



**GNITED MINDS**  
Journals

*Journal of Advances in  
Science and Technology*

*Vol. IV, No. VIII, February-  
2013, ISSN 2230-9659*

**SYNTHESIS OF DIORGANOSILICON (IV)  
COMPLEXES OF 3-HYDROXY-2-PYRIDINE  
CARBOXYLIC ACID AND 2-PYRIDINE  
CARBOXYLIC ACID**

# Synthesis of Diorganosilicon (IV) Complexes of 3-Hydroxy-2-Pyridine Carboxylic Acid and 2-Pyridine Carboxylic Acid

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**Abstract** – Pyridine carboxylic acids and their derivatives belong to the category of legends present in natural products as well as in biological systems. They are of special interest to medicinal chemists, because of the wide variety of physiological properties displayed by the natural and many synthetic derivatives. Nicotinic acid and nicotinamide present in cells as the pyridine nucleotides, belong to coenzymes and vitamins and are necessary for their metabolism. They are also important from the industrial point of view; for example, vanadium 2-pyridine carboxylic acid complexes are used in the nuclear reactor decontamination process. 2-Pyridine carboxylic acid is formed in the body as an intermediate in the triptophan degradation pathway and it is also an approved food supplement. In addition, Chromax, is the trade mark name of the chromium 2-pyridine carboxylic acid complex, which is currently being used as a food additive and has been shown to assist diabetic patients in maintaining glycemic control.

**Key words:** legends, medicinal chemists, synthetic derivatives, food additive.

## INTRODUCTION

Complexes of 3-hydroxy-2-pyridine carboxylic acid are of bioinorganic interest and also pose structural ambiguities since they display a number of possible bonding modes.<sup>141-145</sup> This multidentate ligand contains three functional groups: pyridyl nitrogen atom, two oxygen atoms of the carboxyl group and one oxygen atom of the hydroxyl group leading to the formation of complexes with various structures. 3-Hydroxy-2-pyridine carboxylic acid ligand (HL<sub>2</sub>) is a potential chelate with interesting possibilities, either having N,O-chelation through the pyridine nitrogen and the carboxylate group, forming a five membered chelate ring or O,O-chelation through the carboxylate group and the deprotonated hydroxyl group, forming a six-membered chelate ring. The O,O-chelation is identical to the salicylato coordination mode reported for related ambidentate ligands. In addition, the 3-hydroxy-2-pyridine carboxylate ion can also act as a monodentate or bridging ligand. 2-Pyridine carboxylic acid (HL<sub>3</sub>) contains a carboxylic group in the *ortho*-position to the nitrogen in the pyridine ring, acting as a bidentate ligand by (N,O) coordination (Fig.-2.4).

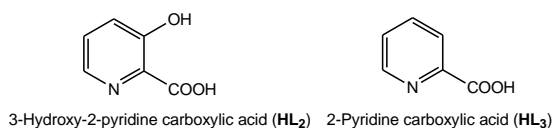
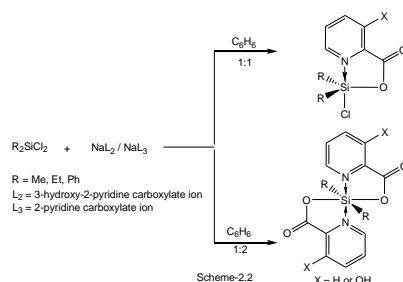


Fig.-2.4

Organosilicon compounds exhibit a broad spectrum of biological activities and the activity of some biologically active compounds was appreciably enhanced on coordination with metal ion or with organosilicon halides. Keeping this in mind we have synthesized diorganosilicon(IV) complexes of 3-hydroxy-2-pyridine carboxylic acid and 2-pyridine carboxylic acid and evaluated them for *in vitro* antimicrobial activity against several bacteria and fungi.

The complexes were obtained by the reaction of diorganodichlorosilanes R<sub>2</sub>SiCl<sub>2</sub> (R = Me, Et or Ph) with the sodium salt of 3-hydroxy-2-pyridine carboxylic acid (NaL<sub>2</sub>) and 2-pyridine carboxylic acid (NaL<sub>3</sub>) in 1:1 and 1:2 molar ratios in dry benzene (Scheme-2.2).



