CHAPTER IV

PREPARATION AND STRUCTURE OF SALICYLIDENE ORTHOAMINOBENZO-
THIOL (SOTB-\textsubscript{H}_2) AND SALICYLIDENE PARAAMINOTHIOARISOL (SPTA-H)

SCHIFF'S BASES AND THEIR METAL COMPLEXES.
Schiff's bases (imines) which are usually known as anilines are the condensation products of aldehyde with aliphatic or aromatic amines. The characteristic group – C = N – contains a nitrogen which acts as donor because of the presence of lone pair of electrons. A wide variety of Schiff's bases can be prepared and the nature and position of donor atoms and groups can be utilized to control the size of chelate ring in its metal complexes. All these factors make Schiff's bases chelating agents of great potential value. Besides finding use in analytical chemistry and biochemical reactions, a number of Schiff's bases and their complexes have been found to exhibit bactericidal, tuberculostatic, fungicidal and anticancer activities (1-8). The Schiff's base metal complexes involving a metal chelate with six-membered ring are found to be particularly important (loc. cit.) in biological systems.

Considerable amount of work on the preparation and determination of composition and structure of Schiff's bases containing various donor sites including sulphur is reported in literature (loc. cit.). Here we report the preparation, determination of composition and structural studies on some
sulphur containing schiff's bases viz. salicylidene-
orthoaminobenzothiol and salicylideneparaminothioanisol.
Similar studies on complexes of salicylideneorthoaminoben-
zothiol are also being reported.

**EXPERIMENTAL**

**Materials:** The chemicals listed below, were obtained from
different chemical companies and their purities were checked
by measuring melting and boiling points.

(a) Salicylaldehyde (Ward Blenkinsop and Co., Ltd., London,
Widens made in England).

(b) Orthoaminobenzothiol (Riedel-de Haen AG, Seelze
Hannover, made in Germany).

(c) Paraaaminothioanisol (BDH made in England).

(d) All other materials employed in the reaction were
(AR, BDH) grade reagents.

**Preparation of schiff's bases:**

The schiff's bases, salicylidene orthoaminobenzothiol
(SOTA-H₂) and salicylidene paraaminothioanisol (SPTA-H) were
prepared by refluxing equimolar quantities of orthoaminoben-
zothiol and paraaminothioanisol, respectively with
salicylaldehyde in minimum amount of pure ethanol for about two hours. After refluxing, the solutions were filtered while hot and allowed to cool in ice. When the respective schiff's bases crystallised out, the product obtained were filtered through Buchner funnel and washed with minimum amount of cold ethanol. The products obtained were recrystallised by redissolving the crystals in minimum amount of hot ethanol (9). The solutions were then cooled and allowed to crystallise. The products of recrystallisation were filtered through buchner funnel and washed with a little amount of cold ethanol. The crystals were dried in oven at 45-55°C and stored in a desiccator for further studies.

The schiff's bases obtained were analysed for sulphur content by fusing the respective schiff's bases (≈0.20g) with 2-3 cm of fusion mixture (Na₂CO₃ + K₂CO₃) and then completing the estimation of sulphur gravimetrically as barium sulphate (10). The percentage of sulphur obtained from the analysis, along with the calculated values for the product II - C = A - are given in Table IV-A. In case of (2CTB-H₂) schiff's base the yield was 70% and m.point 156°C and in case of (2PTA-H) schiff's base, yield was 68% and the m.point was 88°C.
A perusal of the table IV-A indicates that these schiff's bases of the products of the condensation of 1 mol. of amine with 1 mol. of salicylaldehyde.

**Formation of schiff's base:**

\[
R - C \equiv O + H_2N - R' \xrightarrow{\text{H}} R - C \equiv N - R'
\]

(Aldehyde) + (Amine) (Schiff's base)

**ISOLATION OF COMPLEXES**

1. **Salicylideneorthoaminobenzothiol copper(II) complex.**

Cupric nitrate (1.8962 gms) was dissolved in a minimum quantity of sixty percent dioxan-water mixture and was made to react with 2.0 gms. of salicylidene-orthoaminobenzothiol schiff's base dissolved in a minimum quantity of 1,4-dioxan, and refluxed for about thirty minutes. The solution was filtered through Buchner funnel while hot and allowed to stand for about one hour. pH of the reaction mixture was measured and found to be 6.80. Dark green precipitate of copper(II)
complex was formed. The complex was filtered and washed using 50% dioxan water mixture and dried in oven at 50-60°C for 8 to 10 hours.

