CHAPTER VI

SILICON(IV) COMPLEXES WITH POTENTIALLY BIDENTATE
AND TRIDENTATE SCHIFF BASES
INTRODUCTION

In recent years renewed interest in the coordination chemistry of silicon lead to the isolation of some octahedral complexes with ligands like naphthalocyanine\textsuperscript{1}, tropholones\textsuperscript{2} and \(\beta\)-diketone ligands\textsuperscript{3}.

Only a few complexes of silicon of bidentate and multidentate Schiff bases are known in the literature\textsuperscript{4-6}.

The silicon compounds with distorted shape and large size, compared with their carbon analogues have been effectively used in elucidating the process involved in physiological activity\textsuperscript{7,8}. The ability of dimethylchlorosilane to form coordination complexes was brought to light recently\textsuperscript{9,10}.

Silicon tetrahalides are strong Lewis acids and hence they form number of adducts with the ligands containing N, O, P or S donor atoms\textsuperscript{12}.

Silicon is generally known to acquire coordination numbers 4 and 6. However, the existence of five coordinated silicon has been established\textsuperscript{11}.

Silicon(IV) complexes have been prepared\textsuperscript{13-15} from bivalent tridentate Schiff bases.
Biradar et al.\textsuperscript{16} have synthesised and characterised silicon(IV) chloride complexes of Schiff bases derived from sulphonamide. These complexes having 1:2 (metal-ligand) stoichiometry are non-electrolytes.

Coordination behaviour of azomethines of sulpha drugs towards Si(IV) ion has been studied by Tandon et al.\textsuperscript{17} Si(OAc)\textsubscript{2}L.
and \( \text{SiL}_2 \) (\( H_2 L \) = Schiff bases derived from salicylaldehyde and sulphathiazole, sulphaphenazole, sulphapyridine, sulphadiazine, sulphaguamidine) were prepared from \( \text{Si(OAc)}_4 \) and \( H_2 L \) in 1:1 and 1:2 molar ratios. The Schiff base ligands are tridentate forming bipyramidal \( \text{Si(OAc)}_2 L \) and octahedral \( \text{SiL}_2 \). Organosilicon complexes with Schiff bases were prepared and characterised by Saxena and Tandon. \(^{18}\)

Recently Siddiqui and coworkers\(^{19}\) have prepared complexes of group(IV) metals Si, Ge, Sn, Ti and Zr with 5,5'-methylenebis-(salicylaldehyde) \( (H_2 L) \) and its diozone Schiff base \( (L) \). These were characterised by IR spectroscopy, conductivity measurement and mol wt. determination. The complexes are non-ionic in DMSO. An octahedral structure is proposed for all the complexes.

Garcea-Vazquiz et al.\(^{29}\) prepared and characterised coordination complexes of group(IV) halides with monodentate Schiff bases \( \text{Trans} Mx_4 L_2 \) \( (X = \text{Cl}, \text{Br}, \quad L = C_6H_5CH_NC_6H_4R \quad R = H, 2-, 3-, 4-\text{Me,} \quad M = \text{Sn}, X = \text{Cl}, R = H, 3-, 4-\text{Me,} \quad M = \text{Si}) \) complexes were prepared and characterised by elemental analysis and electronic, Raman and IR spectral methods.

Recently Siddiqui and coworkers\(^{30}\) have reported the preparation and characterisation and toxicity studies on complexes N-phenyl-\( \alpha \)-naphthalamine, 2-aminobenzothiazole and 2-4-tolylenediamine.
dithiocarbamates with group(IV) elements, silicon, tin, zirconium and germanium. Their antifungal activities have been investigated against fungi Aspergillus flavus, Aspergillus niger and Alternaria por1.

A limited number of complexes of o-hydroxyacetophenone and other substituted Schiff bases have been reported.20-25 Dey prepared a complex of Fe(III) with Schiff base derived from o-hydroxyacetophenone and ethylenediamine.

![Chemical structure of a complex](image)

Tandon et al 26,27 have prepared and characterised Sn(IV) complexes derived from o-hydroxyacetophenone and aminoalcohol, aniline, n-propylamine, n-butylamine

Oxovanadium(IV) complexes with o-hydroxyacetophenone were prepared by Biradar et al 28
Though there are several references on acetophenone complexes of Sn(IV), only a few references are available on acetophenone complexes of Si(IV).

However, there appears no much information on silicon(IV) complexes with Schiff bases derived from various substituted acetophenones. Hence it was felt worthwhile to study Si(IV) complexes of Schiff bases derived from acetophenone, o-substituted acetophenones, p-substituted acetophenones with 2-aminopyridine, 2-amino-3-methylpyridine.