These diorganosilicon(IV) complexes were white solids, insoluble in most of the common organic solvents except in DMSO and DMF. Low molar

conductance values ( $5\text{-}15\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ ) of these complexes indicated non-electrolytic nature. The monomeric nature of these complexes was confirmed by the molecular weight determinations. The stereochemistry of these complexes was determined by using IR and NMR ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$ ) spectral data.

## REVIEW OF LITERATURE

### IR SPECTRA OF LIGANDS

The infrared spectra of the free ligands 3-hydroxy-2-pyridine carboxylic acid ( $\text{HL}_2$ ) and 2-pyridine carboxylic acid ( $\text{HL}_3$ ) are given in Table-2.4. In the IR spectrum of  $\text{HL}_2$  the bands due to  $\nu(\text{O-H})$ ,  $\nu_{\text{as}}(\text{COO})$ ,  $\nu_{\text{s}}(\text{COO})$  and  $\nu(\text{C=N})$  were present at 3340, 1676, 1323 and 1606  $\text{cm}^{-1}$ , respectively. Whereas, in the IR spectrum of  $\text{HL}_3$  the same bands were present at 3280, 1716, 1293 and 1607  $\text{cm}^{-1}$ , respectively. The bands at 1235 and 1056  $\text{cm}^{-1}$  in the IR spectrum of  $\text{HL}_2$  and at 1254 and 1060  $\text{cm}^{-1}$  in the IR spectrum of  $\text{HL}_3$ , were either due to ring vibrations or hydrogen deformation modes.

### $^1\text{H}$ NMR SPECTRA

The  $^1\text{H}$  NMR spectra of the free ligands  $\text{HL}_2$  and  $\text{HL}_3$  are given in Table-2.5. In  $^1\text{H}$  NMR spectra of the ligands  $\text{HL}_2$  and  $\text{HL}_3$ , single resonance was observed at  $\delta$  14.27 and 9.22, respectively, due to  $-\text{COOH}$  group. The downfield shift in the position of carboxylic acid proton of  $\text{HL}_2$  may be due to its involvement in intramolecular hydrogen bonding with the hydroxyl group present at 3-position of the ring. The presence of intramolecular hydrogen bonding in  $\text{HL}_2$  was also supported by the fact that the singlet due to phenolic proton appearing at  $\delta$  11.12 was broadened. The signals for the aromatic protons of the ligands  $\text{HL}_2$  and  $\text{HL}_3$  were observed in the range  $\delta$  7.22-8.08 and 7.53-8.74, respectively.

### $^{13}\text{C}$ NMR SPECTRA

The  $^{13}\text{C}$  NMR spectra of the free ligands  $\text{HL}_2$  and  $\text{HL}_3$  are given in Table-2.6. For ligand  $\text{HL}_2$  the  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{C}_5$  and  $\text{C}_6$  carbons of pyridine ring showed signals at  $\delta$  137.40, 159.43, 129.42, 129.76 and 140.68 respectively, while for the ligand  $\text{HL}_3$  signals due to the same carbons were observed at  $\delta$  148.43, 128.67, 137.66, 127.23 and 149.20. The carbon of carboxylate group of the ligands  $\text{HL}_2$  and  $\text{HL}_3$  was observed at  $\delta$  175.62 and  $\delta$  167.74, respectively.

### IR SPECTRA OF COMPLEXES

The infrared spectra of the diorganosilicon(IV) complexes of 3-hydroxy-2-pyridine carboxylic acid and 2-pyridine carboxylic acid are given in Table-2.4. The IR spectra of the diorganosilicon(IV) complexes of 3-hydroxy-2-pyridine carboxylic acid showed bands due to  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  in the range 1666-1671 and 1358-1365  $\text{cm}^{-1}$ , respectively. The magnitude of  $\Delta\nu$  [ $\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$ ] was about 303-310  $\text{cm}^{-1}$ .