2. Salicylideneorthoaminobenzothiol nickel(II) complex.

Nickel nitrate (1.5753 gms) was dissolved in a minimum quantity of sixty percent dioxan-water mixture and was made to react with (2.0 gms) of salicylideneorthoaminobenzothiol schiff's base, dissolved in a minimum quantity of 1,4-dioxan and refluxed for about half an hour. The solution was filtered while hot, allowed to stand for about two hours and pH of the reaction mixture was found to be 8.55. Reddish yellow precipitate obtained was washed with 50% water dioxan mixture and dried as in case of copper (II) complex.

3. Salicylideneorthoaminobenzothiol cobalt(II) and iron(II) complexes.

Ferrous sulphate (1.9328 gms) and cobalt chloride (1.9255 gms) were dissolved in a minimum quantity of sixty percent water-dioxan mixture respectively. Such solution was reacted with 2.0 gms of salicylideneorthoaminobenzothiol schiff's base, dissolved in a minimum amount of 1,4-dioxan and refluxed for about
forty minutes. The solution was filtered while hot and allowed to stand for about two hours. pH of the solutions found to be 7.25 and 6.48 respectively. Reddish brown and brownish yellow precipitates separated in case of cobalt (II) and iron(II) respectively. The precipitates were washed with 50% water dioxan mixture and dried as described earlier.

4. Salicylidene orthoaminobenzothiol uranyl(VI) complex.

2.0 gms of salicylideneorthoaminobenzothiol was dissolved in a minimum quantity of 1,4-dioxan and was refluxed with uranyl acetate (1.065 gms) dissolved in 50% dioxan water mixture for about thirty minutes. The solution was filtered while hot and pH of the reaction mixture was found to be 7.15. Yellowish red precipitate obtained was washed with 50% dioxan water mixture and dried.

Analysis:

The complexes were analysed for their metal and sulphur content. The complexes were decomposed twice in aqua regia and the metal contents were estimated. In case of copper (II) complex, copper(II) was estimated as cuprous thiocyanate whereas nickel(I) was estimated as nickel salt of dimethyl glyoxime. Iron(II) was
estimated as oxide whereas cobalt (II) and uranyl(VI) was estimated as oxime (loc. cit.). The sulphur content in the complexes was estimated by fusing the respective schiff's bases and their complexes with excess of fusion mixture (K₂CO₃ + H₂O₂) and then completing the estimation of sulphur gravimetrically as barium sulphate (loc. cit.). The evaluation of composition on the basis of estimation of sulphur and metal ions is reported in Table IV-A.

Infrared spectral studies.

The infra-red spectra of the schiff's base and their metal complexes in potassium bromide discs were recorded on Perkin-Elmer Spectrophotometer in the region 4000-400 cm⁻¹. The infra-red spectral frequencies of schiff's bases i.e., salicylidene orthoaminobenzothiol (SOTB-H₂) and salicylidene paraaminothioanisol (SPTA-H) and their metal complexes like salicylidene orthoaminobenzothiol copper (I), salicylidene orthoaminobenzothiol nickel (II), salicylidene orthoaminobenzothiol cobalt (II), salicylidene orthoaminobenzothiol iron (II) and salicylidene orthoaminobenzothiol uranyl (VI), are given in Table IV-B.
RESULTS AND DISCUSSION

A perusal of the Table IV-A indicates that the products obtained are the 1:1 condensation products as shown below:

(I).

\[
\text{PhCHO} + \text{PhSH} \xrightarrow{} \text{PhC=N} \text{SH}
\]

(II).

\[
\text{PhCHO} + \text{PhNH}_2 \xrightarrow{} \text{PhC=NSCH}_3
\]