The following ligands were used in the preparation of Si(IV) complexes.
I  \( R = H \)
\( R' = H \)  Acetophenone-2-aminopyridine
\( R'' = H \)

II  \( R = H \)
\( R' = OH \)  o-Hydroxyacetophenone-2-aminopyridine
\( R'' = H \)

III  \( R = H \)
\( R' = \text{NH}_2 \)  o-Aminoacetophenone-2-aminopyridine
\( R'' = H \)

IV  \( R = H \)
\( R' = H \)  p-Chloroacetophenone-2-aminopyridine
\( R'' = Cl \)
V  \( R = H \)
\( R' = H \) p-Bromoacetophenone-2-aminopyridine
\( R'' = Br \)

VI  \( R = 3-CH_3 \)
\( R' = H \) Acetophenone-2-amino-3-methylpyridine
\( R'' = H \)

VII  \( R = 3-CH_3 \)
\( R' = OH \) o-Hydroxyacetophenone-2-amino-3-methylpyridine
\( R'' = H \)

VIII  \( R = 3-CH_3 \)
\( R' = NH_2 \) o-Aminoacetophenone-2-amino-3-methylpyridine
\( R'' = H \)

IX  \( R = 3-CH_3 \)
\( R' = H \) p-Chloroacetophenone-2-amino-3-methylpyridine
\( R'' = Cl \)

X  \( R = 3-CH_3 \)
\( R' = H \) p-Bromoacetophenone-2-amino-3-methylpyridine
\( R'' = Br \)
EXPERIMENTAL

All the reactions were carried out under strictly anhydrous conditions and analytical grade chemicals were used for all experiments. Dry benzene was obtained by refluxing benzene (BDH) over sodium wire for several hours. Dimethylformamide was purified and stored in blackened bottle and stoppered. This was used to find out the specific conductivity of complexes. Silicon(IV)chloride (Riedel, pure) was distilled before use.

Preparation of Schiff bases

Schiff bases of acetophenone, o-substituted and p-substituted acetophenones were prepared by mixing the corresponding acetophenone with 2-aminopyridine and 2-amino-3-methylpyridine in equimolar ratio (0.01M) in benzene and refluxing for several hours (6-8h), followed by removal of water benzene azeotropically.

Preparation of Complexes

Calculated quantity of ligand (0.01M in case of o-substituted acetophenone and 0.02M in case of acetophenone and p-substituted acetophenone ligands) was dissolved in dry benzene, in a 250 ml two necked round bottom flask. Silicon(IV)chloride (0.01M) in dry benzene was slowly added to the ligand solution using magnetic stirrer and passing the nitrogen gas through the solution to maintain...
the inert atmosphere during the reaction. After the completion of the reaction the solid compound was immediately separated. It was filtered, washed with dry benzene and was dried under vacuum. Its purity was checked by TLC.

**Analytical Methods and Physicochemical Measurements**

Silicon was estimated gravimetrically as silicon dioxide. Nitrogen was estimated by Dumas method and chloride and bromide estimated as silver chloride and silver bromide. These estimations were done as per the standard methods discussed in Chapter II.

Conductance measurements were done on Elico CM-82 bridge with a cell having cell constant 0.829 cm⁻¹.

The infrared spectra of the ligands and complexes were recorded on the Perkin-Elmer model-580 spectrometer in the range 4000 - 250 cm⁻¹ using KBr pellets and nujol mull.

The PMR spectra of the ligands and complexes were recorded on a WH 270 FT NMR spectrometer.

Tetrasilane was used as the internal standard. DMSO-d₆ was used as the solvent.

The X-ray data were recorded on a DX-GER P12 X-ray.
machine attached with a diffractogram using CuKα radiation (λ = 1.5418 Å). The diffraction pattern was recorded at a chart speed 2°(2θ)/min. at 10-80°(2θ) using the scale 1° = 1 cm. The finely powdered crystalline samples were taken.

The Electron Spectroscopy for Chemical Analysis (ESCA) or the X-ray Photoelectron Spectroscopic (XPS) measurement of the complexes was carried out with ESCA III Mark II spectrometer from VG Scientific Ltd. The AlKα (1486.6 eV) radiation was used. The binding energy was measured with respect to the Fermi level EF.

**Biological Activities**

**Antifungal activity**

The antifungal activity of the pure ligands and complexes was studied by adopting agar plate technique against Aspergillus flavus, Alternaria alternata, Alternaria pori, Aspergillus niger and Fusarium moniliforme as the test fungi. Testing of the ligand and complex was carried out in DMF solution at the concentration of 10 mg ml⁻¹. The zones of inhibition of the test solutions were recorded. The inhibition percentage was calculated by the following equation:

\[
\% \text{ inhibition} = \frac{100(C-T)}{C}
\]

where \( C \) = diameter (mm) of the fungus colony in the control plate agar after 72 hours.

and \( T \) = diameter (mm) of the fungus colony in treated plates after 72 hours.
RESULTS AND DISCUSSION

The complexes are yellow, red, brown and orange in colour, insoluble in common organic solvents. However, they are soluble in DMF and DMSO. This insolubility of complexes did not permit the molecular weight determination. The results of the elemental analysis given in Table VI.1 suggest that these complexes have 1:1 and 1:2 (metal-ligand) stoichiometry.

The molar conductance in DMF at the concentration \( \approx 10^{-3} \text{M} \) fall in the range 25 to 40 \( \Omega^{-1} \text{cm}^2 \text{mol}^{-1} \). The low molar conductance values indicate the complexes to be non-electrolytes.

