CHAPTER IV

LUIJNALDINE
Chemically, an alkaloid usually forms an integral part of a cyclic structure. One of the simplest alkaloids, quinaldine is 2-methyl substituted quinoline (I).

![Quinaldine](image)

Fig. (1).

A little attention has been paid towards the metal-quinaldine complexes. Addition compounds of Cr (VI) oxide with quinaldine and other heterocyclic amines, have been reported by Sisler et al. Ludwig & Wittmann studied the composition of Ni (II) complexes of many heterocyclic amines along with 2-methyl quinoline, spectrophotometrically.

Reaction of bis (salicylato) diaquo copper (II) complexes with nitrogen containing compounds and aromatic amines were studied by Smogrovic. A simple method for preparation of complex compounds was described.

Complexes of niobium oxychloride and titanium tetra-chloride with 2-methyl quinoline were synthesised in benzene. The colored complexes of nickel (II) were prepared by
Majumdar et al.\textsuperscript{5} and mixed ligand complexes of indium trichloride were reported by Sutton.\textsuperscript{6} These complexes behave as uni-univalent electrolyte in HCl. Oxomolybdenum complexes with quinoline-2 and 6 carboxylic acid were prepared and their structure detected. Complexes were paramagnetic and recorded susceptibility was low as 0.73 BM.

Magnetic properties and structure of some cyanate copper (II) complexes with 2 and 4-methyl quinoline and 3-isoquinoline are reported. The susceptibility of Cu\textsubscript{2}I\textsubscript{2} almost follow the curies law and their magnetic moments have values in the upper region for the distorted octahedral complexes of Cu (II). Cu is coordinated in equitorial position by 6 atoms from the NCC groups and 2 in the axial position by 20 atoms for the NCC groups. The NCC group appear as bridge which complete the configuration of the Cu ion with very weak band through oxygen. Their magnetic moments have usually more than 3 BM. Two spin free octahedral complexes of Ni(II), NiL\textsubscript{4}Cl\textsubscript{2} and NiL\textsubscript{4} (SCN)\textsubscript{2}, where L is 2-methyl quinoline, are isolated and characterised.\textsuperscript{9} They undergo thermal decomposition of NiL\textsubscript{4}Cl\textsubscript{2} and NiL\textsubscript{4} (SCN)\textsubscript{2} which can be converted back to tetraakis compounds on treatment with excess ligand. The infra red spectra of thiocyanato compounds indicate the presence of terminal thiocyanato group.
Rao et al.\textsuperscript{10} prepared mixed ligand complexes of nickel acetyl acetone. The complexes were characterised by elemental analyses, conductance measurement, magnetic measurement and infra red of complexes are reported. The complexes were para magnetic and effective magnetic moment indicates the presence of 2 unpaired electrons. Eleven non-electrolytic, penta coordinated mixed ligand complexes were reported\textsuperscript{11} with zinc acetyl acetone and quinolines.

The work described in the proceeding pages consists of determination of the complexes of chlorides of Zn (II), Cd (II), Sb (III), Bi (III) and nitrate of Hg (II) with 2-methyl quinoline. The characterization of the complexes were done by elemental analyses like carbon, hydrogen and nitrogen, conductometric and potentiometric titrations, molar conductances, melting points and infra red spectra. The location of possible coordination sites has been determined on the basis of infra red spectral studies.
EXPERIMENTAL

Reagents:

The reagents used were, chlorides of Zn (II) (B.D.H. product), Cd (II) (U.S.S.R.), Sb (III) (U.S.S.A.), Bi (III) (Poland) and nitrate of Hg (II) (B.D.H.). Alkaloid quinaldine (B.D.H. England), solvents such as ethanol and dimethyl sulfoxide were purified and distilled before use.

Preparation of Complexes:

The compounds reported herein were synthesised from the solution of metal salts in ethanol and appropriate alkaloid in the same solvent. The solution of metal salt was added in the ratio of 1:2 (metal: ligand) but ligand maintained in excess with constant stirring. The precipitate was washed several times with solvent to remove excess of metal ion and ligand. The complexes were dried over vacuo for several days.

Analyses of Complexes:

The analyses of carbon, hydrogen and nitrogen were done by Microanalytical Division of I. I. T., Kanpur. The conductometric titration and conductivities of 1x10^{-3}M solution in dimethyl sulfoxide of the complexes were measured with a Philips conductivity bridge model PA 9500 using a dip type cell (cell constant 0.84) at 25°C. The infra red spectra of complexes and ligand were recorded with Perkin Elmer model 21 spectrophotometer.
in the range of 4000 cm\(^{-1}\) - 600 cm\(^{-1}\). The potentiometric titrations have been performed by Fye type potentiometer. Melting points were determined by the usual method.

