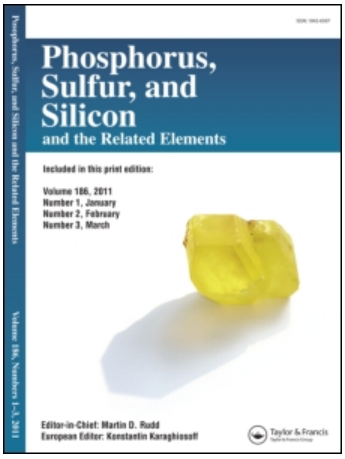

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Dimethylsilicon(IV) Derivatives of Amino Acids

Mala Nath[a]; Sunita Goyal[a]
[a] Department of Chemistry, University of Roorkee, Roorkee, India

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DIMETHYLSILICON(IV) DERIVATIVES OF AMINO ACIDS

Mala Nath and Sunita Goyal
Department of Chemistry, University of Roorkee, Roorkee, India

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Reactions of dichlorodimethylsilane with the sodium salt of amino acids in 1:2 molar ratio led to the formation of a new series of dimethylsilicon(IV) complexes of general formula, Me_2SiL_2 [L = anion of amino acids, viz. glycine (HGly), L-methionine (L-MethH), DL-α-alanine (DL-α-AlaH) L-leucine (L-LeuH), L-valine (L-ValH) and D-phenylalanine (D-PheH)]. The complexes have been characterized by elemental analyses, molar conductance, and electronic spectra, and the bonding in these complexes is discussed in terms of their infrared, ^1H and ^{13}C NMR spectra. A distorted octahedral structure with trans *methyl groups has been tentatively suggested for the complexes. The complexes, found soluble in DMSO, have been tested in vitro against various bacteria, viz.* Escherichia coli*,* Pseudomonas putida-2252*,* Aeromonas formicans*,* Staphylococcus aureus-740*, and fungi, viz.* Aspergillus niger *ORS-4,* Aureobasidium pullulans-1991*,* Verticillium dahliae-2063*, and* Penicillium notatum-1348*.*

Keywords: Amino acids; antimicrobial activity; dichlorodimethylsilicon(IV) complexes; multinuclear NMR

INTRODUCTION

Although organotin and organosilicon compounds find many practical applications, their coordination by biological molecules is not well understood.[1,2] The exponential increase of industrial, agricultural, domestic, and biological applications of organotin[1,3–9] and organosilicon[10–15] compounds during the last 50 years has led to their

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Address correspondence to M. Nath, Department of Chemistry, University of Roorkee, Roorkee - 247 667, India. E-mail: chemt@rurkiu.ernet.in

accumulation in the environment and finally, with man, will surely increase within the next few years giving rise to pollution and toxicological problems. This will require an in depth knowledge of the mechanism of cell detoxification, a process that involves a reaction with biologically important ligands such as amino acids, peptides, reduced glutathione, and nucleotides. A considerable amount of work on organotin derivatives of amino acids and peptides has been reported, and has been compiled in the form of a review.[16] Part of our work in this field concentrates on studies of organo compounds of Group IV elements and amino acids, their derivatives, peptides and appropriate model compounds.[16–25] Accordingly, this article describes six new dimethylsilicon(IV) derivatives of amino acids.