Infrared Spectra

The important infrared frequencies along with their assignments are listed in Table VI.2 and VI.3. The infrared spectra of the ligands and complexes are reproduced in Figs 6.1 to 6.6.

In IR spectra of ligands broad peaks in the region 3376 to 3350 cm\(^{-1}\) are observed due to hydrogen bonded OH. In the present investigations the broad and medium band found in the region of 3340-3334 cm\(^{-1}\) in ligands III and VIII spectra is assigned to NH\(_2\) stretching. The splitting of NH\(_2\) stretch in the complexes...
XIII and XVIII makes it imperative that NH$_2$ has taken part in the coordinate bond formation. In the spectra of ligands II and VII the broad peaks observed in the region 3394 to 3376 cm$^{-1}$ are due to hydrogen bonded OH$^{33}$ In the spectra of complexes XII and XVII, the band due to OH gets shifted to higher wave number region 3408-3403 cm$^{-1}$ showing the coordination of the ligand through phenolic oxygen. In the spectra of Schiff bases a strong band observed in the region 1630-1612 cm$^{-1}$ is assignable to $\nu$ C=N$^{33}$ But in complexes this band is shifted to higher frequency region 1662-1650 cm$^{-1}$ because of an increase in the bond order of the azomethine group$^{34}$ This shows that azomethine nitrogen is linked to silicon in the complexes$^{35}$ In the IR spectra of ligands II and VII a medium intensity band at 1265-1235 cm$^{-1}$ due to CO is observed In the complexes XII and XVII this band is shifted to higher frequency region 1308-1307 cm$^{-1}$ suggesting the participation of the phenolic oxygen in complexation$^{36,37}$ The bands appearing in all the silicon(IV) complexes in the region 420-390 cm$^{-1}$ and 550-520 cm$^{-1}$ are due to Si + N and Si + O$^{33}$. In the present investigations the strong bands in all the silicon(IV) complexes appearing in the region 425-405 cm$^{-1}$ are due to Si + N and the strong bands in the complexes XII and XVII appearing at 518 and 517 cm$^{-1}$ are due to Si + O. The strong bands at 298-296 cm$^{-1}$ in all the complexes arise from Si-Cl vibrations

**Proton Magnetic Resonance Spectra (PMR)**

The PMR data obtained in the course of this study are
<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Compound</th>
<th>Analysis % Found/(Calcd)</th>
<th>Conductance</th>
<th>Ω⁻¹ cm² mol⁻¹</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Si</td>
<td>N</td>
<td>Cl</td>
</tr>
<tr>
<td>XI</td>
<td>Tetrachlorobis(acetophenone-2-aminopyridine)Si(IV) (\text{SiCl}<em>4(\text{C}</em>{13}\text{H}_{12}\text{N}_2)_2)</td>
<td>4.87</td>
<td>9.62</td>
<td>24.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(4.98)</td>
<td>9.96</td>
<td>(25.27)</td>
</tr>
<tr>
<td>XII</td>
<td>Tetrachloro-o-hydroxyacetophenone-2-aminopyridine Si(IV) (\text{SiCl}<em>4(\text{C}</em>{13}\text{H}_{12}\text{N}_2\text{O}))</td>
<td>6.96</td>
<td>7.07</td>
<td>36.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(7.33)</td>
<td>(7.33)</td>
<td>(37.17)</td>
</tr>
<tr>
<td>XIII</td>
<td>Tetrachloro-o-aminoacetophenone-2-aminopyridine Si(IV) (\text{SiCl}<em>4(\text{C}</em>{13}\text{H}_{13}\text{N}_3))</td>
<td>7.10</td>
<td>10.87</td>
<td>36.95</td>
</tr>
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<td></td>
<td></td>
<td>(7.35)</td>
<td>(11.02)</td>
<td>(37.27)</td>
</tr>
<tr>
<td>XIV</td>
<td>Tetrachlorobis(p-chloroacetophenone-2-aminopyridine)Si(IV) (\text{SiCl}<em>4(\text{C}</em>{13}\text{H}_{11}\text{N}_2\text{Cl})_2)</td>
<td>4.21</td>
<td>8.45</td>
<td>33.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(4.44)</td>
<td>(8.87)</td>
<td>(33.76)</td>
</tr>
<tr>
<td>XV</td>
<td>Tetrachlorobis(p-bromoacetophenone-2-aminopyridine)Si(IV) (\text{SiCl}<em>4(\text{C}</em>{13}\text{H}_{11}\text{N}_2\text{Br})_2)</td>
<td>3.65</td>
<td>7.51</td>
<td>18.55</td>
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<td></td>
<td></td>
<td>(3.89)</td>
<td>(7.78)</td>
<td>(19.72)</td>
</tr>
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<td>XVI</td>
<td>Tetrachlorobis(acetophenone-2-amo-3-methylpyridine)Si(IV) (\text{SiCl}<em>4(\text{C}</em>{14}\text{H}_{12}\text{N}_2)_2)</td>
<td>4.54</td>
<td>9.28</td>
<td>23.75</td>
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<td></td>
<td></td>
<td>(4.75)</td>
<td>(9.49)</td>
<td>(24.07)</td>
</tr>
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<td>XVII</td>
<td>Tetrachloro-o-hydroxyacetophenone-2-amo-3-methylpyridine Si(IV) (\text{SiCl}<em>4(\text{C}</em>{14}\text{H}_{14}\text{N}_2\text{O}))</td>
<td>6.86</td>
<td>6.65</td>
<td>35.29</td>
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<td></td>
<td></td>
<td>(7.07)</td>
<td>(7.07)</td>
<td>(35.66)</td>
</tr>
<tr>
<td>XVIII</td>
<td>Tetrachloro-o-aminoacetophenone-2-amo-3-methylpyridine Si(IV) (\text{SiCl}<em>4(\text{C}</em>{14}\text{H}_{15}\text{N}_3))</td>
<td>6.72</td>
<td>10.45</td>
<td>35.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(7.09)</td>
<td>(10.63)</td>
<td>(35.95)</td>
</tr>
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<td>XIX</td>
<td>Tetrachlorobis(p-chloroacetophenone-2-amo-3-methylpyridine)Si(IV) (\text{SiCl}<em>4(\text{C}</em>{14}\text{H}_{13}\text{N}_2\text{Cl})_2)</td>
<td>4.12</td>
<td>8.26</td>
<td>31.08</td>
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<td></td>
<td></td>
<td>(4.25)</td>
<td>(8.50)</td>
<td>(32.32)</td>
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<td>XX</td>
<td>Tetrachlorobis(p-bromoacetophenone-2-amo-3-methylpyridine)Si(IV) (\text{SiCl}<em>4(\text{C}</em>{14}\text{H}_{13}\text{N}_2\text{Br})_2)</td>
<td>3.59</td>
<td>7.20</td>
<td>18.56</td>
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<td></td>
<td></td>
<td>(3.74)</td>
<td>(7.49)</td>
<td>(18.98)</td>
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Table VI.2: INFRARED FREQUENCIES (in cm\(^{-1}\)) OBSERVED IN SCHIFF BASES

