CHAPTER II

REAGENTS AND EXPERIMENTAL METHODS

The details regarding the various reagents employed, the procedure for the preparation of the ligands, the general method for the preparation of the complexes, and the methods used for their analysis are presented in this chapter. A brief description of the instruments used for the physico-chemical studies is also given.

REAGENTS

Metal salts: Most of the metal halides, nitrates and acetates employed for the synthesis of complexes were BDH AR grade samples. When AR samples were not available, metal salts were prepared from metal carbonates (AR) and respective acids.

Metal perchlorates were prepared from AR metal carbonates and perchloric acid (Albright and Wilson Ltd., England). The carbonates were dissolved in hot 60% perchloric acid. A slight excess of metal carbonate was used. The undissolved salt was removed by filtration; and the metal perchlorate was crystallised out. The salt obtained was recrystallised from hot water.
Iron(III) thiocyanate was prepared as follows. 30 ml of an aqueous solution of FeCl₃·6H₂O (10%) was mixed with 70 ml of an aqueous solution of KSCN (10%). The deep red iron(III) thiocyanate was extracted into an ether layer by vigorously shaking the aqueous solution with ether in a separating funnel. The ether layer was collected and dried using anhydrous calcium chloride. This solution was used for the preparation of iron(III) thiocyanate complexes.

**SOLVENTS**

**Acetone, methanol and ethanol:** Commercially available acetone, methanol and ethanol were purified by standard procedure¹⁶¹. BDH spectroscopic grade methanol was used for conductivity measurements.

**Acetonitrile and nitrobenzene:** These solvents used for the conductivity measurements were purified by repeated distillation of BDH samples over P₄O₁₀.

**4-amino-3H-pyrazol-3-one, 1,2 dihydro-1,5-dimethyl-2-phenyl (4-aminoantipyrine)**

4-amino antipyrine (BDH AR grade) was used as such for the synthesis of the ligands.
Other reagents

All other reagent used in the present study were either BDH AR, Merck GR or other analytical reagent grade chemicals.

PREPARATION AND CHARACTERISATION OF THE LIGANDS

In the course of the present study, two Schiff bases of 4-amino antipyrine were used as ligands.

1. Schiff base derived from 4-amino-3H-pyrazol-3-one, 1,2-dihydro-1, 5-dimethyl-2-phenyl (4-aminoantipyrine) and benzil [AAPyBZL].

Solutions of 0.1 mol of benzil and 0.1 mol of 4-amino antipyrine in ethanol were mixed. It was refluxed on a water bath for 2-3 hr. On cooling pale yellow crystals of schiff base were obtained. The crystals were filtered, washed with ethanol and recrystallised from hot ethanol.

2. Schiff base derived from 4-amino-3H-pyrazol-3-one, 1,2-dihydro-1, 5-dimethyl-2-phenyl (4-amino antipyrine) and pyridine-2-aldehyde. [AAPyPyAL]

Solutions of 0.1 mol of 4-amino antipyrine and 0.1 mol of pyridine-2-aldehyde in ethanol were mixed. The resulting solution was kept at room temperature for about half an hour with occasional stirring. The
solution was then poured into ice-cold water when an yellow crystalline solid separated. It was filtered, washed with ethanol and recrystallised from hot ethanol.

Analytical data of the two compounds are given in Table I.

Infrared spectra

The infrared spectra of the two compounds were taken as KBr pellets. The region, 700-1000 cm$^{-1}$ shows large number of bands. The assignments of these bands are made by comparing with the spectra of antipyrine and 4-amino antipyrine.

