CHAPTER V

SYNTHESIS, CHARACTERIZATION, PHYSICO-CHEMICAL AND SPECTRAL STUDIES ON Mn(II), Fe(II), Co(II), Ni(II) AND Cu(II) COMPLEXES WITH (SALOPHEN AND SALMPHEN) QUADRIDENTATE SCHIFF BASE LIGANDS CONTAINING AROMATIC BRIDGES
Salicylaldehyde can be condensed with orthophenylene diamine or metaphenylenediamine to give respective schiff base ligands, bis(salicylaldehyde)orthophenylenediimine (Salophen) (I) and bis(salicylaldehyde)metaphenylenediimine (Salmphen) (II) containing aromatic bridges. The deprotonated schiff base (I or II) forms potential quadridenate ligand by bonding through two nitrogen atoms and two oxygen atoms.

During the complexation process the schiff base ligand can grasp comfortably around dimeric metal ion to form complexes and their stereochemistry largely depends either on the nature of aromatic bridge or on the property of divalent metal ion. For example, nickel(II) complexes of these tetradeinate schiff base ligands give 4-coordinate complexes while cobalt forms 6-coordinate structures. The length of bridging chain in the ligands is another deciding factor of the structure of coordination compounds derived.
from these quadridentate Schiff base ligands. Complexes have been prepared by two independent methods. In the first method complexes are obtained as usual by the use of quadridentate Schiff base ligand and metal ion solution. The second method is a direct one which does not require Schiff base ligand. However, both methods involve the use of carbonyls and corresponding diamine. In the latter method, metal ion serves as template on which carbonyl and diamine are positioned to give complexes possessing coordinated azomethine nitrogen atom. Typical synthesis of nickel complexes is presented in Scheme V-I.

The products of the reactions of these tetradentate Schiff bases with nickel(II) are shown to be monomeric and 1:1 complexes by elemental analyses, chemical degradation, independent synthesis and spectral analyses.

Study of ligands

The synthetic procedures for the preparation of bis-(salicylaldehyde)orthophenylenediimine (Salophen) and bis-(salicylaldehyde)metaphenylenediimine (Salmphen) are given in the Chapter titled "Materials and Methods" along with their yield, melting point and elemental analyses.

The electronic absorption spectra, which are attributed to \(^n\)-electron delocalization of the aromatic rings and locally excited transitions in azomethine groups,
SCHEME V-I

Where,
A = C₆H₄,
B = o-C₆H₄₆

(i) KCN + NaOH
(ii) 1M HCl

OH

A

C = O

H

B — o-C₆H₄

SCHEME V-I
are studied at different pH values. Typical absorption spectra of $5.0 \times 10^{-5}$ M Salophen and Salmphen at different pH values are plotted in Fig. V.1 and V.2 respectively. Spectra of Salophen and Salmphen show bathochromic shifts in acid and alkaline media. Values of $pK_1$ and $pK_2$ are calculated from the variation of absorbance with pH by Phillips and Meritt\textsuperscript{2} method and are respectively found to be 2.45, 7.90 (Salophen) and 2.23, 5.87 (Salmphen).

Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes of Salophen and Salmphen have been studied by elemental analyses, magnetic susceptibility measurements, electronic and infrared spectral data. Electron spin resonance and nuclear magnetic resonance spectral data of representative coordination compounds are also incorporated. All complexes can be obtained by any of the two methods described in Chapter IV. Though the synthetic procedures are different they tend to give only one type of nickel complex. However, studies are made for the complexes obtained by the method which involves the use of carbonyl, diamine and metal ion. The elemental analyses of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes of Salophen and Salmphen are presented in Chapter IV. Elemental analyses indicate 1:1 (metal:ligand) composition for all complexes.

Conductivity experiments

All metal chelates of Salophen and Salmphen are soluble
Fig. V,1. Absorption spectrum of $5.0 \times 10^{-5}$ M Salophen at different pH values.
Fig. V.2. Absorption spectrum of $5.0 \times 10^{-5}$ M Salmphen at different pH values.
in dimethylformamide. Therefore coordination compounds of Salophen and Salmphen are dissolved in dimethylformamide to perform conductivity measurements.

Known quantity of a coordination compound is taken in 25 ml standard flask, dissolved in DMF and diluted to volume with the same solvent. The coordination compound solution thus obtained in DMF is transferred into a 50 ml beaker to measure the molar conductivity. Specific and molar conductance values are calculated using the following equations:

Specific conductance \( K \) = Cell constant \( \times \) Conductance

\[ = 0.90 \times \text{Conductance} \]

Molar conductance \( \Lambda_m \) = \[ \frac{K \times 1000}{C} \]

The experimental results indicate their nonelectrolytic nature which is consistent with the idea that the complex formation is taking place between the deprotonated schiff base and divalent metal ion.