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Legend</th>
<th>(\nu) (NH(_2))</th>
<th>(\nu) (CH(_{\text{ii}}))</th>
<th>(\nu) (C-N)</th>
<th>(\nu) (C=O)</th>
<th>Pyridine ring vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>C(<em>{13})H(</em>{12})N(_2)</td>
<td>3188s</td>
<td>1615s</td>
<td>1480s</td>
<td>1565 &amp; 1460s</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>C(<em>{13})H(</em>{12})N(_2)O</td>
<td>3194s</td>
<td>1623m</td>
<td>1488s</td>
<td>1488s</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>C(<em>{13})H(</em>{13})N(_3)</td>
<td>3190s</td>
<td>1612s</td>
<td>1488s</td>
<td>1488s</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>C(<em>{13})H(</em>{14})N(_2)C(_1)</td>
<td>3190s</td>
<td>1615s</td>
<td>1470s</td>
<td>1470s</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>C(<em>{13})H(</em>{13})N(_2)Br</td>
<td>3180m</td>
<td>1615s</td>
<td>1470m</td>
<td>1470m</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>C(<em>{14})H(</em>{14})N(_2)O</td>
<td>3185m</td>
<td>1613s</td>
<td>1472s</td>
<td>1472s</td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>C(<em>{14})H(</em>{13})N(_3)C(_1)</td>
<td>3185s</td>
<td>1613s</td>
<td>1472s</td>
<td>1472s</td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>C(<em>{14})H(</em>{13})N(_2)Cl</td>
<td>3180m</td>
<td>1613s</td>
<td>1472s</td>
<td>1472s</td>
<td></td>
</tr>
<tr>
<td>IX</td>
<td>C(<em>{14})H(</em>{13})N(_2)Br</td>
<td>3180m</td>
<td>1613s</td>
<td>1472s</td>
<td>1472s</td>
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</tr>
<tr>
<td>X</td>
<td>C(<em>{14})H(</em>{13})N(_2)Cl</td>
<td>3180m</td>
<td>1613s</td>
<td>1472s</td>
<td>1472s</td>
<td></td>
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</table>

b = broad, m = medium, s = sharp
Table VI.3: INFRARED FREQUENCIES (in cm\(^{-1}\)) OF SILICON(IV) COMPLEXES