The assignments of bands in the case of AAPyPyAL is complicated due to the presence of two C=N groups, one within the pyridine ring and other outside the pyridine ring. The C=O vibration is observed at 1635 cm$^{-1}$. A band of medium intensity observed at 1560 cm$^{-1}$ is assigned to the vibration of azomethine group. A strong sharp band observed at 1590 cm$^{-1}$ is assigned to the vibration of the C=N group within the pyridine ring coupled with the C=C vibration. No other band is observed in the region 1500-1700 cm$^{-1}$ which can be assigned to the vibration of the C=N group within the pyridine ring.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>% of Carbon</th>
<th>% of nitrogen</th>
<th>% of hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Observed</td>
<td>Calculated</td>
<td>Observed</td>
</tr>
<tr>
<td>AAPyBZL</td>
<td>Pale yellow</td>
<td>75.94</td>
<td>75.45</td>
<td>10.10</td>
</tr>
<tr>
<td>AAPyPyAL</td>
<td>Yellow</td>
<td>69.06</td>
<td>69.86</td>
<td>18.65</td>
</tr>
</tbody>
</table>
In the IR spectrum of AAPyBZL, a very strong broad band is observed at 1645 cm\(^{-1}\). The compound has two C=O groups and it appears that both the carbonyl groups absorb almost in the same region, 1645 cm\(^{-1}\). The broadness of the band may be due to the overlap of the two bands. Another band of medium intensity observed at 1580 cm\(^{-1}\) is assigned to the vibration of the azomethine group. No other prominent band is observed in the region 1500-1700 cm\(^{-1}\).

NMR spectra

In the NMR spectra of the compounds, the signal of C-CH\(_3\) group of pyrazolone ring appears as a sharp singlet (3H) in the region \(\delta 2.39-2.50\). The N-CH\(_3\) signal is observed as another singlet in the region \(\delta 3.10-3.20\). The aromatic protons of the compounds appear as multiplet between \(\delta 6.97-8.42\). A detailed assignment of the aromatic proton signals is not attempted. The azomethine proton signal of AAPyPyAL appears as a singlet at \(\delta 9.7\).

Mass spectra

The mass spectra of both the compounds were recorded with the aim of finding out the molecular mass. No attempt is made to study the mechanism of fragmentation of
the compounds. Molecular ion peaks are observed in both cases. For the compound AAPyBZL it is observed at m/e 395, with an abundance percentage of 27.7. The base peak is observed at m/e 290. This fragment corresponds to $[\text{P-C}_6\text{H}_5\text{CO}]^+$. The peak due to $[\text{C}_6\text{H}_5\text{CO}]^+$ is observed at m/e 105 (Abundance 51.3%).

For the compound AAPyPyAL, the base peak is observed at m/e 121. This is due to the ion $[\text{C}_6\text{H}_5^-\text{N}^+-\text{NHCH}_3]$, which results from the fragmentation path centered on the pyrazole nucleus\textsuperscript{162}. Another peak noticed at m/e 172 with an abundance of 96.7% is due to the ion $[\text{P-(C}_6\text{H}_5^-\text{N=NCH}_3)]^+$. The molecular ion peak has an abundance of 64.3% and is observed at m/e 292.

The spectral and analytical studies show that the compounds have the structures I and II.
PREPARATION OF THE COMPLEXES

The following general procedure was employed for the preparation of the complexes. To a metal salt solution in ethanol, methanol or acetone, the ligand solution in ethanol or methanol was added. The metal ligand ratio was kept at about 1:1 or 1:2, with the ligand in slight excess. In most cases a colour change was observed, indicating the complex formation. Most of the complexes separated only after refluxing the mixture for about 1-2 hr. The solid complexes were filtered and washed with the solvent used. When a pasty mass was formed, it was repeatedly stirred with ether till a solid separated. All the complexes were dried over anhydrous calcium chloride in a desiccator.

ANALYSIS OF THE COMPLEXES

1. Estimation of halides and perchlorate

For the estimation of halides, the complexes were carefully decomposed with AR sodium carbonate in a nickel crucible at 450 + 20°C. The contents of the crucible were extracted with water and acidified with sufficient AR nitric acid to decompose the excess carbonate. The halides were then estimated by Volhard's method.$^{163}$
Perchlorate was estimated by Kurz's method\textsuperscript{164}. The complex was heated with excess sodium nitrite at $500 \pm 20^\circ$C, so that perchlorate is reduced to chloride. The residue left was extracted with water and the chloride in the solution was estimated by Volhard's method\textsuperscript{163}.

