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Schiff Base Complexes of Silicon(IV)

By

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With 2 Figures

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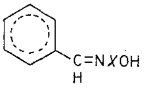
Reactions of silicon tetraacetate with different types of *Schiff* bases have been investigated in anhydrous benzene. Monofunctional bidentate, $C_6H_5CH:NXOH$ and $HORCH::NC_6H_5$ [where $X = CH_2CH_2$, $CH_2CH(CH_3)$ or o-C_6H_4 and $R = $ o-C_6H_4 or 2,1-$C_{10}H_6$], bifunctional tridentate, o-$HOC_6H_4CH::NYOH$ [where $Y = CH_2CH_2$ or $CH_2CH(CH_3)$] and bifunctional tetradentate *Schiff* bases, o-$HOC_6H_4C(CH_3):N(CH_2)_nN::C(CH_3)C_6H_4OH$-o (where $n = 2$ or 3) have been shown to yield derivatives of the type, $Si(OAc)_{4-m}L_m$, $Si(OAc)_{4-2n}L_n'$ and $Si(OAc)_2L''$ (where $m = 1,2$ or 3; $n = 1$ or 2 and HL, H_2L' and H_2L'' represent the molecules of monofunctional bidentate, bifunctional tridentate and bifunctional tetradentate *Schiff* bases resp.) and have been found to be monomeric in boiling benzene. Tentative structures based on IR and in a few cases PMR spectra have been indicated for the resulting derivatives.

Introduction

Extensive studies on the *Schiff* base derivatives of transition elements have been reported in the literature and in recent years such derivatives of even nontransition elements are receiving attention. In earlier communications from these laboratories, *Schiff* base complexes of the main group III elements such as Al(III)[1] and Ga(III)[2] have been reported. In the main group IV, much attention has been paid to the derivatives of Sn(IV)[3, 4] and a few Pb(IV)[5] compounds have also been reported. However, very few references on the silicon—*Schiff* base complexes are so far available.

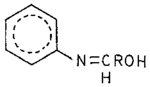
A silicon complex, diethylamino(1-propenylpropylamino)-dichlorosilane, was prepared for the first time by *Breederveld*[6] by the reaction of $EtCH::NPr$ with Et_2NSiCl_3. *Shum*[7] synthesized N-organosilylketimines and studied their UV spectra. *Kovacs* et al.[8] prepared silicon—*Schiff* base complexes by the reaction of p-(triphenylsilyl)benzaldehyde with phenylenediamines. *Orlova* et al.[9] investigated the reactions of $SiCl_4$ with hydroxyanils of the type, $RC_6H_4CH:NC_6H_3R'(OH)$ with the view to obtain heat stable polymers and synthesized complexes of the type, $SiCl_4 \cdot 2\,L$ having trans-octahedral structure.

The present paper reports the reactions of silicon tetraacetate with monofunctional bidentate (I and II), bifunctional tridentate (III) and bifunctional tetradentate *Schiff* bases (IV).



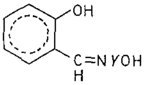
I

$X = CH_2CH_2$ or $CH_2CH(CH_3)$ or $o-C_6H_4$



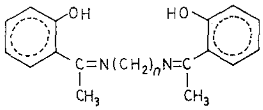
II

$R = o-C_6H_4$ or $2,1-C_{10}H_6$



III

$Y = CH_2CH_2$ or $CH_2CH(CH_3)$



IV

$n = 2$ or 3

Experimental

As silicon tetraacetate and the resulting products are moisture sensitive, all the reactions were carried out under completely anhydrous conditions and the apparatus fitted with quickfit interchangeable joints was used throughout.

Materials

Benzene (B.D.H.) was dried over Na wire by refluxing for several hours and finally distilled azeotropically with ethanol. Ether was stored over $CaCl_2$ for several days and filtered. It was then refluxed over Na wire and distilled. Silicon tetraacetate was prepared by the reaction of freshly distilled $SiCl_4$ and tertiary butylacetate as described by *Mehrotra* et al.[10]. It was sublimed before use and analyzed:

$Si(OAc)_4$ Calcd.: Si 10.63, OAc 89.37%.
Found: Si 10.98, OAc 88.30%.