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Complex</th>
<th>(\nu) OH</th>
<th>(\nu) NH(_2)</th>
<th>(\nu) CH</th>
<th>(\nu) C=N</th>
<th>(\nu) C=C</th>
<th>(\nu) C-O</th>
<th>(\nu) M-O</th>
<th>(\nu) M-N</th>
<th>(\nu) M-Cl</th>
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</thead>
<tbody>
<tr>
<td>XI</td>
<td>SiCl(<em>4)(C(</em>{13})H(_{12})N(_2))(_2)</td>
<td>-</td>
<td>-</td>
<td>3250w</td>
<td>1660s</td>
<td>1548s</td>
<td>-</td>
<td>-</td>
<td>423s</td>
<td>296s</td>
</tr>
<tr>
<td>XII</td>
<td>SiCl(<em>4)(C(</em>{13})H(_{12})N(_2))O</td>
<td>3408m</td>
<td>-</td>
<td>3235w</td>
<td>1655s</td>
<td>1567s</td>
<td>1308s</td>
<td>517s</td>
<td>410s</td>
<td>297m</td>
</tr>
<tr>
<td>XIII</td>
<td>SiCl(<em>4)(C(</em>{13})H(_{13})N(_3))</td>
<td>-</td>
<td>3320</td>
<td>3256w</td>
<td>1660s</td>
<td>1548s</td>
<td>-</td>
<td>-</td>
<td>425s</td>
<td>298m</td>
</tr>
<tr>
<td>XIV</td>
<td>SiCl(<em>4)(C(</em>{13})H(_{11})N(_2))Cl(_2)</td>
<td>-</td>
<td>-</td>
<td>3235w</td>
<td>1660s</td>
<td>1547s</td>
<td>-</td>
<td>-</td>
<td>423s</td>
<td>296s</td>
</tr>
<tr>
<td>XV</td>
<td>SiCl(<em>4)(C(</em>{13})H(_{11})N(_2))Br(_2)</td>
<td>-</td>
<td>-</td>
<td>3238w</td>
<td>1662s</td>
<td>1548s</td>
<td>-</td>
<td>-</td>
<td>420s</td>
<td>296s</td>
</tr>
<tr>
<td>XVI</td>
<td>SiCl(<em>4)(C(</em>{14})H(_{14})N(_2))(_2)</td>
<td>-</td>
<td>-</td>
<td>3248w</td>
<td>1650s</td>
<td>1560s</td>
<td>-</td>
<td>-</td>
<td>410s</td>
<td>299s</td>
</tr>
<tr>
<td>XVII</td>
<td>SiCl(<em>4)(C(</em>{14})H(_{14})N(_2))O</td>
<td>3403m</td>
<td>-</td>
<td>3250w</td>
<td>1650s</td>
<td>1565s</td>
<td>1307s</td>
<td>518ms</td>
<td>410s</td>
<td>298s</td>
</tr>
<tr>
<td>XVIII</td>
<td>SiCl(<em>4)(C(</em>{14})H(_{15})N(_3))</td>
<td>-</td>
<td>3320</td>
<td>3225w</td>
<td>1660s</td>
<td>1555s</td>
<td>-</td>
<td>-</td>
<td>413s</td>
<td>298s</td>
</tr>
<tr>
<td>XIX</td>
<td>SiCl(<em>4)(C(</em>{14})H(_{13})N(_2))Cl(_2)</td>
<td>-</td>
<td>-</td>
<td>3240w</td>
<td>1660s</td>
<td>1548s</td>
<td>-</td>
<td>-</td>
<td>405s</td>
<td>298s</td>
</tr>
<tr>
<td>XX</td>
<td>SiCl(<em>4)(C(</em>{14})H(_{13})N(_2))Br(_2)</td>
<td>-</td>
<td>-</td>
<td>3240w</td>
<td>1658s</td>
<td>1547s</td>
<td>-</td>
<td>-</td>
<td>408s</td>
<td>297s</td>
</tr>
</tbody>
</table>

\(w = \text{weak}, \ m = \text{medium}, \ ms = \text{medium sharp}, \ s = \text{sharp}\)
shown in Table VI.4. The representative PMR spectra of the ligands and complexes are reproduced in Figs. 6.7 to 6.10.

Characteristic signals of NH$_2$ protons are noticed in the region 2.45 to 2.52 ppm. The resonance due to orthohydroxy group (13.52 ppm.) of the ligand appears in the complex but shows a shift to lower field (14.19 ppm.) indicating that coordination has taken place through -OH of the Schiff base. The sharp signal of methine proton is observed around 7.6 to 7.86 ppm. There is a downfield shift of =CH resonance of the ligand. This downfield shift is probably due to coordination of the azomethine nitrogen with Si(IV) which results in deshielding of the methine proton. In the ligand II, VIII and the complexes XII and XVIII, the signal observed around 1.98 to 2.18 ppm is assigned to the methyl protons substituted to the 2-aminopyridine.
Fig. 6.1
o-Hydroxyacetophenone-2-amino-3-methylpyridine

WAVELENGTH (CM\(^{-1}\))
3600 3400 3200 3000 1600 1400 1200 1000
Fig. 6.2 o-Aminoacetophenone-2-amino-3-methylpyridine
Fig 6.3  p-Chloroacetophenone-2-amino-3-methylpyridine
Fig 6.4  Tetrachloro-o-hydroxyacetophenone-2-amino-3-methylpyridine Si(IV)
Fig 6.5
Tetrachloro-o-aminoacetophenone-2-amino-3-methylpyridine (IV)
Fig. 6.6 Tetrachlorobis(p-chloroacetophenone-2-amino-3-methylpyridine)Si(IV)
### Table V I . 4 : THE PROTON MAGNETIC RESONANCE CHEMICAL SHIFTS OF ACETOPHENONE SCHIFF BASES AND THEIR COMPLEXES OF S I ( I V ) .