Magnetic susceptibility measurements

The structures of various metal chelates have been supported by magnetic measurements, the magnetic moments of various transition metal complexes derived from Salophen and Salmphen are presented in Table V.1.
### Table V.1 - Magnetic moments of Schiffbase complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Magnetic moments B.M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(II) - Salophen</td>
<td>6.05</td>
</tr>
<tr>
<td>Fe(II) - (Salophen)(H₂O)₂</td>
<td>0.97</td>
</tr>
<tr>
<td>Fe(II) - (Salmphen)(H₂O)₂</td>
<td>2.81</td>
</tr>
<tr>
<td>Co(II) - (Salophen)₂O₂</td>
<td>0.79</td>
</tr>
<tr>
<td>Co(II) - Salmphen</td>
<td>2.88</td>
</tr>
<tr>
<td>Ni(II) - Salophen</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>Ni(II) - Salmphen</td>
<td>3.57</td>
</tr>
<tr>
<td>Cu(II) - Salophen</td>
<td>1.34</td>
</tr>
<tr>
<td>Cu(II) - Salmphen</td>
<td>1.92</td>
</tr>
</tbody>
</table>
Mn(II) complexes

Compounds of bivalent manganese are known in both high spin or low spin states. The high spin compounds are expected to show magnetic moments very close to the spin only value (5.92 B.M) and independent of temperature. Irrespective of whether the ligand arrangement is octahedral, tetrahedral or lower symmetry, the magnetic moments of Mn(II) compounds with schiff bases range from 4.74 BM to upto 5.74 BM. at room temperature. Mn-phthalo-cyanin complex which is known to be square planar has a magnetic moment value of 4.5 B.M. The magnetic moments of some tetrahedral complexes are also close to 5.9 B.M. This magnetic moment value of manganese compounds is independent of the structure.

Mn-Salophen complex has magnetic moment value of 6.05 B.M. and found it to have no significant antiferromagnetism, and can be best formulated as monomeric species. As the magnetic moment value of this complex corresponds to high spin Mn(II) compound, the oxidation state of manganese in Mn-Salophen is only +2 and not +3.

Fe(II) complexes

Fe(II)-Salophen shows very low magnetic moment (0.97 B.M) essentially corresponds to low spin Fe(II) complex. This complex undergoes antiferro magnetic interaction.
The obtained magnetic moment value (2.81 B.M) of Fe(II)-Salophen complex approaches the spin only value of high spin octahedral complex.

**Co(II) complexes**

The cobalt complex of Salophen has a magnetic moment value of 0.79 B.M. It may be assumed that Co(III) complex is formed by the aerobic reaction of CoCl₂ with Salophen in aqueous methanolic medium. A number of binuclear complexes of cobalt in which the two metal atoms are bridged by a -O₂- group are paramagnetic, giving magnetic moments near or rather below the spin only value for one unpaired electron (1.73 B.M) at room temperature⁶. These cobalt complexes have been preferably regarded as derivatives of trivalent cobalt with the unpaired electron located on the -O₂- group.

The magnetic moment value (2.88 B.M) of Co(II)-Salphen complex suggests a spin paired square planar geometry. The magnetic properties of square planar Co(II) complex have not been accurately predicted in terms of spin orbit coupling and orbital contribution. According to Figgis the moments rather higher than the spin only value (1.73 B.M) are expected⁷. These compounds show a magnetic moments of about 2.22 to 2.90 B.M. In the case of cobalt(II)-phthalocyanin complex which is known to have
square planar configuration, the observed moment is higher than spin only value i.e., 2.73 B.M. The magnetic moment value of this complex is well comparable to either methoxy or ethoxy derivatives of Co(II)-Salen.

**Ni(II) complexes**

Ni(II) complex of Salophen is diamagnetic and possess square planar configuration. Ni(II)-Salmphen complex has a magnetic moment value of 3.57 B.M which correspond to two unpaired electrons and is independent of temperature. It is presumed that due to longer chain length and less steric strain, the nickel-nitrogen bond has been changed its conformation from normal square planar configuration and hence the complex prefers to have tetrahedral structure.

**Cu(II) complexes**

The low magnetic moment for Cu(II)-Salophen complex (1.34 B.M) shows square planar geometry. The low magnetic moment may be due to the presence of short metal-metal distance which permit a direct and partial spin-spin coupling accompanied by super exchange mechanism. Cu(II)-Salmphen possess a magnetic moment value of 1.92 B.M indicating that cupric ions assumed to be too far apart for direct spin exchange and are at opposite ends of 12-membered ring. This further suggests that an increase in chain length causes some distortion than that of Cu(II)-Salophen and
possess tetrahedral (distorted square planar) structure.

**Electronic spectral data**

The electronic spectral studies have been used for the structural characterization of transition metal complexes. Electronic spectral data of various metal complexes of Salophen and Salmphen are given in Table V.2.