Preparation of Schiff Bases

Benzylidene-2-hydroxyethylamine, benzylidene-2-hydroxy-1-propylamine, salicylidene-2-hydroxyethylamine and salicylidene-2-hydroxy-1-propylamine were prepared by refluxing equimolar amounts of aldehyde with aminoalcohol in benzene for several hours. Water formed in the reaction was removed azeotropically. After drying, products were distilled under reduced pressure.

Benzylidene-o-aminophenol, salicylideneaniline and 2-hydroxy-1-naphthylideneaniline were prepared by refluxing equimolar amounts of aldehyde and amine in alcohol and distilled under reduced pressure. Bis-o-hydroxyacetophenoneethylenediimine and bis-o-hydroxyacetophenone-1,3-propylenediimine were synthesized by heating two moles of o-hydroxyacetophenone with one mole of diamine in alcohol and purified by recrystallization.

1. Benzylidene-2-hydroxyethylamine, $C_6H_5CH:NCH_2CH_2OH$; orange liquid; B.P. 99–100/0.1–0.2 °C/mm.
2. Benzylidene-2-hydroxy-1-propylamine, $C_6H_5CH:NCH_2CH(CH_3)OH$; white solid; M.P. 64–66 °C, B.P. 95–97/0.3–0.4 °C/mm.
3. Benzylidene-o-aminophenol, $C_6H_5CH:NC_6H_4OH$; light yellow solid; M.P. 90–91 °C, B.P. 156–158/2.5–2.7 °C/mm.
4. Salicylideneaniline, $HOC_6H_4CH:NC_6H_5$; yellow solid; M.P. 51 to 52 °C, B.P. 148–151/1.8–2.0 °C/mm.
5. 2-Hydroxy-1-naphthylideneaniline, $HOC_{10}H_6CH:NC_6H_5$; yellow solid; M.P. 92–93 °C, B.P. 192/0.6 °C/mm.
6. Salicylidene-2-hydroxyethylamine, $HOC_6H_4CH:NCH_2CH_2OH$; yellow viscous liquid; B.P. 137–139/1.0 °C/mm.
7. Salicylidene-2-hydroxy-1-propylamine, $HOC_6H_4CH:NCH_2CH(CH_3)OH$; yellow solid; M.P. 62–65 °C, B.P. 127–129 °C/0.1 mm.
8. Bis(o-hydroxyacetophenone)ethylenediimine, $HOC_6H_4C(CH_3):NCH_2CH_2N:C(CH_3)C_6H_4OH$; fine yellow crystals; M.P. 188–189 °C.
9. Bis(o-hydroxyacetophenone)-1,3-propylenediimine, $HOC_6H_4C(CH_3):NCH_2CH_2CH_2N:C(CH_3)C_6H_4OH$; shining yellow crystals; M.P. 128 °C.

Analysis (C, H, N) proved identity and purity of Cpds. 1.–9.

Synthesis of Silicon Schiff Base Complexes

Silicon tetraacetate was dissolved in dry benzene and refluxed with the requisite amount of the *Schiff* base for several hours on an oil bath ($\approx$ 110 °C). The complexes were isolated by removing the excess of the solvent and then drying under reduced pressure. In some cases, the compounds could be recrystallized from benzene.