Whereas, in the case of diorganosilicon(IV) complexes of 2-pyridine carboxylic acid the bands due to  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  were in the range 1704-1710 and 1324-1336  $\text{cm}^{-1}$ , respectively and the magnitude of  $\Delta\nu$  was about 372-383  $\text{cm}^{-1}$ . The large magnitude of  $\Delta\nu$  in both the cases indicated that the carboxylate ligand functions as monodentate ligand and the bridging or chelation and ionic bonding can be excluded.<sup>100,101</sup> The infrared spectra of the diorganosilicon(IV) complexes of  $\text{HL}_2$  showed a strong absorption in the region 3212-3268  $\text{cm}^{-1}$ , assigned to the stretching vibrations of the O-H bond in the hydroxyl group of the ligand.

## MATERIAL AND METHOD

In the IR spectra of diorganosilicon(IV) complexes of  $\text{HL}_2$  and  $\text{HL}_3$ , the  $\nu(\text{C=N})$  band was shifted towards lower frequencies due to the displacement of electron density from nitrogen to silicon on coordination, and was present in the range 1587-1593 and 1586-1592  $\text{cm}^{-1}$ , respectively.<sup>119</sup> The formation of the resulting complexes was also supported by the presence of new bands which were absent in the free ligands. In the IR spectra of the diorganosilicon(IV) complexes of  $\text{HL}_2$  the bands due to  $\nu(\text{Si-O})$ ,  $\nu(\text{Si-N})$  and  $\nu(\text{Si-Cl})$  were present at 800-818, 510-522 and 495-504  $\text{cm}^{-1}$ , respectively. Similarly, in the IR spectra of the diorganosilicon(IV) complexes of  $\text{HL}_3$  these bands were present at 802-820, 515-530 and 497-508  $\text{cm}^{-1}$ , respectively. In dimethyl- and diethylsilicon(IV) complexes of  $\text{HL}_2$  and  $\text{HL}_3$ , the bands at 1440-1480 and 1235-1265  $\text{cm}^{-1}$  were attributed to the asymmetric and symmetric deformation vibrations of methyl and ethyl groups attached to silicon. In diphenylsilicon(IV) complexes of  $\text{HL}_2$  and  $\text{HL}_3$ , the weak to strong intensity bands around 1485-1489, 1125-1131, 743-750 and 697-703  $\text{cm}^{-1}$  have been assigned to  $\nu(\text{Si-C}_6\text{H}_5)$  modes.<sup>59</sup>

**Table-2.4: Infrared spectral characteristics ( $\text{cm}^{-1}$ ) of 3-hydroxy-2-pyridine carboxylic acid, 2-pyridine carboxylic acid and their diorganosilicon(IV) complexes**

Ligand/Complex	$\nu(\text{C=N})$	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$	$\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$	$\nu(\text{Si-O})$	$\nu(\text{Si-N})$	$\nu(\text{Si-Cl})$	Si-Me/Et/Ph	Other bands
$\text{HL}_2$	1606 s	1676 s	1323 s	353	-	-	-	-	3340 bs, 3025 m, 1235m, 1056 w
$\text{Me}_2\text{SiCl}(\text{L}_2)$	1588 s	1670 s	1360 s	310	805 s	522 s	495 m	1467 s, 1260 m	3245 bs, 3022 m, 2968 m, 2865 w, 1248 m, 1046 m
$\text{Me}_2\text{Si}(\text{L}_2)_2$	1589 w	1668 s	1362 m	306	800 s	515 s	-	1440 m, 1235 s	3268 bs, 3038 m, 2971 m, 2870 m, 1243 w, 1050 w
$\text{Et}_2\text{SiCl}(\text{L}_2)$	1587 m	1666 s	1358 s	308	820 s	520 s	504 m	1453 m, 1263 s	3305 bs, 3025 m, 2935 m, 2857 m, 1238 w, 1065 m
$\text{Et}_2\text{Si}(\text{L}_2)_2$	1589 w	1671 s	1361 m	310	810 m	522 w	-	1457 s, 1248 m	3260 bs, 3022 m, 2945 m, 2855 m, 1241 w, 1055 m
$\text{Ph}_2\text{SiCl}(\text{L}_2)$	1591 s	1668 s	1365 s	303	818 m	510 m	500 m	1485 s, 1125 s, 750 s, 703 m	3212 bs, 3028 m, 1236 w, 1107 m
$\text{Ph}_2\text{Si}(\text{L}_2)_2$	1593 s	1668 s	1360 m	308	816 s	512 w	-	1488 s, 1126 w, 744 m, 700 w	3215 bs, 3032 m, 1240 m, 1058 w

Contd....