<table>
<thead>
<tr>
<th>SI No.</th>
<th>Compound</th>
<th>Hydroxy proton of ketonic group</th>
<th>CH$_3$ protons</th>
<th>Phenyl protons</th>
<th>Methine protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>o-Hydroxyacetophenone-2-amino-3-methylpyridine</td>
<td>13.52</td>
<td>2.08</td>
<td>7.42</td>
<td>6.5</td>
</tr>
<tr>
<td>VIII</td>
<td>o-Aminoacetophenone-2-amino-3-methylpyridine</td>
<td>7.65</td>
<td>-</td>
<td>6.37</td>
<td>7.90</td>
</tr>
<tr>
<td>XII</td>
<td>Tetrachloro-o-hydroxyacetophenone-2-amino-3-methylpyridine(SI(IV))</td>
<td>6.58</td>
<td>2.45</td>
<td>6.82</td>
<td>7.83</td>
</tr>
<tr>
<td>XVIII</td>
<td>Tetrachloro-o-aminoacetophenone-2-amino-3-methylpyridine(SI(IV))</td>
<td>6.86</td>
<td>2.18</td>
<td>7.32</td>
<td>6.62</td>
</tr>
</tbody>
</table>
Fig 6.7  o-Hydroxyacetophenone-2-amino-3-methylpyridine
Fig 6.8  o-Aminoacetophenone-2- amino-3-methylpyridine
Fig. 6-9  Tetrachloro-o-hydroxyacetophenone-2-amino-3-methylpyridine Si(IV)
Tetrachloro-o-aminoacetophenone-2-amino-3-methylpyridineS(IV)
Powder X-ray Diffraction Studies

The diffractograms of tetrachloro-o-hydroxyacetophenone-2-amino-3-methylpyridine Si(IV) and tetrachloro-o-aminoacetophenone-2-amino-3-methylpyridine Si(IV) have been shown in Figs. 6.11 & 6.12 with 12 reflections for complex XVII and 10 reflections for complex XIII respectively between 10° and 80°(2θ) with maxima at 2θ = 26.8° and 2θ = 25.4° respectively which corresponds to d = 3.3233 Å and 3.5032 Å respectively. The 2θ values for prominent peaks have been listed in Tables VI.5 and VI.6. All the main peaks have been indexed and their Sin^2θ values compared with the calculated ones. Comparison of these values reveal that there is a good agreement between calculated and observed values of Sin^2θ. The unit cell has been calculated by the trial and error method. The observed values fit well in cubic system for both the complexes XVII and XIII, to give a unit cell with lattice constants a=b=c=10.6967 Å, cell volume = 1223.9098 Å^3 and a=b=c=11.6178 Å, cell volume = 1568.0924 Å^3 respectively. Substitution of this cell volume primitive lattice (n=1) for the complex XVII gives the theoretical value of density equal to 1.9485 g cm^-3 which is fairly in agreement with the experimental value 1.9498 g cm^-3 within the limits of experimental error. Substitution of the cell volume primitive lattice (n=1) for the complex XIII gives the theoretical value of density equal to 1.4633 g cm^-3 which is in agreement with the experimental value 1.4672 g cm^-3 within the limits of experimental errors.
Table VI.5: X-Ray Data of Silicon(IV) Complexes.

Complex XVII: SiCl₄(C₁₄H₈N₂O)
Cubic System

<table>
<thead>
<tr>
<th>Peak no</th>
<th>d spacing Å</th>
<th>Relative Intensity X 100 I/IO</th>
<th>Observed ²Sinθ</th>
<th>Calcd. ²Sin²θ</th>
<th>(hkl)</th>
<th>²θ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.6162</td>
<td>38.2</td>
<td>0.01021</td>
<td>0.01021</td>
<td>110</td>
<td>11.6</td>
</tr>
<tr>
<td>2</td>
<td>6.1425</td>
<td>27.2</td>
<td>0.01570</td>
<td>0.01524</td>
<td>111</td>
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</tr>
<tr>
<td>3</td>
<td>4.6164</td>
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<td>0.02782</td>
<td>0.02591</td>
<td>210</td>
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</tr>
<tr>
<td>4</td>
<td>3.7598</td>
<td>35.4</td>
<td>0.04195</td>
<td>0.04176</td>
<td>211</td>
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</tr>
<tr>
<td>5</td>
<td>3.4890</td>
<td>38.6</td>
<td>0.04871</td>
<td>0.04826</td>
<td>221</td>
<td>25.5</td>
</tr>
<tr>
<td>6</td>
<td>3.3233</td>
<td>125.8</td>
<td>0.0570</td>
<td>0.0570</td>
<td>311</td>
<td>26.8</td>
</tr>
<tr>
<td>7</td>
<td>3.0653</td>
<td>40.0</td>
<td>0.06311</td>
<td>0.06218</td>
<td>222</td>
<td>28.1</td>
</tr>
<tr>
<td>8</td>
<td>2.9753</td>
<td>60.4</td>
<td>0.06698</td>
<td>0.06736</td>
<td>320</td>
<td>30.1</td>
</tr>
<tr>
<td>9</td>
<td>2.6644</td>
<td>36.4</td>
<td>0.08335</td>
<td>0.08291</td>
<td>400</td>
<td>33.6</td>
</tr>
<tr>
<td>10</td>
<td>2.4984</td>
<td>29.1</td>
<td>0.09498</td>
<td>0.09328</td>
<td>420</td>
<td>35.9</td>
</tr>
<tr>
<td>11</td>
<td>2.4783</td>
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<td>0.09846</td>
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<tr>
<td>12</td>
<td>2.0036</td>
<td>27.3</td>
<td>0.1477</td>
<td>0.1503</td>
<td>520</td>
<td>45.2</td>
</tr>
</tbody>
</table>