1. $Si(OAc)_3 \cdot (C_6H_5CH:NCH_2CH_2O)$; yellow viscous liquid miscible with benzene.
2. $Si(OAc)_2 \cdot (C_6H_5CH:NCH_2CH_2O)_2$; yellow viscous liquid miscible with benzene.
3. $Si(OAc) \cdot (C_6H_5CH:NCH_2CH_2O)_3$; yellow viscous liquid miscible with benzene.
4. $Si(OAc)_3 \cdot [C_6H_5CH:NCH_2CH(CH_3)O]$; yellow viscous liquid miscible with benzene.
5. $Si(OAc)_2 \cdot [C_6H_5CH:NCH_2CH(CH_3)O]_2$; yellow viscous liquid miscible with benzene.
6. $Si(OAc) \cdot [C_6H_5CH:NCH_2CH(CH_3)O]_3$; yellow viscous liquid miscible with benzene.
7. $Si(OAc)_3 \cdot (C_6H_5CH:NC_6H_4O)$; greenish black solid, sparingly soluble in benzene, no change up to 240 °C.
8. $Si(OAc)_2 \cdot (C_6H_5CH:NC_6H_4O)_2$; greenish black solid, sparingly soluble in benzene, no change up to 240 °C.

9. $Si(OAc) \cdot (C_6H_5CH : NC_6H_4O)_3$; greenish black solid, sparingly soluble in benzene, no change up to 240 °C.

10. $Si(OAc)_3 \cdot (OC_6H_4CH : NC_6H_5)$; yellow solid, crystallizable from benzene, decomposes at 215 °C.

11. $Si(OAc)_2 \cdot (OC_6H_4CH : NC_6H_5)_2$; yellow solid, crystallizable from benzene, melts with decomposition at 250 °C.

12. $Si(OAc) \cdot (OC_6H_4CH : NC_6H_5)_3$; yellow solid, crystallizable from benzene, melts with decomposition at 236 °C.

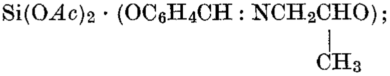
13. $Si(OAc)_3 \cdot (OC_{10}H_6CH : NC_6H_5)$; yellow solid, soluble in benzene, decomposes beyond 205 °C.

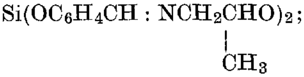
14. $Si(OAc)_2 \cdot (OC_{10}H_6CH : NC_6H_5)_2$; yellow solid, soluble in benzene, does not melt up to 210 °C and thereafter decomposes.

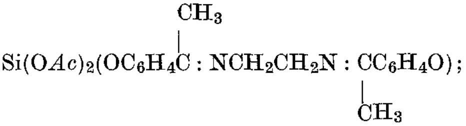
15. $Si(OAc) \cdot (OC_{10}H_6CH : NC_6H_5)_3$; yellow solid, soluble in benzene, decomposes at 240 °C.

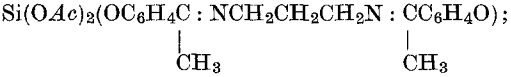
16. $Si(OAc)_2 \cdot (OC_6H_4CH : NCH_2CH_2O)$; yellow solid, crystallizable from benzene, does not melt up to 240 °C.

17. $Si(OC_6H_4CH : NCH_2CH_2O)_2$; yellow solid, crystallizable from benzene, does not melt up to 240 °C.

18. 
$Si(OAc)_2 \cdot (OC_6H_4CH : NCH_2\underset{CH_3}{\underset{|}{C}}HO)$; yellow solid, crystallizable from benzene, melts at 88–90 °C.

19. 
$Si(OC_6H_4CH : NCH_2\underset{CH_3}{\underset{|}{C}}HO)_2$; yellow solid, crystallizable from benzene, melts at 128–130 °C.

20. 
$Si(OAc)_2(OC_6H_4\overset{CH_3}{\overset{|}{C}} : NCH_2CH_2N : \underset{CH_3}{\underset{|}{C}}C_6H_4O)$; light yellow solid, crystallizable from benzene.

21. 
$Si(OAc)_2(OC_6H_4\underset{CH_3}{\underset{|}{C}} : NCH_2CH_2CH_2N : \underset{CH_3}{\underset{|}{C}}C_6H_4O)$; yellow solid, soluble in benzene.

Analysis (Si, N, OAc) and molecular weight determinations proved identity and purity of complexes 1.–21.