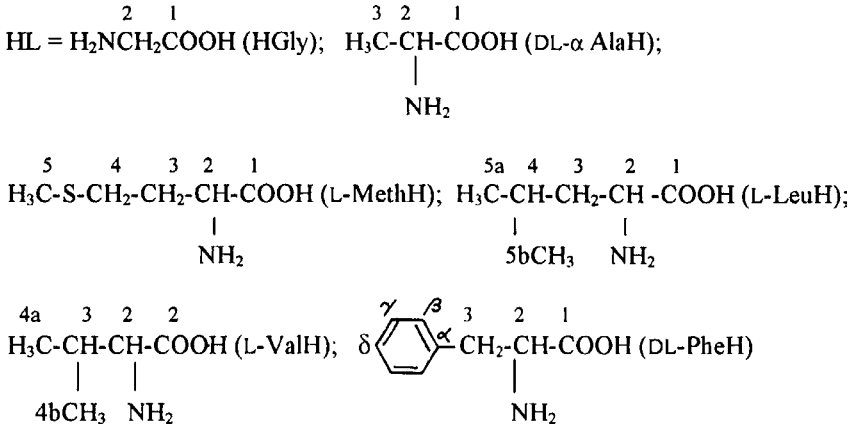
RESULTS AND DISCUSSION

Reactions of Me_2SiCl_2 with the sodium salt of amino acids in 1:2 molar ratio led to the formation of the complexes according to Eqs. 1 and 2.

$$HL + NaOMe \rightarrow NaL + MeOH \quad (1)$$

$$2NaL + Me_2SiCl_2 \rightarrow Me_2Si(L)_2 + 2NaCl \quad (2)$$

where,



The above reactions were found to be facile and were complete within 8–9 h of refluxing. The resulting complexes were obtained in good yield (60–90%) and were white to cream yellow solids, except $Me_2Si(Meth)_2$, which was a viscous semi solid (Table I). They were readily soluble in methanol, except $Me_2Si(Gly)_2$ and $Me_2Si(Phe)_2$, which were sparingly soluble, while $Me_2Si(Gly)_2$, $Me_2Si(Leu)_2$, and $Me_2Si(Phe)_2$ were soluble

TABLE I Analytical Data and Physical Characteristics of Dimethylsilicon(IV) Complexes of Amino Acids

S. N.	Complexes (empirical formula)	m.p. (°C)	Yield (%)	Color and physical state	Analysis (%) obsd. (calcd.)				Molar conductance Ω^{-1} cm^2 mol^{-1}
					C	H	N	Si	
1.	$Me_2Si(Gly)_2$	190–192d	73	Cream	35.44	7.24	13.19	13.98	[a]
	$[C_6H_{14}O_4N_2Si]$			Solid	(34.94)	(6.84)	(13.58)	(13.62)	
2.	$Me_2Si(Ala)_2$	125	89	Yellow	40.59	7.34	11.49	12.40	64.20[b]
	$[C_8H_{18}O_4N_2Si]$			Solid	(41.01)	(7.74)	(11.95)	(11.99)	
3.	$Me_2Si(Meth)_2$	—	70	Cream	40.97	7.80	7.54	8.31	24.01[b]
	$[C_{12}H_{26}O_4N_2S_2Si]$			Semi-solid	(40.65)	(7.39)	(7.90)	(7.92)	
4.	$Me_2Si(Leu)_2$	190d	64	White	53.30	9.89	8.51	9.22	19.99[b]
	$[C_{14}H_{30}O_4N_2Si]$			Solid	(52.80)	(9.49)	(8.80)	(8.82)	
5.	$Me_2Si(Val)_2$	—	65	White	49.33	9.42	9.40	9.80	60.21[b]
	$[C_{12}H_{26}O_4N_2Si]$			Semi-solid	(49.63)	(9.02)	(9.65)	(9.67)	
6.	$Me_2Si(Phe)_2$	192–193	61	White	62.40	6.30	6.76	7.70	[a]
	$[C_{20}H_{26}O_4N_2Si]$			Solid	(61.15)	(6.78)	(7.25)	(7.27)	

[a] Insufficient solubility.
[b] In methanol.

in DMSO and DMF. They were either insoluble or very poorly soluble in all other common organic solvents.

Satisfactory elemental analyses have been obtained for all the complexes, in good agreement with the proposed 1:2 stoichiometry between the organosilicon moiety and the amino acid (Table I). All of the complexes were moisture-sensitive and decomposed when exposed to air. The molar conductance values (19.99–64.20 ohm^{-1} cm^2 mol^{-1}) of 10^{-3} M solutions of the complexes in methanol have indicated their non electrolytic nature, but the possibility of the hydrolysis to some extent can not be ignored.