**Mn(II) complexes**

The crystal field spectra of Mn(II) complexes with organic ligands is not very clear as even the very weak tail of ligand absorption into the visible region is often enough to mask d-d bands. The spectra of tetrahedral Mn(II) complexes fall into 3 well defined regions, because of fairly low Dq values (\( \geq 300 \text{ cm}^{-1} \)) involved. Thus transitions to the components of the \( ^4G \) term lie between 21000-24000 cm\(^{-1} \) those to \( ^4P \) and \( ^4D \) between 26000-29000 cm\(^{-1} \) and those to \( ^4P \) lie between 35000-38000 cm\(^{-1} \). The electronic spectra of Mn(II) Salophen in toluene solvent shows bands at 21280, 29850 and at 34250 cm\(^{-1} \) indicating the presence of tetrahedral structure\(^{12} \) for this complex. In the presence of pyridine (Fig. V.3) a band at 21280 cm\(^{-1} \) observed in toluene is disappeared indicating the possible existence of pyridine adduct in this solvent.

**Fe(II) complexes**

Fe(II) complexes of Salophen and Salmphen exhibit
Fig. V, 3. Electronic spectra of Mn-Salophen complex; (1) in toluene and (2) in pyridine.
TABLE V.2 - Electronic spectral data of transition metal complexes of Salophen and Salmphen

<table>
<thead>
<tr>
<th>Complex</th>
<th>Spectral bands($\nu$ cm$^{-1}$; $\varepsilon$, $L$-mol$^{-1}$ cm$^{-1}$)</th>
<th>Toluene</th>
<th>Pyridine</th>
<th>Dimethylformamide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda$(nm)</td>
<td>$\nu$</td>
<td>$\varepsilon$</td>
<td>$\lambda$(nm)</td>
</tr>
<tr>
<td>Mn(II)-Salophen</td>
<td>470</td>
<td>21275</td>
<td>(0132)</td>
<td>335</td>
</tr>
<tr>
<td></td>
<td>335</td>
<td>29850</td>
<td>(1127)</td>
<td>336</td>
</tr>
<tr>
<td></td>
<td>292</td>
<td>34245</td>
<td>(3100)</td>
<td>304</td>
</tr>
<tr>
<td>Fe(II)-(Salophen)(H$_2$O)$_2$</td>
<td>390</td>
<td>25640</td>
<td>(400)</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>302</td>
<td>33115</td>
<td>(695)</td>
<td>334</td>
</tr>
<tr>
<td></td>
<td>292</td>
<td>34245</td>
<td>(742)</td>
<td>320</td>
</tr>
<tr>
<td>Fe(II)-(Salmphen)(H$_2$O)$_2$</td>
<td>345</td>
<td>28985</td>
<td>(17285)</td>
<td>344</td>
</tr>
<tr>
<td></td>
<td>302</td>
<td>33115</td>
<td>(13842)</td>
<td>344</td>
</tr>
<tr>
<td>(Co(II)-Salophen)$_2$O$_2$</td>
<td>390</td>
<td>25640</td>
<td>(2750)</td>
<td>397</td>
</tr>
<tr>
<td></td>
<td>296</td>
<td>33785</td>
<td>(3825)</td>
<td>314</td>
</tr>
<tr>
<td></td>
<td>296</td>
<td>33785</td>
<td>(3825)</td>
<td>314</td>
</tr>
<tr>
<td>Co(II)-Salmphen</td>
<td>358</td>
<td>27935</td>
<td>(15675)</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>342</td>
<td>29240</td>
<td>(16760)</td>
<td>340</td>
</tr>
<tr>
<td></td>
<td>302</td>
<td>33115</td>
<td>(15140)</td>
<td>275</td>
</tr>
</tbody>
</table>

Contd.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Spectral bands (ν, cm⁻¹; ε, 1. mol⁻¹ cm⁻¹)</th>
<th>Toluene</th>
<th>Pyridine</th>
<th>Dimethylformamide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ (nm) ν ε</td>
<td></td>
<td>λ (nm) ν ε</td>
<td>λ (nm) ν ε</td>
</tr>
<tr>
<td>Ni(II)-Salophen</td>
<td>490 20410 (2750) 956 11680 (71)</td>
<td></td>
<td>480 20830 (3300) 475 21050 (6411)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>460 21740 (2230) 440 22730 (3750)</td>
<td></td>
<td>380 26320 (8760) 376 26660 (21860)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>385 25970 (8320)</td>
<td></td>
<td>368 27170 (10365)</td>
<td></td>
</tr>
<tr>
<td>Ni(II)-Salmphen</td>
<td>440 22730 (2450) 350 28750 (8000)</td>
<td>350 28750 (8000)</td>
<td>345 28990 (16570)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>370 27030 (8820) 368 27170 (10365)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(II)-Salophen</td>
<td>435 23000 (22220) 429 23310 (21465)</td>
<td></td>
<td>422 23695 (24965)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>310 32260 (22970) 310 32260 (23195)</td>
<td></td>
<td>306 32680 (30855)</td>
<td></td>
</tr>
<tr>
<td>Cu(II)-Salmphen</td>
<td>330 30305 (1710) 330 29850 (1516)</td>
<td></td>
<td>340 29410 (16830)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>290 34480 (4570) 306 32680 (1430)</td>
<td></td>
<td>275 36365 (25055)</td>
<td></td>
</tr>
</tbody>
</table>
intense charge transfer spectra (Table V.2) predominantly of the M → L class. The intense red colour associated with any Fe(II) complexes of unsaturated amines arises from this source.