The important features in the infra-red absorption spectra of the schiff's bases is the band of medium intensity at 1610 cm\(^{-1}\) and 1615 cm\(^{-1}\) respectively which shows the existence of C = N stretching and confirms the formation of schiff's bases. The bands at 1150 cm\(^{-1}\) corresponds to C - C stretching. The bands in the region 900-650 cm\(^{-1}\) are due to out of plane bending modes of the ring and C - H bands.
Another feature is a weak band at 3250 cm\(^{-1}\) which can be ascribed to the partially ionic \(-\mathrm{NH}\) bands. The significant feature is a weak band for S-H stretching vibrations which are observed at 2650 cm\(^{-1}\) and 2510 cm\(^{-1}\) for the \(\text{(SOTB-H}_2\text{)}\) and \(\text{(SPTA-H)}\) schiff's bases respectively. This weak and broad band indicates that the sulphydryl proton is probably shifted to the \(-\mathrm{N}^-\). This assumption is further supported by the existence of broad peak for \(\mathrm{N-H}\) band. On this basis, the real structure of schiff's base is probably a resonance structure involving the structure I and II as given below:

![Chemical Structure](image)

The other bands at 1350 cm\(^{-1}\) and 1280 cm\(^{-1}\) observed for \(\text{(SOTB-H}_2\text{)}\) and \(\text{(SPTA-H)}\) schiff's base are assigned to the C-O stretching frequencies. The schiff's base shows medium peaks at 755 cm\(^{-1}\) and 780 cm\(^{-1}\) which are assigned to C-S stretching in case of salicylideneorthoaminobenzothiol and salicylidene-paraaminothioanisol schiff's bases respectively. The 0-H stretching frequencies for C-OH are observed as broad peaks.
at 3250 cm\(^{-1}\) and 3160 cm\(^{-1}\) for (DOTS-H\(_2\)) and (EPA-H) Schiff's bases respectively.

1. Salicylideneorthaminobensothiol copper(II) complex:

This complex corresponds to the composition CuL. The infra red spectra of Schiff's base exhibits a band at 1615 cm\(^{-1}\) assignable to C = N stretching frequency. In the copper (II) Schiff's base complex the said frequency is observed to occur at 1605 cm\(^{-1}\). The lowering of the C = N stretching frequency is an indication of the coordination of amine nitrogen and thus indicating less double bond character in the C = N bond (11). The C-H frequency at 3250 cm\(^{-1}\) disappears and the C-O stretching mode of the phenolimine form of the Schiff's bases occurring at 1345 cm\(^{-1}\) are found to shift to 1280 cm\(^{-1}\)
in the copper (II) complex which indicates the bonding of copper (II) through oxygen of C-O group (12). The infra red spectra also show peaks at 510 cm\(^{-1}\) and 600 cm\(^{-1}\) which is assigned to the (M-N) and (M-O) stretching frequencies (13). The C=S frequency was observed to shift from 755 cm\(^{-1}\) to 715 cm\(^{-1}\), which indicates the bonding through sulphur also.
2. **Salicylideneorthoaminobenzothiol cobalt (II) complex.**

The infra red spectra of the salicylideneorthoaminobenzothiol exhibits a band at 1615 cm\(^{-1}\) assignable to \(\text{C} = \text{N}\) stretching frequency. In cobalt (II) Schiff's base complex the frequency is observed to be shifted to 1570 cm\(^{-1}\). This shift in frequency is an indication that the metal coordinates through nitrogen. The shift has been observed in C-O stretching, in Schiff's base from 1345 cm\(^{-1}\) to 1330 cm\(^{-1}\) in complex. Besides this the absence of band at 3250 cm\(^{-1}\) assignable to O-H frequency supports that metal coordinates through oxygen. This is further supported by the appearance of a band at 590 cm\(^{-1}\) which can be assigned to M-O stretching. The shift in C-S stretching frequency has also been observed, which is at 755 cm\(^{-1}\) in Schiff's base and at 715 cm\(^{-1}\) in complex. All these factors support that metal coordinates through oxygen, nitrogen as well as sulphur.