For complex XVII (cubic system), a=b=c=10.6967 Å, cell volume (V = 1223 9098 Å³), mol wt. = 396, density (ρ) (Calcd.) = 1.9485 g cm⁻³, density (ρ) (obs.) = 1.9498 g cm⁻³.

For cubic system \( \sin^2 \theta = \frac{\lambda^2}{4a^2}(h^2+k^2+l^2) \)
Fig 6-11 Diffraction pattern of Tetrachloro-o-hydroxyacetophenone-2-amino-3-methylpyridineSi(IV)
Fig 6.11 Diffraction pattern of Tetrachloro-o-hydroxyacetophenone-2-amino-3-methylpyridineSi(IV)
**Table VI.6 : X-RAY DATA OF SILICON(IV) COMPLEXES.**

**COMPLEX XIII : SiCl$_4$(C$_{13}$H$_{13}$N$_3$)**

Cubic System

<table>
<thead>
<tr>
<th>Peak no.</th>
<th>d spacing A$^0$</th>
<th>Relative Intensity X 100</th>
<th>Observed $\sin^2\theta$</th>
<th>Calcd $\sin^2\theta$</th>
<th>(hkl)</th>
<th>$2\theta^0$ values</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>8.1672</td>
<td>43.6</td>
<td>0.0089</td>
<td>0.008786</td>
<td>110</td>
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</tr>
<tr>
<td>2</td>
<td>5.1197</td>
<td>57.3</td>
<td>0.02262</td>
<td>0.02196</td>
<td>210</td>
<td>17.3</td>
</tr>
<tr>
<td>3</td>
<td>4.1287</td>
<td>34.5</td>
<td>0.03479</td>
<td>0.03514</td>
<td>220</td>
<td>21.50</td>
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<tr>
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<td>3.6702</td>
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<td>0.04113</td>
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<td>0.1335</td>
<td>0.1318</td>
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</table>

For complex XIII (cubic system), $a=b=c=11.6178$ A$^0$, cell volume (V) = 1568.0924 A$^{3}$, mol.wt. = 381, density ($\rho$) (Calcd) = 1.4633 g cm$^-3$.

For cubic system $\sin^2\theta = \frac{\lambda^2(h^2+k^2+l^2)}{4a^2}$.
Fig. 6-12 Diffraction pattern of Tetrachloro-o-aminoacetophenone-2-aminopyridine Si(IV)
Electron Spectroscopy for Chemical Analysis (ESCA)

Or [X-ray Photoelectron Spectroscopy (XPS)]

The results are summarised in Table VI.7.

The spectra of the complex tetrachloro-o-hydroxyacetophenone-2-aminopyridine Si(IV) are reproduced in Figs 6.13 to 6.17. The complex contains C, O, N, Cl and Si elements. XP Spectrum of Si 2P_{1/2} core level shows a sharp (single) symmetric photoelectron peak at 105.6 eV. The absence of additional peaks like satellite lines or multiple splitting of 2p_{1/2} core level clearly indicates that the complex is diamagnetic. The presence of only one type of nitrogen atom (imine nitrogen) is revealed by XP Spectrum of Nls core level showing the intense peak at 402.2 eV. Further, XP Spectrum of Cls core level indicates the presence of one type of carbon atom. The sharp peak at 286.2 eV corresponds to the carbon atom of benzene ring. XP Spectrum of Ols core level shows the presence of only one type of oxygen atom indicated by the sharp peak at 534.5 eV. The presence of chlorine atom is revealed by a sharp peak at 200.0 eV shown by XP Spectrum of Cl 2p_{3/2}.

This reveals that Si(IV) chloride has undergone complexation with o-Hydroxyacetophenone-2-aminopyridine ligand forming the complex which is diamagnetic in nature.
Table VI.7: BINDING ENERGIES FOR VARIOUS LEVELS

<table>
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<th>Level</th>
<th>Binding energy (eV)</th>
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<tbody>
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<td>Cls</td>
<td>286.2</td>
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<tr>
<td>Nls</td>
<td>402.2</td>
</tr>
<tr>
<td>Ols</td>
<td>534.5</td>
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<tr>
<td>Cl 2p3/2</td>
<td>200.0</td>
</tr>
<tr>
<td>Si 2p1/2</td>
<td>105.6</td>
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</table>
ESCA XP SPECTRUM OF NITROGEN 1s CORE LEVEL

Fig. 6.14
Fig. 6-16 ESCA XP SPECTRUM OF Cl$_2$P$_{3/2}$ CORE LEVEL

B.E (eV)
**Biological Activities**

**Antifungal activity**

The results are summarised in Tables VI.8 & VI.9.