Co(II) complexes

The electronic spectra of cobalt complexes have been studied in toluene and pyridine. The former solvent has no coordinating ability while pyridine has ability to coordinate cobalt. Typical electronic spectra of Co-Salophen complex is given in Fig. V.4. Co-Salophen complex in pyridine solvent shows an intense band centred at 25190 cm⁻¹ with a shoulder around 21740 cm⁻¹. Whereas in toluene solvent it exhibits maximum absorbance at 25640 cm⁻¹ with some detectable bands at 19230 cm⁻¹ and 17240 cm⁻¹.

The electronic spectra of metal dioxygen complexes have been studied in detail by Lever and Gray¹³. They have presented a reasonable picture of charge transfer transitions involving d⁶ low spin metal centres and end-on super oxo, end-on bridging peroxo and side-on peroxo groups. However, the electronic spectra of cobalt dioxygen complexes could not unequivocally identify the existence of peroxo and superoxo bridging species.

Cobalt-Salophen complex, however, shows bands at 25640, 19230 and 17240 cm⁻¹ in toluene. The first band
Fig. V, 4. Electronic spectra of Co-Salophen complex; (1) in toluene and (2) in pyridine.
bas been assigned as a charge transfer transition from the $\pi h^*$ orbital to an appropriate $d \sigma^*$ level on the metal centre. Another weak features observed at 19230 and 17240 cm$^{-1}$ have been attributed to a $d\pi \rightarrow \pi V^*$ charge transfer transitions, possibly in favour of superoxo di-Co(III) species. The $d\pi \rightarrow \pi V^*$ charge transfer transition can be considered as $\pi V^* \rightarrow d\sigma^*$ transition. The $\pi h^* \rightarrow d \sigma^*$ and $\pi h^* \rightarrow \pi V^*$ transitions are thus detectable in Co-Salophen complex. In pyridine solvent only $\pi h^* \rightarrow d \sigma^*$ charge transfer transition is observed for this complex.

The electronic spectra of Co-Salophen complex shows only one band centred at 29400 cm$^{-1}$ that corresponds to $\pi h^* \rightarrow d \sigma^*$ charge transfer transition. The orbital energy level diagram for a planar cis Co(II)L$_2$O$_2$ of $C_{2v}$ symmetry is given in the Fig. V.5.

\[
\begin{align*}
\Delta 4 & \quad d_{x^2-y^2} \quad \text{b1} \\
\Delta 3 & \quad d_{xy} \quad \text{a1} \\
\Delta 2 & \quad 1/J_2 (d_{xz} + d_{yz}) \quad \text{b2} \\
\Delta 1 & \quad 1/J_2 (d_{xz} - d_{yz}) \quad \text{a2} \\
\quad & \quad d_{z^2} \quad \text{a1}
\end{align*}
\]

Fig. V.5.
Due to the presence of strong charge transfer band a clear absorption band around 15000 cm\(^{-1}\) could not be observed in the spectrum of this complex in analogy\(^{16,17}\) with other square planar complexes.

**Ni(II) complexes**

Ni-Salophen complex display visible band at 20410 cm\(^{-1}\) possibly due to \(^{1}A_{1g} \rightarrow ^{1}B_{1g} \rightarrow (\gamma_2)\) transition. Typical absorption spectra of Ni-Salophen in toluene and pyridine are presented in Fig. V.6. The electronic spectra of Ni-Salophen complex in pyridine solvent shows shifts in maximum absorbance with increased molar absorptivity indicating the existance of 6-coordinate nickel in solution. This view is also supported by the appearance of a new band around 10500 cm\(^{-1}\) (\(\varepsilon \approx 70\)) in the electronic spectra of this complex in pyridine.

\[
\text{Ni(II)-TSB} + 2 \text{C}_5\text{H}_5\text{N} \rightleftharpoons \text{Ni(II)-TSB.2C}_5\text{H}_5\text{N}
\]

... (1)

where TSB is Salophen. The pyridine adduct of Salophen has been isolated from pyridine solvent. Spectral measurements in toluene solution indicate that the reaction (1) is reversed.