Analyses

Silicon was estimated as oxide by direct ignition of the sample after treating with two drops of sulphuric and nitric acids (AR). Acetoxy content was estimated by titrating against $0.05N$ solution of NaOH and nitrogen by *Kjeldahl*'s method.

Physical Measurements

Molecular weights of the complexes were determined ebullioscopically in benzene with the help of a semi-micro ebulliometer (Gallenkamp) using thermistor sensing.

Infrared spectra of the *Schiff* bases and their silicon complexes were recorded in the range 4000–400 cm^{-1} with the help of Perkin-Elmer 337

IR Spectrophotometer. Mostly the spectra were recorded as nujol mulls and in a few cases neat liquids were also used.

PMR spectra were recorded in CCl_4 on Varian A 60 D Spectrometer using *TMS* as internal standard.

Thermogravimetric analysis was carried out on a Stanton (Mass flow type) Automatic Recording Thermogravimetric balance. The weighed quantity of the sample was heated under a controlled rate of heating (4 °C/min).

Results and Discussion

Triacetoxy silicon *Schiff* base, diacetoxy silicon bis-*Schiff* base and acetoxy silicon tris-*Schiff* base derivatives have been synthesized by the reaction of silicon tetraacetate with monofunctional bidentate *Schiff* bases in different stoichiometric ratios as represented by the following general equation:

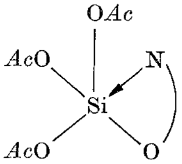
$$\mathrm{Si}(\mathrm{O}Ac)_4 + m\,\mathrm{H}L \rightarrow \mathrm{Si}(\mathrm{O}Ac)_{4-m}L_m + m\,Ac\mathrm{OH}$$

(where $m = 1$, 2, or 3).

All these reactions are highly exothermic and due to the presence of acetoxy groups all the resulting compounds are very much susceptible to moisture. The derivatives of benzylidene-2-hydroxyethylamine and benzylidene-2-hydroxy-1-propylamine are yellow viscous liquids, whereas those of salicylideneaniline and 2-hydroxy-1-naphthylideneaniline are yellow solids soluble in benzene. Benzylidene-o-aminophenol rather yields greenish black solids, which are sparingly soluble in benzene.

The reactions in 1 : 4 molar ratio were also attempted, but these were found to proceed only up to 1 : 3 stoichiometry. The resulting acetoxy silicon tris-*Schiff* base derivatives were obtained together with the remaining excess of the *Schiff* base, which was removed by repeated washing with ether. The nonformation of $\mathrm{Si}L_4$ type of complexes may be due to the steric factors and small size of the central silicon atom (1.32 Å). However, in the case of Ti(IV)[11] and Zr(IV)[12], it has been possible to synthesize tetrakis-*Schiff* base derivatives. The formation of octacoordinated complexes may probably be due to their larger atomic radii (Ti 1.47; Zr 1.60 Å) as compared to that of silicon. The octacoordination in the case of Zr(IV) has also been confirmed on the basis of PMR spectra and single crystal X-ray studies[12].

All these complexes of silicon have been found to be monomeric as evidenced by their molecular weights determined ebullioscopically in boiling benzene. In the triacetoxy silicon *Schiff* base complexes, the central silicon atom appears to be pentacoordinated (V) as shown below:

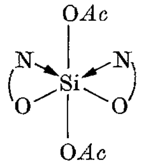


V

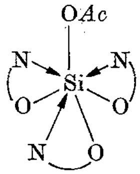
(where N⌒OH represents the *Schiff* base molecule)

Pentacoordination for silicon is rather unusual, but it has been claimed in the case of a few compounds. *Frye*[13] has studied the reactions of heterocyclic pinacol derivative of silicon with aminoalcohols and isolated quite stable complexes with a pentacoordinated silicon atom where both oxygen and nitrogen atoms are linked to silicon atom. In $[SiCl_3 \cdot 2\,NMe_3]ClO_4$ also the central silicon atom has been shown to be pentacoordinated with D_{3h} symmetry[14].

