solidify the Schiff bases except N-2-hydroxynaphthalideneglycine [H_2L^1; m.p. 206–207°C (206–208°C)[16]] by using various solvents were failed. The viscous oily mass was dried over P_4O_{10} under vaccum for several hrs. and redissolved in 10 mL of absolute methanol. To this was added sodium methoxide, prepared by dissolving sodium (0.25 g, 11.0 mmol) in absolute methanol (20 mL) under dry nitrogen and the mixture was again refluxed for 2–3 h. The viscous oils thus obtained were purified by repeated washings with petroleum ether (b.p. 60–80°C). Several attempts to solidify the disodium salts [Na_2L] of the Schiff bases [H_2L] by using various solvents were also failed. Therefore, they were used in situ for the synthesis of complexes.

Synthesis of Dimethylsilicon(IV) Complexes [Me_2SiL] of Schiff Bases

The complexes were prepared under anhydrous conditions by slow addition of a dry and hot methanol solution (25 mL) of the dimethylsilicon(IV) dichloride (0.65 g, 5.0 mmol) to the preformed solution of the disodium salts of the Schiff bases (5.0 mmol) in 1:1 molar ratio. The mixture was refluxed with constant stirring for 4–5 h and filtered to remove sodium chloride and the unreacted sodium salt of the Schiff base. Excess of solvent was removed under reduced pressure. The complexes thus obtained were purified by repeated washings with dry n-hexane (60–80°C) and recrystallized from a mixture (3:2 v/v, 10 mL) of methanol and n-hexane (60–80°C). The complexes were dried in vacuo and stored under dry nitrogen.

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