Electronic Spectra

The electronic spectra of HGly, DL-α-AlaH, L-MethH, L-LeuH, DL-PheH and L-ValH in water exhibit a very intense band at 193 (ε_{max}: molar absorption coefficient, 1946), 201 (ε_{max}, 2524), 201 (ε_{max}, 1678), 194 (ε_{max}, 169), 213 (ε_{max}, 2883), and 194 nm (ε_{max}, 173), respectively, which may be due to the n-π^* transition of the (COO) chromophore.[26] The corresponding absorption in the spectra of the organosilicon(IV) complexes has been observed at 223 ± 8 nm. Two bands are observed in $Me_2Si(Phe)_2$ at 247 and 273 nm, which may be due to the π-π^* (B) bands of the phenyl group of phenylalanine.

Infrared Spectra

Structural proposals are based on vibrational data, which are collected in Table II. Infrared NH_2 stretching frequencies were used to distinguish coordinated from free amino groups.[16–20,27] The amino acids themselves exist in a zwitterionic from $RCH(NH_3^+)$ COO^-, in the solid state, in which there are NH_3^+ groups. Free NH_2 groups are found in the amino acid salts, but here the species are anionic. The proper comparison is with the matrix-isolated species, but, unfortunately, only the vibrational data for glycine are known to us. For this species, $\nu(NH_2)$ is 3414 and 3411 cm^{-1}, for the asymmetric and symmetric modes respectively.[28] Taking the highest energy absorption which is generally the most intense, 3414 cm^{-1} for the matrix-isolated species can be compared with 3380 cm^{-1} for the sodium salt and 3166 cm^{-1} for the zwitterion in which the amino group is protonated. Coordination to metal centres also gives rise to a substantial shift, and x-ray structures are available which show NH_2 groups coordinated to tin atom in several chelated organotin(IV) complexes of the amino acids.[16,29,30] The $\nu(NH_2)$ in all the amino acids used in the present study is observed in the region 3166–2795 cm^{-1}, whereas their sodium salts show the corresponding

TABLE II Infrared Frequencies (in cm^{-1}) of Dimethylsilicon(IV) Complexes of Amino Acids

Amino acid/ complex	$\nu(NH_2)$	$\nu_{as}(COO)$[a] $\nu_s(COO)$	$\Delta\nu$	$\nu_{as}(Si{-}O)$ $\nu_s(Si{-}O)$	$\nu(Si \leftarrow N)$	$\nu(Si{-}C)$	$\delta_{as}(Si{-}C)$ $\delta_s(Si{-}C)$
HGly	3166 w	1610 m	198	—	—	—	—
	3132 m	1412 w					
	3091 w						
	2931 m						
$Me_2Si(Gly)_2$	3165 m	1640 vs	224	868 w	554 w	772 w	1448 w
	3081 sh	1416 w		620 w			1256 w
	2942 w						
	2811 m						
DL-α-AlaH	3100 w	1598 vs	186	—	—	—	—
	2954 br	1412 s					
$Me_2Si(Ala)_2$	3030 w	1642 vs	218	892 w	548 w	740 w	1440 w
	2833 sh	1424 w		680 w			1257 m
L-MethH	2973 s	1581 vs	171	—	—	—	—
	2900 sh	1410 s					
	2800 w						
$Me_2Si(Meth)_2$	2985 m	1667 sh	250	817 m	557 m	746 m	1450 m
	2938 w	1417 m		675 m			1214 m
	2898 w						
	2823 vs						
L-LeuH	3100 s	1589 vs	185	—	—	—	—
	2956 vs	1404 s					
$Me_2Si(Leu)_2$	3095 m	1635 s	229	884 w	550 w	748 sh	1469 w
	2929 s	1406 m		652 w			1255 w
	2824 w						
L-ValH	3067 sh	1588 vs	191	—	—	—	—
	2965 vs	1397 s					
	2835 sh						
$Me_2Si(Val)_2$	2975 w	1652 sh	254	844 w	564 sh	791 w	1448 m
	2900 w	1398 s		611 w			1245 sh
	2832 w						
D-PheH	3064 vs	1610 sh	205	—	—	—	—
	3003 sh	1405 s					
	2795 m						
$Me_2Si(Phe)_2$	3018 w	1679 m	259	865 m	516 m	788 m	1444 m
	2943 m	1420 m		644 m			1248 m
	2820 w						
	2766 w						