In the diacetoxy silicon bis-*Schiff* base complexes, the silicon atom appears to be hexacoordinated (**VI**), whereas in the case of acetoxy silicon tris-*Schiff* base complexes, it may probably be heptacoordinated (**VII**).



VI



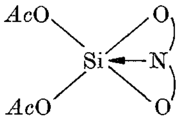
VII

The reactions of silicon tetraacetate with the bifunctional tridentate *Schiff* bases, H_2L' in 1 : 1 and 1 : 2 molar ratios may be represented as follows:

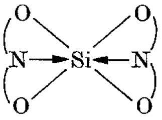
$$Si(OAc)_4 + n\,H_2L' \rightarrow Si(OAc)_{4-2n}L_n' + 2n\,AcOH$$

(where $n = 1$ or 2)

These reactions are also highly exothermic and the resulting diacetoxy silicon *Schiff* base and silicon bis-*Schiff* base derivatives have been obtained as yellow solids soluble in benzene and carbon tetrachloride. The acetoxy compounds have a tendency to hydrolyse when exposed to the atmosphere, whereas the bis-*Schiff* base derivatives are quite stable and do not appear to undergo hydrolytic reactions. These are monomeric in benzene indicating pentacoordination in the acetoxy derivatives (**VIII**) and stable hexacoordination in the bis-*Schiff* base derivatives (**IX**).



VIII



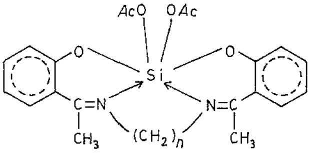
IX

(where HO⌒N⌒OH represents the *Schiff* base molecule)

The 1 : 1 molar reactions of silicon tetraacetate with bifunctional tetradentate azomethines, H_2L'', have yielded the monomeric diacetoxy silicon *Schiff* base derivatives according to the following equation:

$$Si(OAc)_4 + H_2L'' \rightarrow Si(OAc)_2L'' + 2\,AcOH.$$

The probable structure **X** with the central silicon atom in the hexacoordinated environment may be indicated for these derivatives.



X

In an attempt to synthesize octacoordinated complexes of the type, SiL_2'', reactions in 1 : 2 molar ratios were also carried out but found to be unsuccessful. With bis-o-hydroxyacetophenoneethylenediimine a crystalline product could be isolated from the reaction mixture, but this was found to be the same as the derivative of 1 : 1 molar reaction. Similarly, with bis-o-hydroxyacetophenone-1,3-propylenediimine the analysis of the resulting solid product corresponded to a mixture of 1 : 1 derivative with an excess of the *Schiff* base. This further supports the nonformation of *Schiff* base complexes of Si(IV) with octacoordinated environment. With similar tetradentate azomethines of salicylaldehyde, even Ti(IV)[15] and Sn(IV)[4] have been reported to form only hexacoordinated complexes.

Thermogravimetric Analysis

With a view to have an idea about the thermal stability of these compounds, the *TGA* of silicon bis-salicylidene-2-hydroxy-1-propylamine as well as the *Schiff* base was carried out. The *TGA* curve (Fig. 1, Curve A) of the ligand does not show any change up to a temperature of 200 °C. Thereafter, a heavy loss in weight due to its decomposition was recorded. The silicon complex was found to be stable up to 150 °C and thereafter a rapid decomposition was observed up to 340 °C. It finally gets converted to SiO_2 at 760 °C (Fig. 1, Curve B).

Infrared Spectra

The infrared spectra of a few azomethines and their silicon complexes have been recorded. In the spectra of the *Schiff* bases, broad absorption bands in the region, 3400—3200 cm^{-1} are observed which may be assigned to the hydrogen bonded OH. However, in the case of silicon complexes these bands disappear indicating chelation of oxygen to the silicon atom.