Ligand/ Complex	$\nu(\text{C}=\text{N})$	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$	$\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$	$\nu(\text{Si}-\text{O})$	$\nu(\text{Si}-\text{N})$	$\nu(\text{Si}-\text{Cl})$	Si-Me/Et/Ph	Other bands
HL <sub>3</sub>	1607 s	1716 s	1293 s	423	-	-	-	-	3280 bs, 3024 m, 1254 w, 1060 m
Me <sub>2</sub> SiCl(L <sub>2</sub> )	1586 w	1704 s	1328 s	376	820 m	522 s	506 m	1446 s, 1258 m	3021 m, 2973 m, 2870 m, 1245 m, 1054 w
Me <sub>2</sub> Si(L <sub>2</sub> ) <sub>2</sub>	1587 s	1708 m	1336 s	372	802 m	527 w	-	1453 m, 1265 s	3026 m, 2980 m, 2868 m, 1247 w, 1049 m
Et <sub>2</sub> SiCl(L <sub>2</sub> )	1588 m	1706 s	1327 m	379	815 w	525 m	508 m	1468 s, 1264 s	3035 m, 2963 m, 2858 m, 1235 w, 1060 w
Et <sub>2</sub> Si(L <sub>2</sub> ) <sub>2</sub>	1589 s	1710 s	1330 w	380	812 s	530 s	-	1480 s, 1256 m	3016 m, 2957 m, 2853 w, 1246 m, 1058 m
Ph <sub>2</sub> SiCl(L <sub>2</sub> )	1590 s	1707 s	1324 m	383	810 w	515 m	497 m	1487 s, 1131 m, 743 m, 697 w	3017 m, 1242 w, 1067 m
Ph <sub>2</sub> Si(L <sub>2</sub> ) <sub>2</sub>	1592 s	1705 m	1328 w	377	807 m	517 w	-	1489 s, 1128 s, 746 m, 698 m	3022 m, 1247 w, 1065 w

## <sup>1</sup>H NMR SPECTRA

The <sup>1</sup>H NMR spectra of diorganosilicon(IV) complexes of HL<sub>2</sub> and HL<sub>3</sub> are given in Table-2.5. The peak due to carboxylic acid proton was absent in the spectra of the complexes, indicating the coordination of oxygen of carboxylate ion after the deprotonation of the carboxylic acid proton to silicon moiety. Further in <sup>1</sup>H NMR spectra of diorganosilicon(IV) complexes of HL<sub>2</sub> a sharp singlet at  $\delta$  11.28-11.52 was observed due to the phenolic proton, which showed that it was not involved in coordination as well as in intramolecular hydrogen bonding in the complexes.

In the <sup>1</sup>H NMR spectra of the complexes the signals for the aromatic protons of the ligands HL<sub>2</sub> and HL<sub>3</sub> were slightly deshielded and appeared as multiplet at  $\delta$  7.28-8.72 and 7.70-9.10, respectively. Methyl groups attached to silicon in the complexes appeared as a singlet at  $\delta$  0.90-0.93, while the ethyl and phenyl groups attached to the silicon gave multiplets at  $\delta$  0.92-1.32 and 7.18-7.75, respectively.

## <sup>13</sup>C NMR SPECTRA

The <sup>13</sup>C NMR spectra of diorganosilicon(IV) complexes of HL<sub>2</sub> and HL<sub>3</sub> are given in Table-2.6. In the <sup>13</sup>C NMR spectra of diorganosilicon(IV) complexes of HL<sub>2</sub>, the C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub> and C<sub>6</sub> carbons showed signals at  $\delta$  130.34-132.52, 148.67-149.64, 127.47-128.33, 127.79-128.20 and 143.12-143.51, respectively. In the case of diorganosilicon(IV) complexes of HL<sub>3</sub>, the signals due to same carbons were at  $\delta$  141.34-142.33, 128.14-128.32, 139.18-139.47, 127.10-127.43 and 149.16-149.59, respectively.