[a] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

absorption in the region 3385–2900 cm^{-1}. In the IR spectra of the dimethylsilicon(IV) complexes (Table II), this band has undergone a substantial lowering (3165–2766 cm^{-1}) from the values for the matrix-isolated glycine (3414 cm^{-1}) and sodium salt of the amino acids (3385–2900 cm^{-1}), indicating the coordination of the amino acids through

the amino group to the central silicon atom. Similar results have been reported for R_3SnAA and $R_2Sn(AA)_2$ (AA = amino acid anion)[16–19] and R_2SnL (H_2L = dipeptides).[20] The zwitterionic forms of the amino acids in the solid state have symmetric anionic carboxylate groups, as do their salts. The sodium salts of the amino acids and the zwitterionic forms of the amino acids have $\nu_{as}(COO)$ in the regions 1590–1588 and 1610–1581 cm^{-1} respectively. The $\nu_{as}(COO)$ and $\nu_s(COO)$ in the dimethylsilicon(IV) complexes were observed at 1657 ± 22 and 1411 ± 13 cm^{-1}, respectively, indicating that the $\nu_{as}(COO)$ moved to higher frequencies and the $\nu_s(COO)$ absorptions either remained at the same values or moved to higher frequencies than in the amino acids themselves. Strong interactions between carboxylate carbonyl and the silicon atom were ruled out on this basis.[16–20] The band position and also $\Delta\nu$ values [$\nu_{as}(COO)$–$\nu_s(COO)$] were in the range (218–259 cm^{-1}) (Table II) and were comparable with those obtained[16–20] for $R_3Sn(AA)$, $R_2Sn(AA)_2$, and R_2SnL, indicating that the carboxylate groups act as monodenate; ionic as well as bridging or chelated (COO) groups, which would give $\Delta\nu < 200$ cm^{-1}, were thus excluded.[16–20,31] The conclusions drawn above were further supported by the presence of new bands in all the complexes at *ca.* 855 ± 38, 646 ± 35, and 540 ± 24 cm^{-1}, which may be assigned to $\nu_{as}(Si–O)$, $\nu_s(Si–O)$, and $\nu(Si \leftarrow N)$ respectively.[32–34]

The IR spectra of $Me_2Si(AA)_2$ (where AA = anion of amino acids used) show two bands at 1455 ± 15 and 1236 ± 22 cm^{-1}, which have been assigned to the asymmetric and symmetric deformation modes of CH_3–Si respectively.[25,35] A weak to medium intensity band at 766 ± 26 cm^{-1} may be due to ν(Si–C) modes. Several octahedral neutral silicon complexes containing two organic groups and four electronegative ligands possess a mutually *trans* geometry for the silicon-carbon bonds.[36,37] Similarly, a number of octahedral cationic,[38] neutral,[38,39] and anionic[40] diorganotin(IV) complexes possess *trans* geometry for the tin-carbon bonds (with a few exceptions). Therefore, a *trans* distorted octahedral structure has been tentatively proposed for the $Me_2Si(AA)_2$, as shown in Figure 1.

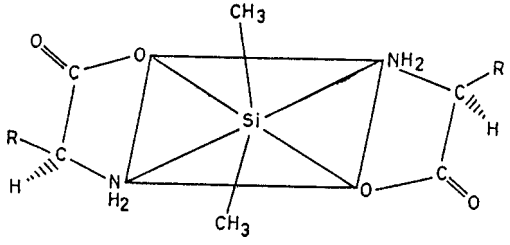


FIGURE 1 Structure of dimethylsilicon(IV) complexes of amino acids.