In the acetoxy silicon *Schiff* base complexes, bands in the region, 1740—1670 cm^{-1} appear and these may be attributed to C=O bond of the acetoxy group.

A strong band at 1635—1625 cm^{-1} is observed in the *Schiff* bases and this may be assigned to ν C=N vibrations. The coordination of nitrogen to silicon is expected to reduce the electron density in the azomethine link causing a reduction in the ν C=N frequency. However, this band appears at almost identical position or shifts slightly in the case of the silicon complexes. In the literature, shift of this frequency to higher[16] as well as lower[17] wave number side has been reported and in some cases even no change has been noted[18].

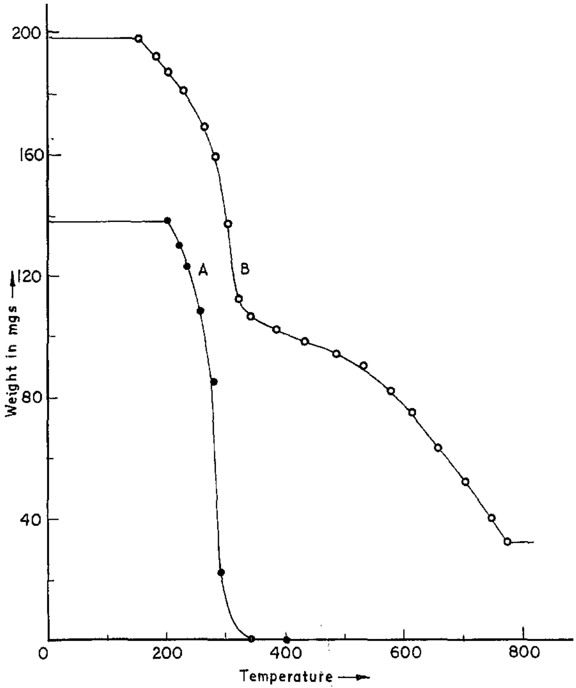
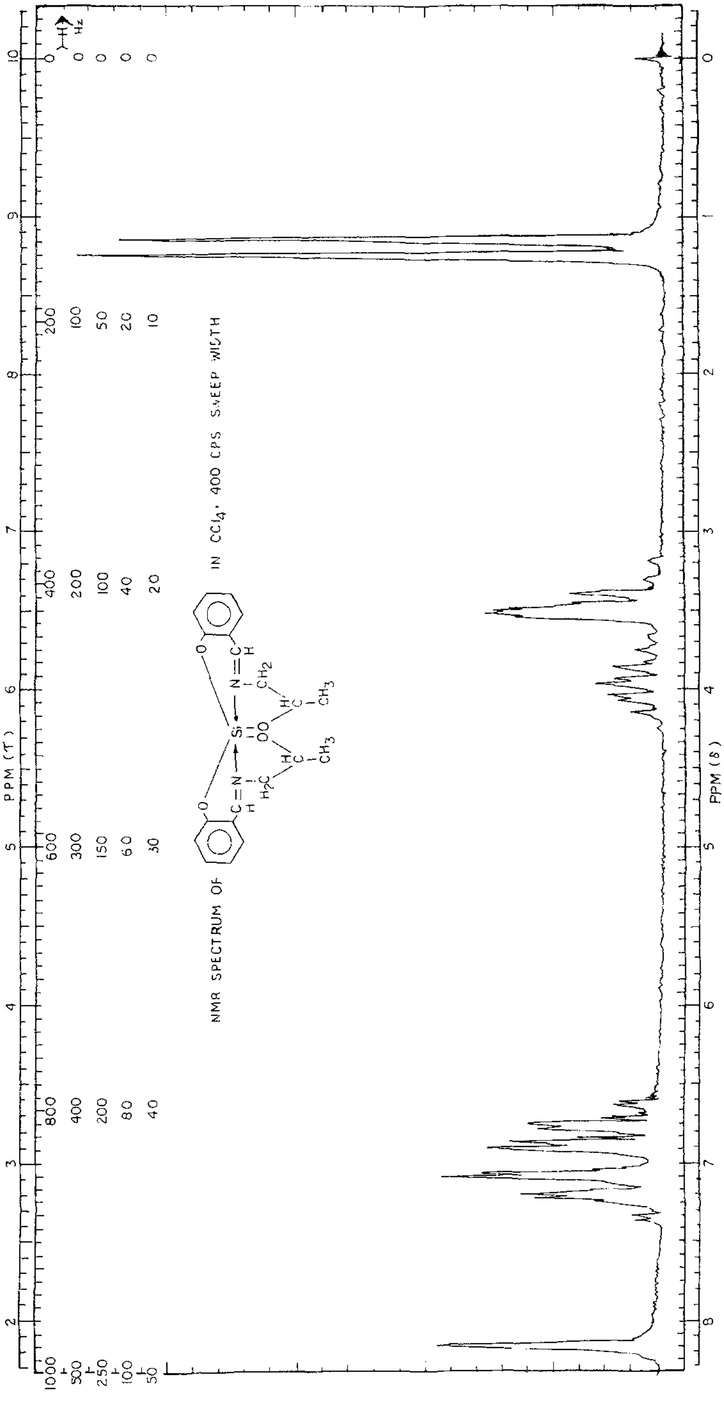