**RESULTS AND DISCUSSION**

The conductometric and potentiometric titrations and elemental analyses for carbon, hydrogen and nitrogen show that interaction of quinaldine with chlorides of zinc, cadmium, antimony, bismuth and nitrate of mercury occurs in the molar ratio of 1:2 and following formulas have been established.

\[
\begin{align*}
C_{20}H_{16}Cl_2N_2Zn \\
C_{20}H_{16}Cl_2CdN_2 \\
C_{20}H_{16}Cl_2SbN_2 \\
C_{20}H_{16}HgN_4O_6 \\
C_{20}H_{16}BiCl_3N_2
\end{align*}
\]

Just like other complexes described in previous chapters, the complexes decompose when subjected for melting points.

**Molar conductances:**

The molar conductances of the complexes were recorded in dimethyl sulfoxide at \(10^{-3} M\) concentration. The molar conductances fall in the range 8.4 - 44.2 cm\(^2\) mol\(^{-1}\) cm\(^{-1}\) mole\(^{-1}\). The range
is compatible with non-electrolytes. Non-electrolytic behavior of the complexes of quinaldine with certain metal ions has been reported by Farooq & Malik\textsuperscript{12} and Ramna Rao et al\textsuperscript{13}. The range of non-electrolytes in case of complexes has been discussed before (Chapter I).

**Infra-red Spectra**

In the case of quinaldine the only position available for coordination is the heterocyclic nitrogen. In the spectra of quinaldine a strong band observed at 2955 cm\textsuperscript{-1} attributed to CH stretching vibrations\textsuperscript{14} of heterocyclic ring. The strong bands at 1527, 1597, 1576, 1506 and 1422 cm\textsuperscript{-1} may be assigned for CC and CN stretchings\textsuperscript{15}. The bands at 1392, 1321, 1233, 1156 and 1125 cm\textsuperscript{-1} (CH in plane deformation)\textsuperscript{16}, 1069, 1057, 1017 cm\textsuperscript{-1} (ring skeletal vibration) and 640, 601 and 754 cm\textsuperscript{-1} (CH out of plane deformation)\textsuperscript{17} were found in the spectra of quinaldine.

On the complexation, there is reduction in the number of bands. No change has been observed to CH stretching vibration. There is appreciable shifting in the bands of CC and tertiary nitrogen. The 1597, 1422, 1321 and 1233 cm\textsuperscript{-1} bands of quinaldine go down in frequency on coordination.
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>Formula</th>
<th>ΧC</th>
<th>ΧH</th>
<th>ΧN</th>
<th>M cm⁻¹</th>
<th>Colour</th>
<th>M. D. t °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Quinaldine</td>
<td>C₁₀H₉N₆</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Zn(0d)₂Cl₂</td>
<td>C₂₀H₁₆Cl₂₂₂₂n (59.92) (4.50) (7.14)</td>
<td>59.70</td>
<td>4.47</td>
<td>7.11</td>
<td>Light pinkish</td>
<td>&gt;250°</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Cd(0d)₂Cl₂</td>
<td>C₂₀H₁₆Cl₂Cd₂ (51.03) (3.67) (5.63)</td>
<td>50.61</td>
<td>3.61</td>
<td>5.60</td>
<td>Dark yellow</td>
<td>&gt;250°</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Sb(0d)₂Cl₃</td>
<td>C₂₀H₁₈Cl₃₂₀₃₂₃ (46.70) (3.54) (5.51)</td>
<td>45.65</td>
<td>3.50</td>
<td>5.44</td>
<td>White</td>
<td>250-50D</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Hg(0d)₂(NO₃)₂</td>
<td>C₂₀H₁₆Hg₄O₆ (40.01) (2.96) (9.20)</td>
<td>39.34</td>
<td>2.95</td>
<td>9.16</td>
<td>White</td>
<td>&gt;360°</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Bi(0d)₂Cl₃</td>
<td>C₂₀H₁₈BiCl₃₂ (41.21) (3.10) (4.69)</td>
<td>40.02</td>
<td>3.00</td>
<td>4.66</td>
<td>Finkish</td>
<td>236°</td>
<td></td>
</tr>
</tbody>
</table>

Observed values are given in parentheses.
Plate No. 37 IR Spectrum of Quinaldine
REFERENCES


13. Ref. 9.