TABLE III ^{1}H NMR and ^{13}C NMR Spectral Data of Dimethylsilicon(IV) Derivatives of Amino Acids

Complexes	δ (ppm)
^{1}H NMR	
$Me_2Si(Gly)_2$	8.02, m, 4H(—NH_2*); 3.35, s, 4H (H-2); 1.23, s, 6H [$(CH_3)_2Si$]
$Me_2Si(Leu)_2$	7.55 br, 4H(—NH_2^*); 3.75, t, 2H (H-2; $J_{2.3} = 6.5$; 7.6); 1.70 m, 4H (H-3); 1.83, m, 2H (H-4); 0.95, 12H (H-5a and H-5b); 0.90, s, 6H [$(CH_3)_2Si$)]
$Me_2Si(Phe)_2$	7.65, br, 4H (–NH_2^*); 3.89, t, 2H (H-2; $J_{2.3} = 6.2$, 7.5); 3.75, m, 4H (H-3);7.25, m, 10H (C_6H_5); 0.90, s, 6H [$(CH_3)_2Si$]
^{13}C NMR	
$Me_2Si(Gly)_2$	C-1, 170.5; C-2, 48.9; C-α', 10.0
$Me_2Si(Leu)_2$	C-1, 171.4; C-2, 50.8; C-3, 31.0; C-4, 24.5; C-5a, 23.1; C-5b, 22.3; C-α', 7.5
$Me_2Si(Phe)_2$	C-1, 178.7; C-2, 57.5; C-3, 42.0; C-α, 140.8; C-β, 127.9; C-γ, 129.2; C-δ, 125.5; C-α', 4.0

C-α', $Si—\overset{\alpha'}{C}H_3$; solvent, DMSO-$d_6$; DRX-300 MHz FTNMR Spectrometer; J values in Hz; s, singlet; t, triplet; m, multiplet; br, broad.

^{1}H NMR Spectra

The chemical shifts (δ, ppm) of various protons in $Me_2Si(Gly)_2$, $Me_2Si(Leu)_2$, and $Me_2Si(Phe)_2$, which are sufficiently soluble in DMSO-d_6, are given in Table III. The ^{1}H NMR as well as ^{13}C NMR spectra of all other complexes could not be recorded due to their very low solubility in $CDCl_3$ and DMSO-d_6. The absence of a signal due to the —OH proton at $\delta = 12.0$–13.0 ppm suggests deprotonation of the carboxylic oxygen atom of the amino acids on complexation.[16–20] The NH signal of the amino group is shifted to lower field, $\delta = 8.02$–7.55 ppm, indicating the coordination of the NH_2 group to silicon. Similarly, the —NCH< signal is shifted up field [$\delta = 3.35$ ppm for $Me_2Si(Gly)_2$; $\delta = 3.75$ ppm for $Me_2Si(Leu)_2$; and $\delta = 3.89$ ppm for $Me_2Si(Phe)_2$] on complexation in comparison with the free zwitterionic form [—NCH< at $\delta = 4.03$ ppm for HGly; $\delta = 4.17$ ppm for HLeu and $\delta = 4.44$ ppm for HPhe in D_2O[41]]. A sharp singlet due to the $Si—CH_3$ protons has also been assigned in the region $\delta = 1.23$–0.90 ppm. 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 ^{13}C chemical shifts of the various carbon atoms in $Me_2Si(Gly)_2$, $Me_2Si(Leu)_2$, and $Me_2Si(Phe)_2$ in DMSO-d_6 are presented in Table III. The COO resonances for the amino acids are observed at lower field

($\delta = 171.4$–170.5 ppm) except $Me_2Si(Phe)_2$ ($\delta = 178.7$ ppm) on complexation as compared with those of free amino acids[41]: HGly shows COO at $\delta = 173.5$ ppm, HLeu, $\delta = 175.8$ and HPhe, $\delta = 174.3$ ppm at pH 6.5–7.0. The shifts observed in C-2 and C-3 [for $Me_2Si(Leu)_2$ and $Me_2Si(Phe)_2$] resonances of amino acids in the organosilicon derivatives are due to the coordination of the amino acids through the NH_2 and COO groups to silicon. The ^{13}C chemical shifts of methyl groups attached to silicon are observed at $\delta = 7.0 \pm 3.0$ ppm and are consistent with the reported values.[25,36] Due to very low solubility of these complexes in $CDCl_3$ and DMSO-d_6, their ^{29}Si NMR spectra could not be recorded.