3. **Salicylideneorthoaminobenzothiol iron(II) complex.**

The iron(II) complex corresponds to the composition \(\text{Fe(II)}(\text{C}_{13}\text{H}_{11}\text{O}_{6}\text{S})\ (\text{H}_2\text{O})_3\). The important infra red frequencies and their tentative assignments are given in Table IV-8. The \(\text{C} = \text{N}\) stretching frequency in \((\text{SCTB-H}_2)\) Schiff's base was observed at 1615 cm\(^{-1}\) whereas in
complex it was shifted to 1600 cm$^{-1}$. The C-O stretching in \((\text{SOTB-}H_2)\) schiff's base found at 1345 cm$^{-1}$ whereas in complex it was at 1300 cm$^{-1}$. The N-O frequency was observed at 590 cm$^{-1}$ whereas M-N stretching was observed at 545 cm$^{-1}$ and C-S stretching frequency shifted to 730 cm$^{-1}$. These observations confirm the coordination of metal through nitrogen, oxygen and sulphur.

4. **Salicylidene orthoaminobenzothiol nickel(II) complex.**

   The C-N stretching in schiff's base was observed at 1615 cm$^{-1}$ which was shifted to 1595 cm$^{-1}$ in complex. The shift in C-O stretching was observed at 1345 cm$^{-1}$ to 1330 cm$^{-1}$. The other frequencies observed at 605 cm$^{-1}$, 505 cm$^{-1}$ and 705 cm$^{-1}$ respectively for M-O, M-N and C=S bands.

5. **Salicylideneorthoaminobenzothiol uranyl(VI) complex.**

   The important infra red frequencies and their tentative assignments are given in Table IV-B. The C=O stretching frequency in the \((\text{SOTB-} H_2)\) schiff's base was observed at 1615 cm$^{-1}$. This band in the uranyl(VI) complex has shifted to 1580 cm$^{-1}$. The lowering of C = N stretching frequency is an indication of the coordination through nitrogen, thus indicating less double bond character.
In the C=O bond (13). The C=O stretching in the Schiff's base was observed at 1345 cm\(^{-1}\) and shifted in the complex towards 1285 cm\(^{-1}\). This shift confirms M=O bond formation. Similar observations were made by Martoll et al. (14) in the case of Schiff's base transition metal complexes. This view is also confirmed by the appearance of peak in their spectra (12, 13, 15) at 620 cm\(^{-1}\) and 535 cm\(^{-1}\) which are due to metal-oxygen (M=O) and metal-nitrogen (M=N) band stretchings.

On the basis of these studies, it is concluded that the Schiff's base i.e. salicylidene orthoaminobenzothiol acts as a tridentate ligand which binds the metal ion through nitrogen, oxygen and sulphur.

The complexes were slightly soluble in water. Their solubility in common organic solvents is also very low which indicates the polymeric nature of the complexes. On the basis of infra red spectra and the behaviour of the complexes as polymers, the following structures are proposed.

1. Polymeric tetracoordinated copper(II) complex
2. **Polymeric hexacoordinated cobalt(II) complex**:

3. **Polymeric hexacoordinated iron(II) complex**:

4. **Polymeric tetraacordinated nickel(II) complex**:

5. **Polymeric hexacoordinated chelated structure of uranyl(VI) Complex**
Percentage composition data and colour of the sulphur containing Schiff's bases viz. salicylidene orthoaminobenzothiol and salicylidene paraaminothioanisol and their metal complexes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Name and molecular formulae</th>
<th>Colour of the compounds</th>
<th>%age of metal ion</th>
<th>%age of sulphur</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calculated</td>
<td>Found</td>
</tr>
<tr>
<td>1.</td>
<td>Salicylidene orthoaminobenzothiol ( C_{13}H_{11}O_{13}S )</td>
<td>Yellow</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>2.</td>
<td>Salicylidene paraaminothioanisol ( C_{14}H_{13}O_{13}S )</td>
<td>Shinning yellow</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>3.</td>
<td>Salicylidene orthoaminobenzothiol copper(II) ( [Cu(II)(C_{13}H_{11}O_{13}S)] )</td>
<td>Dark green</td>
<td>21.71</td>
<td>21.05</td>
</tr>
<tr>
<td>4.</td>
<td>Salicylidene orthoaminobenzothiol cobalt(II) ( [Co(II)Cl_{2}(C_{13}H_{11}O_{13}S)] )</td>
<td>Reddish brown</td>
<td>16.41</td>
<td>17.40</td>
</tr>
<tr>
<td>5.</td>
<td>Salicylidene orthoaminobenzothiol iron(II) ( [Fe(II)(C_{13}H_{11}O_{13}S)(H_{2}O)_{3}] )</td>
<td>Brownish yellow</td>
<td>16.47</td>
<td>16.25</td>
</tr>
<tr>
<td>6.</td>
<td>Salicylidene orthoaminobenzothiol nickel(II) ( [Ni(II)(C_{13}H_{11}O_{13}S)] )</td>
<td>Reddish yellow</td>
<td>20.40</td>
<td>20.12</td>
</tr>
<tr>
<td>7.</td>
<td>Salicylidene orthoaminobenzothiol uranyl(VI) ( [UO_{2}(VI)(C_{13}H_{11}O_{13}S)] )</td>
<td>Reddish yellow</td>
<td>50.95</td>
<td>50.54</td>
</tr>
</tbody>
</table>
Infrared spectrum frequencies of the Schiff's bases viz. salicylidene orthoaminobenzothiol (C₈H₇-N₂) and salicylidene paraaminothioanisol (C₈H₉-N₂) and their metal complexes.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name &amp; molecular formulae of the compounds</th>
<th>V(C = N)</th>
<th>V(C – O)</th>
<th>V(C=O)</th>
<th>V(=O)</th>
<th>V(C = S)</th>
<th>V(=S-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Salicylidene orthoaminobenzothiol (C₁₃H₁₁O₃S)</td>
<td>1615cm⁻¹</td>
<td>1345cm⁻¹</td>
<td>3250cm⁻¹</td>
<td>—</td>
<td>755cm⁻¹</td>
<td>—</td>
</tr>
<tr>
<td>2.</td>
<td>Salicylidene paraaminothioanisol (C₁₄H₁₃O₃S)</td>
<td>1610cm⁻¹</td>
<td>1280cm⁻¹</td>
<td>3160cm⁻¹</td>
<td>—</td>
<td>780cm⁻¹</td>
<td>—</td>
</tr>
<tr>
<td>3.</td>
<td>Salicylidene orthoaminobenzothiol copper(II) [Cu(II)(C₁₃H₁₁O₃S)]</td>
<td>1605cm⁻¹</td>
<td>1280cm⁻¹</td>
<td>—</td>
<td>600cm⁻¹</td>
<td>715cm⁻¹</td>
<td>510cm⁻¹</td>
</tr>
<tr>
<td>4.</td>
<td>Salicylidene orthoaminobenzothiol cobalt(II) [Co(II)Cl₂(C₁₃H₁₁O₃S)]</td>
<td>1570cm⁻¹</td>
<td>1330cm⁻¹</td>
<td>—</td>
<td>590cm⁻¹</td>
<td>715cm⁻¹</td>
<td>580cm⁻¹</td>
</tr>
<tr>
<td>5.</td>
<td>Salicylidene orthoaminobenzothiol iron(II) [Fe(II)(C₁₃H₁₁O₃S)(H₂O)]</td>
<td>1600cm⁻¹</td>
<td>1300cm⁻¹</td>
<td>—</td>
<td>590cm⁻¹</td>
<td>730cm⁻¹</td>
<td>540cm⁻¹</td>
</tr>
<tr>
<td>6.</td>
<td>Salicylidene orthoaminobenzothiol nickel(II) [Ni(II)(C₁₃H₁₁O₃S)]</td>
<td>1595cm⁻¹</td>
<td>1330cm⁻¹</td>
<td>—</td>
<td>605cm⁻¹</td>
<td>705cm⁻¹</td>
<td>505cm⁻¹</td>
</tr>
<tr>
<td>7.</td>
<td>Salicylidene orthoaminobenzothiol uranyl(VI) [UO₂(VI)(C₁₃H₁₁O₃S)]</td>
<td>1580cm⁻¹</td>
<td>1285cm⁻¹</td>
<td>—</td>
<td>620cm⁻¹</td>
<td>720cm⁻¹</td>
<td>535cm⁻¹</td>
</tr>
</tbody>
</table>
REFERENCES


15. Hao, C. K. H. ... "Chemical applications of infrared spectroscopy".