Typical tetrahedral complexes shows bands at 16000, 8000 and 4000 cm\(^{-1}\) corresponding to \(^{3}T_1 \rightarrow ^{3}T_1 (p) \ldots (\gamma_3)\),
Fig. V.6. Electronic spectra of Ni-Salophen in toluene and pyridine
transitions respectively. In present nickel complexes strong bands around 20000 cm\(^{-1}\) are observed due to \(3T_1(F)\rightarrow 3T_1(P)\) transition\(^{18}\). Due to strong \(\pi\)-electron delocalization of aromatic rings charge transfer bands in these complexes shadows the \(\nu_2\) transitions and could not be detected.

**Cu(II) complexes**

Two bands of equal intensity are observed in the electronic spectrum of Cu(II) - Salophen complex at 23000 and 32260 cm\(^{-1}\). The former band may be due to \(2B_{1g}\rightarrow 2A_{1g}\) transition confirming the presence of square planar geometry\(^{19,20}\). The latter band can be assigned to Cu(II) \(\rightarrow\) phenolate \(\nu_1^*\) transition\(^{21}\). In the electronic spectra of Cu(II) - Salophen complex in toluene solvent a clear shoulder band is observed at 25000 cm\(^{-1}\) which is absent in pyridine solvent (Fig. V.7).

**Cu(II) - Salphen complex shows a strong band at 34480 cm\(^{-1}\) and moderately strong band at 30305 cm\(^{-1}\) in toluene solvent. Whereas the same complex in pyridine solvent shows only latter band. The latter band has been considered as a characteristic of the binuclear nature of copper complexes\(^{22}\).**
Fig. V.7. Electronic spectra of Cu-Salophen in toluene and pyridine
Infrared spectral analyses

Infrared spectral bands (in KBr) of ligands (Salophen and Salmphen) and their metal complexes are presented in Table V.3. Monomeric schiff bases of salicylaldehyde are prepared by the condensation of salicylaldehyde and ortho phenylenediamine or metaphenylenediamine to get the corresponding schiff bases. The IR spectra of free ligands has been compared to the IR spectra of metal complexes so as to assign the coordinating atoms present in respective complexes. Free ligands show no absorption bands due to the amine and carbonyl groups indicating the condensation to obtain schiff bases. Salophen and Salmphen show broad bands at 3450 and 3435 cm\(^{-1}\) are essentially due to the O-H stretching vibration indicating the presence of weak hydrogen bond as a part of a resonating ring system\(^{23}\).

\[ \text{I} \]

\[ \text{II} \]
TABLE V.3 - Important infra-red spectral bands (cm$^{-1}$) of Schiff bases and their complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{\text{OH}}$</th>
<th>$\nu_{\text{C=N}}$</th>
<th>$\nu_{\text{C-O}}$</th>
<th>$\nu_{\text{M-N}}$</th>
<th>$\nu_{\text{M-O}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salophen</td>
<td>3450(B)</td>
<td>1611(S)</td>
<td>1115(S)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn(II) - Salophen</td>
<td>-</td>
<td>1608(S)</td>
<td>1127(W)</td>
<td>541(W)</td>
<td>332(W)</td>
</tr>
<tr>
<td>Fe(II) - Salophen</td>
<td>3066</td>
<td>1609(S)</td>
<td>-</td>
<td>439(M)</td>
<td>338(W)</td>
</tr>
<tr>
<td>Co(II) - Salophen</td>
<td>-</td>
<td>1610(S)</td>
<td>1121(S)</td>
<td>467(M)</td>
<td>360(W)</td>
</tr>
<tr>
<td>Ni(II) - Salophen</td>
<td>-</td>
<td>1609(S)</td>
<td>1126(S)</td>
<td>409(M)</td>
<td>335(M)</td>
</tr>
<tr>
<td>Cu(II) - Salophen</td>
<td>-</td>
<td>1609(S)</td>
<td>1127(S)</td>
<td>508(W)</td>
<td>323(M)</td>
</tr>
<tr>
<td>Salmphen</td>
<td>3435(B)</td>
<td>1622(S)</td>
<td>1107(M)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(II) - Salmphen</td>
<td>3057</td>
<td>1619(S)</td>
<td>1149(S)</td>
<td>478(M)</td>
<td>340(M)</td>
</tr>
<tr>
<td>Co(II) - Salmphen</td>
<td>-</td>
<td>1619(S)</td>
<td>1150(S)</td>
<td>477(M)</td>
<td>325(M)</td>
</tr>
<tr>
<td>Ni(II) - Salmphen</td>
<td>-</td>
<td>1619(S)</td>
<td>1150(S)</td>
<td>478(M)</td>
<td>335(M)</td>
</tr>
<tr>
<td>Cu(II) - Salmphen</td>
<td>-</td>
<td>1607(S)</td>
<td>1150(S)</td>
<td>539(M)</td>
<td>334(M)</td>
</tr>
</tbody>
</table>
Though resonance requires that each 6-membered ring including the replaceable hydrogen be coplanar with the phenyl ring, the two bicyclic ring system cannot be in the same plane because of the steric hindrance and the electrostatic repulsion of N....HO groups. These factors accounts the presence of weak hydrogen bonds in Salophen or Salmphen. In the chelates, both rings can be fixed in the same plane without steric hindrance by the central metal which usually prefers to have a square planar coordination with the tetradequate ligands.