The pure ligands and complexes were screened for their antifungal activity against *Aspergillus flavus*, *Alternaria alternata*, *Alternaria porri*, *Aspergillus niger* and *Fusarium moniliforme* as the test fungi by cup-plate method as described in the beginning of this chapter under biological study. Testing was carried out at the concentration of 10 mg ml\(^{-1}\) (in DMF) of the ligands and complexes. The diameter of the fungus colony in control and the treated set was measured after 72 hr. The zones of inhibition were recorded (Table VI.8) and % inhibition was calculated. The ligands I, II, III, IV and complexes XIII, XIV, XVIII, XIX found to possess more activity against all the test fungi. The ligands V and X were less active. The ligands VI, VII, VIII and IX have fairly significant activity. The complexes XI, XV, XVI and XX are less active. The complexes XII and XVII are moderately active against all test fungi.

All the ligands and their complexes of Silicon(IV) (except bromosubstituted) exhibited fairly good activity against test fungi. The chlorosubstituted ligands and complexes were highly toxic. The amino-substituted ligands and their complexes are moderately toxic. Introduction of methyl group in 3-position in ligands and their complexes of Si(IV) resulted in the decrease of activity. The bromosubstituted ligands and complexes are less active. The antifungal activity on complexation has shown the decrease in activity.
Table VI.8: ANTIFUNGAL SCREENING DATA OF SCHIFF BASES.

Antifungal assay:

<table>
<thead>
<tr>
<th>Compound no. (ligand)</th>
<th>Aspergillus flavus</th>
<th>Alternaria alternata</th>
<th>Alternaria pori</th>
<th>Aspergillus niger</th>
<th>Fusarium moniliforme</th>
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<td>++</td>
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<td>78.7</td>
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<td>21.78</td>
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</table>

Less active = + = 12-15 mm
Moderately active = ++ = 16-24 mm
More active or highly active = +++ = 25-36 mm
Inactive = -- = < 12 mm
### Table VI.9: ANTIFUNGAL SCREENING DATA OF COMPLEXES.

<table>
<thead>
<tr>
<th>Sl. no</th>
<th>Compound (complex)</th>
<th>Aspergillus flavus</th>
<th>Alternaria alternata</th>
<th>Alternaria porri</th>
<th>Aspergillus niger</th>
<th>Fusarium moniliforme</th>
</tr>
</thead>
<tbody>
<tr>
<td>XI</td>
<td>Tetrachlorobis(acetophenone-2-aminopyridine)Si(IV)</td>
<td>++</td>
<td>+</td>
<td>*</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
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<td>Tetrachloro-o-hydroxyaceto-phenone-2-aminopyridine Si(IV)</td>
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<td>+</td>
<td>+</td>
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<td>++</td>
<td>+</td>
<td>+++</td>
<td>++</td>
</tr>
<tr>
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<td>Tetrachlorobis( p-chloro-acetophenone-2-aminopyridine) Si(IV)</td>
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<td>+++</td>
<td>++</td>
<td>+++</td>
<td>++</td>
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<tr>
<td>XV</td>
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<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
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<tr>
<td>XVI</td>
<td>Tetrachlorobis(acetophenone-2-amino-3-methylpyridine)Si(IV)</td>
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<td>+</td>
<td>+</td>
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<tr>
<td>XVII</td>
<td>Tetrachloro-o-hydroxyacetophenone-2-amino-3-methylpyridine Si(IV)</td>
<td>++</td>
<td>++</td>
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<td>++</td>
<td>+</td>
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<tr>
<td>XVIII</td>
<td>Tetrachloro-o-aminoaceto-phenone-2-amino-3-methylpyridine Si(IV)</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>+</td>
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<tr>
<td>XIX</td>
<td>Tetrachlorobis( p-chloro-acetophenone-2-amino-3-methylpyridine)Si(IV)</td>
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<td>+++</td>
<td>++</td>
<td>+++</td>
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<tr>
<td>XX</td>
<td>Tetrachlorobis( p-bromoacetophenone-2-amino-3-methylpyridine)Si(IV)</td>
<td>-</td>
<td>+</td>
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<td>-</td>
</tr>
</tbody>
</table>

Less active = + = 12-15 mm  
Moderately active = ++ = 16-24 mm  
More or highly active = +++ = 25-36 mm  
Inactive = - = < 12 mm
The spectral evidences, analytical data and the conductance measurements suggest that Silicon(IV) exhibits coordination number six in these complexes. These can be regarded as octahedral Complexes can be represented by the following structures.

\[
\begin{align*}
R &= \text{H, 3-CH}_3 \\
R' &= \text{H, Cl, Br} \\
\end{align*}
\]

\[
\begin{align*}
R &= \text{H, 3-CH}_3 \\
R' &= \text{OH, NH}_2 \\
\end{align*}
\]
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