Standard solutions of silver nitrate and ammonium thiocyanate were prepared as described by Vogel\textsuperscript{163}.

2. Estimation of acetate and nitrate

The percentage of nitrate or acetate was indirectly fixed by carrying out elemental analysis for carbon, hydrogen and nitrogen by microanalytical methods. Microanalysis were done at CDRI, Lucknow.

3. Estimation of thiocyanate

Sulphur in thiocyanate complexes was oxidised to sulphate with concentrated nitric acid and bromine. Sulphate was then estimated as barium sulphate\textsuperscript{163}

4. Estimation of metals

The complexes were decomposed with concentrated nitric acid or concentrated sulphuric acid and a few drops
of perchloric acid. The resulting solutions were evaporated to dryness and the residue extracted with water. The aqueous solutions thus obtained were used for estimation.

Cobalt was estimated gravimetrically. From nearly neutral solution of cobalt, the metal was precipitated as cobalt pyridine thiocyanate\textsuperscript{163}.

Copper was estimated iodometrically by the addition of KI and subsequent titration of liberated iodine by standard thiosulphate solution\textsuperscript{163}.

Nickel was determined as dimethyl glyoximate\textsuperscript{163}.

Spectrophotometric procedure was adopted for the estimation of manganese. Weighed quantity of the manganese complex was digested with concentrated sulphuric acid and perchloric acid. The clear solution was transferred to a beaker quantitatively. Potassium periodate was added and the solution was kept over a boiling water bath for about 20 minutes. The absorbance of the pink solution was measured at 545 nm. A calibration curve was constructed using standard permanganate solution. The manganese content of the complex was read from the calibration curve\textsuperscript{163}.

Iron was estimated by direct pyrolysis of the complex to its oxide. For the estimation of iron in perchlorate complex, peaceful pyrolysis was adopted\textsuperscript{165}.
PHYSICAL MEASUREMENTS

1. Electrical conductance

Conductance measurements were carried out on an Elico direct reading conductivity meter. The cell constant of the conductivity cell used was 1.2499 cm$^{-1}$. Data were collected for methanol, acetonitrile and nitrobenzene solutions. Approximately 1x10$^{-3}$ M solutions were used.

2. Magnetic susceptibility

The magnetic susceptibility measurements were made using a Gouy balance at room temperature. Susceptibilities at other temperatures were not determined for want of facilities. The Gouy tube was standardised using Hg[Co(NCS)$_4$] as calibrant$^{166,167}$. Gram susceptibility was calculated using the formula

$$\chi = \frac{\alpha + \beta F'}{w}$$

where $\alpha$ = air displacement constant,
$\beta$ = tube constant,
$F'$ = change in weight in milligrams and
$w$ = Weight of sample in grams.
Diamagnetic corrections were applied using Pascal's constants taking into consideration the magnetic contributions of various atoms and structural units\cite{166, 3, 4}. The effective magnetic moment $\mu_{\text{eff}}$, was calculated using the formula

$$\mu_{\text{eff}} = 2.84 \sqrt{X'_M x T},$$

where $X'_M$ = molar susceptibility corrected for diamagnetism and $T$ = temperature.

3. Electronic spectra

In the solid state the electronic spectra of the complexes were obtained in the range 350-800 nm using reflectance technique on a Shimadzu-UV-200 S double beam spectrophotometer or a Shimadzu-UV-240 spectrophotometer. MgO was used as a reference material.

4. Infrared spectra

The infrared spectra of the complexes and the ligands were recorded on a Perkin-Elmer 397 or Perkin-Elmer 983 spectrophotometer. KBr disc technique was employed.
NMR spectra

The NMR spectra of the ligands were taken on a Varian instrument EM-360 60 MHz NMR spectrophotometer in CDCl₃. TMS was used as the reference material.

6. Mass spectra

Mass spectra of the ligands were recorded using Hewlett-Packard HP 5995 mass spectrophotometer.