CHAPTER IX

SUMMARY AND CONCLUSION OF PRESENT WORK
Open chain quadridentate Schiff base ligands containing mixed donor (N$_2$O$_2$) atoms formed by the aromatic carbonyls and aromatic diamines have not received much attention for the preparation and characterization of transition and group II-B metal complexes.

In an attempt to prepare extended model systems for vitamin B$_{12}$, cobalt complexes were prepared$^1$ with different equatorial ligands and comparison of properties revealed different electronic situations in the complexes. Since then no attempt is made to study Schiff base complexes of remaining transition metals and group II B elements. Further there is no report available in the literature (Chapter II) on the transition metal complexes of bis(2-hydroxy-1-naphthaldehyde)orthophenylenediimine and bis(2-hydroxy-1-naphthaldehyde)metaphenylenediimine.

In view of lacuna identified and biochemical relevance of these quadridentate Schiff base complexes as model compounds it was considered important to study the magnetic and spectral properties of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes with a series of quadridentate Schiff bases than available before. Hence the following Schiff bases (I-IV) have been prepared and studied in the light of ligand formation and characterization.

I bis(Salicylaldehyde)orthophenylenediimine (Salophen)
II bis(Salicylaldehyde)metaphenylenediimine (Salmphen)
III bis(2-Hydroxy-1-naphthaldehyde)orthophenylenediimine (Nalophen)

IV bis(2-Hydroxy-1-naphthaldehyde)metaphenylenediimine (Nalmphen)

The absorption spectra were recorded at different pH values and their pKa values are calculated. Only one pK value is expected since both replaceable protons have identical chemical environment. However, the present ligands have two pK values in analogy with previous observation.

Nearly 40 metal complexes with a series of quadridentate schiff bases have been prepared and characterized and structures are tentatively assigned based on the magnetic susceptibility measurements, electronic and infrared spectral data.

Complexes are prepared in two different ways. The first method involves the use of quadridentate ligands and corresponding metal salt solutions. In the second variation 'template method' is employed for the preparation of metal complexes. Complexes obtained in both ways give corresponding ligand on treatment with alkali cyanide. This has been particularly done in the case of nickel complexes.

From an appreciation of elemental analyses, conductivity data, magnetic susceptibility measurements, electronic spectra, infrared spectral analyses, NMR and ESR spectral data, structures are assigned for the present complexes.
Though the complex formation between bivalent metal ion and quadridentate Schiff bases appears to be straightforward, yet these complexes have some interesting structural features. The coordination geometries of these complexes are governed by two factors.

1. The configuration of Schiff base ligand
2. Nature of central metal ion

The coordination geometries of the present complexes are classified into four groups (Table IX.1). They are tetrahedral, square planar, square pyramidal and octahedral complexes. While Ni(II)-Salophen and Ni(II)-Nalophen complexes have square planar geometry, Ni(II)-Salmphen and Ni(II)-Nalmphen possess tetrahedral structure. The former complexes form adducts (6-coordinate complexes) in coordinating solvents. For this reason the electronic spectra of all complexes are made in toluene as well as in coordinating solvents such as pyridine and dimethylformamide.

The magnetic moment, electronic and IR spectra of Co-Salophen complex infer the presence of bridged $-\cdot O_2\cdot$ group. This complex can be regarded as model for superoxocobalamin (Structure, p. 163). Octahedral geometry is assigned for all Fe(II) complexes. The electronic spectra of these complexes are also studied after saturating with oxygen at low temperatures to verify the reversible binding of oxygen in the presence of axial base.
**TABLE IX.1 - Tentative structures of complexes at a glance**

<table>
<thead>
<tr>
<th>Tetrahedral</th>
<th>Square planar</th>
<th>Square pyramidal</th>
<th>Octahedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu-Salophen]₂</td>
<td>Ni-Salophen</td>
<td>[Cu-Nalophen]₂</td>
<td>Fe(Salophen)₂(H₂O)₂</td>
</tr>
<tr>
<td>[Cu-Nalophen]₂</td>
<td>Ni-Nalophen</td>
<td>[Co-Salophen]₂O₂</td>
<td>Fe(Nalophen)₂(H₂O)₂</td>
</tr>
<tr>
<td>[Co-Nalophen]₂</td>
<td>Co-Nalophen</td>
<td>[Mn-Nalophen]₂</td>
<td>Fe(Salophen)₂(H₂O)₂</td>
</tr>
<tr>
<td>[Ni-Salophen]₂</td>
<td>Mn-Salophen</td>
<td></td>
<td>Fe(Nalophen)₂(H₂O)₂</td>
</tr>
<tr>
<td>[Ni-Nalophen]₂</td>
<td>Zn-BDTSC</td>
<td></td>
<td>CH₃Co(Salophen)Py</td>
</tr>
<tr>
<td></td>
<td>Cd-BDTSC</td>
<td></td>
<td>CH₃Co(Nalophen)Py</td>
</tr>
<tr>
<td></td>
<td>Hg-BDTSC</td>
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</tbody>
</table>
Based on magnetic moment value of Cu(II)-Salophen complex a dimeric structure is assigned with short metal-metal distance. The electron spin resonance spectra of Cu(II) complexes are studied in detail. The ESR spectra of Cu(II)-Nalophen has some interesting features with 6-absorption signals in $g_\parallel$ region. The spin-Hamiltonian and orbital reduction parameters are also calculated. Copper(II)-Nalophen is found to be diamagnetic and has square pyramidal structure (p 195).

Organo-cobalt complexes of Salophen and Nalophen have been prepared and these structures are assigned based on magnetic susceptibility data, electronic, infrared and NMR spectral data. These are found to be low spin octahedral complexes with a strong equatorial plane and two ligands in axial position.

The coordination geometry of group II-B metal complexes is different. The bonding is taking place only through the negativity charged phenolic oxygen atoms of schiff bases as these ligands are reaching the metal ion in 'zwitter-ionic' form. Zn(II) and Hg(II) complexes have tetragonal structure, while Cd is 6-coordinate in the presence of acetate anion as expected. The presence of 'zwitter-ionic' form of ligand and relatively large size of central metal ion perhaps made the schiff base to bind only through phenolic oxygen atoms.
The coordination geometry of group II-B complexes with benzildithiosemicarbazone (BDTSC) have been studied to have some comparison with metal complexes of quadridentate schiff base ligands. In BDTSC complexes the ligand bind through two nitrogen atoms and two sulphur atoms. The BDTSC ligand has more flexible conformation than the present schiff base complexes.
REFERENCES