The carbon of carboxylate group of the free ligands HL<sub>2</sub> and HL<sub>3</sub> was shifted to  $\delta$  166.53-167.75 and 157.61-158.87 on complexation, indicating the involvement of oxygen atom of COO<sup>-</sup> group. The signals due to carbons of methyl groups attached to silicon in the complexes appeared at  $\delta$  1.91-1.99, while carbons of ethyl groups appeared at  $\delta$  5.52-5.84

and 2.22-2.32. The phenyl rings attached to silicon in the complexes gave four signals which were observed in the range  $\delta$  137.37-137.53, 135.58-135.78, 133.23-133.63 and 129.50-130.49.

**Table-2.5: <sup>1</sup>H NMR spectral characteristics ( $\delta$ ) of 3-hydroxy-2-pyridine carboxylic acid, 2-pyridine carboxylic acid and their diorganosilicon(IV) complexes**

Ligand/ Complex	-COOH	-OH	Pyridine ring protons	Si-Me/Et/Ph
HL <sub>2</sub>	14.27 (s)	11.12 (bs)	7.22-8.08 (m, 3H)	-
Me <sub>2</sub> SiCl(L <sub>2</sub> )	-	11.28 (bs)	7.35-8.71 (m, 3H)	0.92 (s, 6H)
Me <sub>2</sub> Si(L <sub>2</sub> ) <sub>2</sub>	-	11.29 (bs)	7.33-8.72 (m, 6H)	0.93 (s, 6H)
Et <sub>2</sub> SiCl(L <sub>2</sub> )	-	11.32 (bs)	7.29-8.69 (m, 3H)	0.92-1.29 (m, 10H)
Et <sub>2</sub> Si(L <sub>2</sub> ) <sub>2</sub>	-	11.35 (bs)	7.28-8.70 (m, 6H)	0.91-1.28 (m, 10H)
Ph <sub>2</sub> SiCl(L <sub>2</sub> )	-	11.50 (bs)	7.30-8.69 (m, 3H)	7.18-7.26 (m, 10H)
Ph <sub>2</sub> Si(L <sub>2</sub> ) <sub>2</sub>	-	11.52 (bs)	7.31-8.68 (m, 6H)	7.19-7.30 (m, 10H)
HL <sub>3</sub>	9.22	-	7.53-8.74 (m, 4H)	-
Me <sub>2</sub> SiCl(L <sub>3</sub> )	-	-	7.72-8.88 (m, 4H)	0.90 (s, 6H)
Me <sub>2</sub> Si(L <sub>3</sub> ) <sub>2</sub>	-	-	7.71-8.89 (m, 8H)	0.92 (s, 6H)
Et <sub>2</sub> SiCl(L <sub>3</sub> )	-	-	7.70-8.87 (m, 4H)	0.97-1.30 (m, 10H)
Et <sub>2</sub> Si(L <sub>3</sub> ) <sub>2</sub>	-	-	7.73-8.89 (m, 8H)	0.96-1.32 (m, 10H)

## CONCLUSION

The <sup>29</sup>Si NMR of 1:1 diorganosilicon(IV) complexes gave sharp signals at  $\delta$  -80 to -110 and the spectra of 1:2 diorganosilicon(IV) complexes gave sharp signals at  $\delta$  -160 to -180, which clearly indicated the penta- and hexa-coordinated environment, respectively, around the silicon atom.

Thus, on the basis of the foregoing spectral features and monomeric behavior of the complexes, penta coordinated trigonal bipyramidal and hexa coordinated octahedral geometries, have been suggested for the 1:1 and 1:2 diorganosilicon(IV) complexes, respectively. In the <sup>1</sup>H NMR spectra of the complexes the signals for the aromatic protons of the ligands HL<sub>2</sub> and HL<sub>3</sub> were slightly deshielded and appeared as multiplet at  $\delta$  7.28-8.72 and 7.70-9.10, respectively. Methyl groups attached to silicon in the complexes appeared as a singlet at  $\delta$  0.90-0.93, while the ethyl and phenyl groups attached to the silicon gave multiplets at  $\delta$  0.92-1.32 and 7.18-7.75, respectively.

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