On the basis of spectral studies, a distorted octahedral structure with *trans* methyl groups for $Me_2Si(IV)$ derivatives of amino acids, as shown in Figure 1, has been tentatively proposed. Intermolecular hydrogen bonds between carboxyl oxygen of one molecule and amino group of another can not be ignored, however and it may be responsible for very low solubility of these compounds.

Antimicrobial Activity

In vitro antimicrobial results (MIC, minimum inhibitory concentration in μg mL^{-1}) against a wide spectrum of bacteria and fungi, of the organosilicon(IV) compounds, which are sufficiently soluble in DMSO, as well as the MIC values of Me_2SiCl_2 are given in Table IV. All the three complexes and Me_2SiCl_2 showed MIC values greater than 25 μg mL^{-1} and were found to be inactive against all strains of bacteria and fungi except *Aureobasidium pullulans*.

TABLE IV Antimicrobial Activity Data of Dimethylsilicon(IV) Derivatives of Amino Acids

	Minimum inhibitory concentration in μg mL^{-1}							
	Bacteria				Fungi			
Complex	1	2	3	4	5	6	7	8
Me_2SiCl_2	<100	<50	<50	>100	<50	<100	<100	>100
$Me_2Si(Gly)_2$	<100	<50	<100	<100	<100	<25	<50	<100
$Me_2Si(Leu)_2$	<100	<50	<50	<100	<100	<25	<50	<100
$Me_2Si(Phe)_2$	<100	<100	<50	<100	<100	<25	<50	<100

1, *Escherichia coli*; 2, *Pseudomonas putida*-2252; 3, *Aeromonas formicans*; 4, *Staphylococcus aureus*-740; 5, *Aspergillius niger* ORS-4; 6, *Auerobasidium pullulans*-1991; 7, *Verticillium dahliae*-2063; 8, *Penicillium notatum*-1348; Solvent, DMSO.

EXPERIMENTAL

All reagents, viz. dimethyldichlorosilane (Merck, Germany), glycine (Richie Renolds Chemicals, Inc., U.S.A.), L-methionine (Sisco Research Laboratory, India), L-leucine(Sigma, U.S.A.), DL-α-alanine and L-valine (B.D.H., England) were used as received. Strictly anhydrous conditions were maintained during the preparation of the complexes, since dimethyldichlorosilane and the product complexes are moisture-sensitive.

Silicon was determined gravimetrically as silicon dioxide and nitrogen by Kjeldahl's method as reported earlier[24,25] C, H, and N in some complexes were determined on Carlo Erba, 1108, Heraeus. CHN analyzer at CDRI, Lucknow. 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 methanol were measured at $25 \pm 1^{\circ}$C with an Elico CM 180 conductivity meter. The electronic spectra were recorded on a Beckman DU-6 spectrophotometer in methanol. 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 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.[25]

Synthesis of Dimethylsilicon(IV) Complexes of Amino Acids

Dimethylsilicon(IV) complexes of amino acids have been synthesized by the interaction of dimethylsilicon(IV) dichloride and various amino acids (Eqs. 1 and 2). The method adopted to prepare them is given below:

The amino acid (14.0 mmol) was dissolved in the minimum amount (40 mL) of absolute methanol. To this was added sodium methoxide, prepared by dissolving sodium (0.32 g, 15.0 mmol) in absolute methanol (15 mL) under dry nitrogen, and the resulting solution was refluxed for 2–3 h with constant stirring. A methanolic solution of dimethylsilicon(IV) dichloride (0.90 g, 7.0 mmol) in 1:2 (dimethylsilicon : amino acid) molar ratio was added to the solution of the sodium salt of the amino acids. The mixture was again refluxed with constant stirring for 5–6 h. It was centrifuged and filtered to remove the sodium chloride, and any excess of solvent was removed under reduced pressure. The semisolid product thus obtained was solidified by trituration with hexane (60–80°C). The complexes were recrystallized from a 3:2 (v/v)

mixture of methanol and hexane (b.p. 60–80°C). The complexes were dried in vacuo and stored under dry nitrogen atmosphere.

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