Salophen and Salmphen show their characteristic azomethine stretching frequency at 1611(S) and 1622(S) cm$^{-1}$ respectively. These stretching vibrations are shifted to lower frequency by (5 cm$^{-1}$ to 15 cm$^{-1}$, in metal complexes, suggesting coordination of schiff bases through azomethine nitrogen$^{24}$. The strong band of the phenolic C-O stretching vibrations are observed at 1115 and 1107 cm$^{-1}$ in Salophen and Salmphen ligands respectively. In all complexes, these bands due to C-O stretching vibration are shifted towards higher frequency on complexation indicating that oxygen atom of hydroxy group present in schiff bases takes part in complex formation.

In IR spectra of all complexes the $\gamma$O-H band disappers showing that Salophen and Salmphen have been deprotonated$^{25}$ on complex formation.
In Fe(II) complexes of Salophen and Salmphen bands at 3066 and 3057 cm\(^{-1}\) respectively are assigned to \(\nu O-H\) stretching of coordinated water.

Co(II)-Salophen complex shows a medium band at 1149 cm\(^{-1}\) which superimposes the C-O stretching vibration present in this complex. However, some other Co(II) Schiff base complexes loose coordinated oxygen with raise in temperature. Additional support for this assignment comes from the observation that gaseous oxygen has a Raman active absorption at 1555 cm\(^{-1}\) and that O-O stretching of solid H\(_2\)O\(_2\) occurs at 1380 cm\(^{-1}\). This makes our assignment at 1149 cm\(^{-1}\) a reasonable one, since we would expect the O-O stretching frequency to be shifted to lower energy upon coordination. Infrared spectra of some representative Schiff base complexes are given in Fig. V.8a and V.8b.

Metal ligand vibrations are difficult to assign on an empirical basis, since their frequencies are sensitive to both the metal and ligand and often couple with low frequency modes in metal chelate compounds. However, the coordination through the azomethine nitrogen and bonding between phenolic oxygen and metal are further corroborated by the appearance of additional M-N and M-O vibrations in the regions (Table V.3) 541-409 and 362-320 cm\(^{-1}\) respectively, in the far IR spectra of metal complexes.
Fig. V, 8a. IR spectra of schiff base metal complexes.
Fig. V,8b. IR spectra of Schiff base metal complexes
Electron spin resonance spectra

Cu(II) ion has in its outermost shell nine d electrons, a configuration which can be considered equivalent to one unpaired "hole". In square planar or tetragonally elongated geometry (ground state $d_{x^2-y^2}$) the $g$ factors deviate from the free electron value (2.0023) according to the following equations

$$g_{||} = 2.0023 \left(1 - \frac{8 \alpha^2 \lambda}{\Delta_{xy}}\right)$$
$$g_{\perp} = 2.0023 \left(1 - \frac{2 \alpha^2 \lambda}{\Delta_{xz}}\right)$$

where $\alpha$ is the coefficient of $d_{x^2-y^2}$ in the molecular orbital containing d unpaired electron, $\lambda$ is the spin orbit coupling constant (-828 cm$^{-1}$ for the free Cu(II) ion), $\Delta_{xy}$ and $\Delta_{xz}$ are the energy separations of the $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals relative to the ground state. The ESR hyperfine structure is due to the interaction of the unpaired electron with the $^{63,65}$Cu nuclei, where $I = 3/2$, and has contribution from Fermi contact, dipolar nuclear spin - electron spin, and nuclear spin - electron orbit mechanisms.

The copper(II) ion with a $d^9$ configuration, has an effective spin of $S = 1/2$ and associated spin angular momentum of $m_s = \pm 1/2$ leading to a doubly degenerate spin energy state in the absence of a magnetic field. On application of a magnetic field this degeneracy is removed and
transitions occurs between the two levels given by the condition \( h \nu = g \beta H \). For a free electron, the Lande splitting factor \( g \) has the value 2.0023, whilst for an electron in crystal field the value can differ from 2.0023. The Lande splitting factor (\( g \)) is only isotropic in a cubic environment, in axial and rhombic crystal field, two and three different \( g \) values are obtained. The expressions for these are summarized in a recent review. In practice the observed crystal \( g \)-values for copper(II) complexes will be determined by the symmetry of ligand field about the copper(II) ion and whether the tetragonal axes of the copper(II) ion present in the unit cell are aligned parallel. If all the tetragonal axes are aligned parallel then the crystal \( g \) values accurately reflect the local copper(II) ion environment.