Fig. 1. Thermolysis curves. Curve A ($C_{10}H_{13}NO_2$): wt. of the compd. taken = 138 mg; wt. left = nil. Curve B [$Si(C_{10}H_{11}NO_2)_2$]: wt. of the compd. taken = 198 mg; wt. left = 32 mg; calc. wt. for SiO_2 = 31 mg

Bands of strong to medium intensity in the region, 840—800 cm^{-1} and 1075–1025 cm^{-1} in the silicon complexes may probably be attributed to ν Si—O.


NMR SPECTRUM OF
IN CCl4, 400 CPS SWEEP WIDTH
PPM (τ)
PPM (δ)
Hz
Si
N
C
H
O
CH2
H2C
CH3
10
9
8
7
6
5
4
3
2
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1
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200
80
40

Fig. 2

PMR Spectra

The PMR spectra of the Schiff base, o-$HOC_6H_4CH : NCH_2CH(CH_3)OH$ and its complex $Si[OC_6H_4CH : NCH_2CH(CH_3)O]_2$ (Fig. 2) have been recorded in carbon tetrachloride. The methyl protons exhibit a doublet at 8.82 τ in the case of the *Schiff* base as well as silicon complex due to coupling with the methine (CH) proton. A doublet due to methylene (CH_2) protons is observed at 6.62 τ in both the ligand and the complex on account of the coupling with the methine (CH) proton adjacent to the methyl group. The methine (CH) proton gives a sextet centered at 6.10 τ due to coupling with both CH_2 and CH_3 protons. A complex multiplet due to ring protons appears at different positions in the two spectra. In the case of ligand, it is centered at 3.60 τ, whereas in the complex at 3.07 τ. The shift of the ring protons to lower field suggests the chelation of ligand to the silicon atom.

The azomethine proton (N : CH) exhibits a singlet at 2.38 τ in the spectrum of the ligand. This singlet is shifted considerably to down field in the complex and appears at 1.88 τ. This is due to the considerable deshielding of the proton caused by coordination of nitrogen of the ligand moiety to silicon atom. Similar down field shift of azomethine proton signal has been reported from 1.70 τ to 0.82 τ in $Ti(OC_6H_4CH : : NC_6H_5)_4$[19] and from 1.98 τ to 1.41 τ in $Ti(OC_6H_4CH : NCH_2CH_2O)_2$[20]. In the PMR spectra of Al(III)[21] complexes of 2-hydroxy-1-naphthylidenealkylamines also the azomethine proton signal is shifted down field. However, in the case of thorium complexes of salicylideneanilines, *Biradar* and *Kulkarni*[22] have reported shift of this peak to down as well as higher fields.

Acknowledgements

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