The nature of the copper(II) site in \( \text{N}_2\text{O}_2 \) coordination environment(III) has received much attention primarily due to the resemblances with galactose oxidase. Galactose oxidase is a copper containing enzyme which catalyzes the conversion of primary alcohols to the corresponding aldehydes.

\[
\begin{array}{c}
\text{X} \\
\text{N} | \text{N} \\
\text{Cu} \text{---} \text{X} \\
\text{O} \quad \text{O}
\end{array}
\]

(III)
The complex, N,N'-ethylene bis(trifluoroacetylacetoneiminato)-
copper(II) was proposed as a model of the equatorial coordination of the copper(II) in galactose oxidase. Results obtained in ESR studies indicate that the model is an appropriate one for galactose oxidase.

Electron spin resonance spectra of copper(II) - Salophen in polycrystalline state is presented in Fig. V.9 ESR spectrum of copper(II) - Salophen is isotropic in nature indicating that this complex has a lower symmetry than octahedral structure containing grossly misaligned axes. Copper(II)-Salophen complex in polycrystalline state has an isotropic g-value of 2.079.

Solution spectra (Fig.V.10a&b) provide a measure of the average or isotropic g value ($g_i^i$) as well as the isotropic hyperfine structure constant ($A_o^{Cu}$) and the isotropic ligand hyperfine structure constant ($A_o^{N}$). Employing data obtained from the ESR spectra of solids and solutions the following relationship can be verified.

$$g_{av} = \frac{1}{3} (g_i^i + 2 g_\perp)$$

$$A_{av} = \frac{1}{3} (A_i^i + 2 A_\perp)$$

This verification leads to the evaluation of the spin Hamiltonian for the copper(II) ion in tetragonal crystal field.
Fig. V,9. ESR spectrum of Cu-Salophen in polycrystalline state at room temperature.
Fig. V,10,a. Cu(II)-Salophen in DMF at room temperature.
Fig. V,10,b.  Cu(II)-Salophen in DMF at -120°C.
The spin Hamiltonian parameters have been calculated and presented in Table V.4. Kivelson and Neiman\textsuperscript{33} have shown that $g_{||}$ is a moderately sensitive function for indicating covalency. For ionic environments $g_{||}$ is normally 2.3 or larger. For covalent compounds $g_{||}$ should be less than 2.3. Copper(II)-Salophen complex has a $g_{||}$ value of 2.29 indicating the presence of covalent bonds in complex formation. According to Hathway\textsuperscript{30,34} two types of axial spectras are observed depending on the value of lowest $g$ factor; 1) Lowest $g > 2.04$; such a spectrum can be observed for a copper(II) ion in axial symmetry with all the principal axes aligned parallel and would be consistent with elongated tetragonal, octahedral and square planar stereo-chemistries. In such axial spectra, the $g$ values are related by

$$G = \frac{g_{||} - 2}{g_{\perp} - 2} \leq 4.0$$

Adherence to this expression indicates the presence of a $d_{x^2-y^2}$ ground state. If $G > 4.0$, then the local tetragonal axes are aligned parallel or only slightly misaligned. If $G < 4.0$, significant exchange coupling is present and the misalignment is appreciable.
### TABLE V.4 - Spin Hamiltonian and orbital reduction parameters of Cu-Salophen complex (at -120°C).

<table>
<thead>
<tr>
<th></th>
<th>g_up</th>
<th>g_down</th>
<th>g</th>
<th>A_up</th>
<th>A_down</th>
<th>A*</th>
<th>d-d</th>
<th>K^2_up</th>
<th>K^2_down</th>
<th>G</th>
</tr>
</thead>
<tbody>
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<td>(ave)</td>
<td>(ave)</td>
<td>(ave)*</td>
<td>(ave)*</td>
<td>band**</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2.24</td>
<td>2.05</td>
<td>2.11</td>
<td>135</td>
<td>28</td>
<td>63.6</td>
<td>23000</td>
<td>0.825</td>
<td>0.662</td>
<td>4.98</td>
<td></td>
</tr>
</tbody>
</table>

* Units x 10^{-4} cm^{-1}

** in cm^{-1}, only one peak observed.
The Cu(II)-Salophen complex gives rise to anisotropic spectrum both at room temperature and at -120°C. The room temperature (30°C) spectrum of this complex shows two peaks of small intensity towards left and another two peaks of high intensity towards right.

In square planar or elongated octahedral Cu(II) complexes the low intensity peak(s) that appear towards left correspond to $g_{||}$ component and the large intensity peak(s) towards right to $g_{\perp}$ component.

The spectrum at -120°C shows good resolution that the peaks have been further split up. In this low temperature spectrum four peaks of small intensity have been identified, which are considered to have originated from $g_{||}$ component. The $g_{||}$ component splitting into four peaks is as expected for the interaction of the unpaired electron on Cu(II) with Cu nucleus whose nuclear spin ($I$) value is equal to 3/2. That means four peaks are expected when the unpaired electron interacts with Cu nucleus and the same have been observed. These four peaks have appeared at 2655, 2845, 3035 and 3095 G.

The $g_{\perp}$ component in the low temperature spectrum shows still better resolution that more than four peaks have been observed. This indicates that the unpaired
electron not only interacts with copper nucleus but also with the nitrogens (nitrogen is magnetically active with \( I = 1 \)) associated with the complex. If the unpaired electron interacts with one Cu nucleus and two nitrogens present in the complex, altogether twenty peaks are to be observed. But the number of peaks actually observed in the \( g_{\perp} \) component of the present complex is more than four and less than twenty. This is common in practice because overlapping of narrow separated peaks results in less number of peaks being observed. However, four out of many peaks observed have been chosen which appear at 3115, 3145, 3175 and 3205 from which four \( g_{\perp} \) values have been calculated.

The calculated \( g_{||} \) values are 2.44, 2.28, 2.14, 2.10 and 2.24 may be designated as \( g_{||}(1) \), \( g_{||}(2) \), \( g_{||}(3) \) and \( g_{||}(4) \) respectively. The \( g_{||}(\text{average}) \) gives a value of 2.24. Similarly \( g_{\perp}(1) \), \( g_{\perp}(2) \), \( g_{\perp}(3) \) and \( g_{\perp}(4) \) have been calculated and respectively found to be 2.08, 2.06, 2.04, 2.02 with \( g_{\perp}(\text{average}) \) value of 2.05.

The \(|g|\) is calculated using the following equation

\[
|g| = \frac{g_{||} + 2g_{\perp}}{3}
\]

and found to be 2.11.
The g tensor values of Cu(II) complexes can be used to derive the ground state. In an elongated octahedral and square planar complexes, the unpaired electron lies in \( d_{x^2-y^2} \) orbital giving \( ^2B_{1g} \) as the ground state with \( g|| > g\perp \). In a compressed octahedron, on the other hand, the unpaired electron lies in \( d_{z^2} \) orbital giving \( ^2A_{1g} \) as the ground state with \( g|| < g\perp \). For the present complex, the \( g|| > g\perp \) indicating that the unpaired electron lies predominantly in the \( d_{x^2-y^2} \) orbital. The \( g|| \) value for the present complex is less than 2.3 suggesting covalent character of the metal ligand bond.

The axial symmetry parameters \( G \) is shown to be a measure of exchange interaction between copper centres in polycrystalline solids. If the \( G \) value is higher than 4, the exchange interaction is negligible, while \( G \) values of less than 4 indicate considerable interaction. This value for the present complex is 4.98, which indicates no interaction. The Hamiltonian parameters of this complex are included in Table V.4. The \( K_{||} > K_{\perp} \) for the present complex indicates out of plane Pi-bonding.
The dimeric nature of copper(II)-Salmphen complex was first discovered by Pfeiffer and Pfitzner\textsuperscript{35}. The molecular structure is depicted in Fig. V.11. The coordination geometry at each copper ion is almost midway between cis-planar and tetrahedral. Jeter and Hatfield\textsuperscript{36} studied the EPR characteristics of this complex. Later Hendrickson et al.\textsuperscript{37} presented improved EPR results on this complex.

In order to have verification and comparison with EPR studies of copper(II)-Salophen complex, ESR studies are extended to this complex. The X-band EPR spectrum for the pure powdered solid exhibited a very strong absorption near 3150 gauses while its X-band spectrum for a dimethylformamide liquid nitrogen temperature glass show 6 peaks in analogy\textsuperscript{37} with previous observation.

\textbf{\textsuperscript{1}H NMR spectra}

In the nuclear magnetic resonance spectra of nickel complexes, multiplet signals correspond to aromatic protons and singlet signal at low field strength indicates the presence of -N=C-H protons. \textsuperscript{1}H NMR (\textit{d}_6-DMSO-Me\textsubscript{4}Si) Ni-Salophen, 6.35-7.25 (m, 12H, phenyl); 8.25 (S, 2H, \textsuperscript{=}CH): Ni-Salmphen, 6.93-7.85 (m, 12H, phenyl); 8.60 (S, 2H, \textsuperscript{=}CH). All NMR signal positions are in ppm.
Fig. V,11. Molecular structure of Cu(II)-Salmphen.
Structures

Based on the appreciation of the results obtained in elemental analyses, conductivity measurements, magnetic susceptibility studies, electronic, infrared, (NMR and ESR) spectral studies, octahedral structure (IV) for [Fe(Salophen)(H₂O)₂] and [Fe(Salmphen)(H₂O)₂] complexes; superoxo bridged structure (V) for [(Co-Salophen)₂O₂] complex; square planar geometry (VI) for Ni-Salophen complex; dimeric structure for (Cu-Salophen)₂ complex and binuclear and tetrahedral structure (VIII) in which two metal centers are separated far apart for Cu-Salmphen and Ni-Salmphen are assigned.
Where $M = \text{Cu or Ni}$
REFERENCES


6 L. Malatesta, Gazzetta, 72 (1942) 287.


