Studies on Iron(III), Cobalt(II), Nickel(II) and Copper(II) Complexes of N-Benzoyl-N'(4-antipyrylmethylidene) hydrazine
This chapter deals with the synthesis and characterisation of nineteen complexes of iron(III), cobalt(II), nickel(II) and copper(II) with the Schiff base N-Benzoyl-N'-(4-antipyrylmethylidene)hydrazine (BAMH).

![Chemical structure of BAMH]

Fig. 4.1. N-Benzoyl-N'-(4-antipyrylmethylidene)hydrazine (BAMH)

The ligand BAMH would be expected to behave as a neutral tridentate ligand coordinating through both the carbonyl oxygens and the azomethine nitrogen forming two chelate rings (one six membered and the other five membered) incorporating the metal ion. But the possibility of non-participation of any one of the donor sites cannot be ruled out.

**Experimental**

The details of the preparation of the ligand and metal salts were described in chapter 2.
4.1 Preparation of the Complexes

Iron(III) Complexes

Perchlorate, Thiocyanate Chloride and Bromide Complexes

A quantity of one mmol of Fe(ClO$_4$)$_3$, Fe(SCN)$_3$, FeCl$_3$, FeBr$_3$ or FeI$_3$ in ethyl acetate (10 mL) was added to a boiling suspension of 2.2 mmol of BAMH in ethyl acetate (100 mL). The mixture was refluxed for about 3 h on a steam bath. The resulting solution was concentrated and cooled. The complexes, which precipitated on cooling, were filtered and washed several times with hot benzene to remove the excess ligand. These were recrystallised from methanol and dried under vacuum over phosphorus(V)oxide.

Nitrate Complex

A quantity of one mmol of Fe(NO$_3$)$_3$ in methanol (10 mL) was added to a boiling suspension of 2.2 mmol of BAMH in ethyl acetate (100 mL). The mixture was refluxed for about 2 h on a steam bath. The resulting solution was concentrated and cooled. The complex, which precipitated on cooling, was filtered and washed several times with hot benzene to remove the excess ligand. It was recrystallised from acetonitrile and dried under vacuum over phosphorus(V)oxide.

Cobalt(II) Complexes

Perchlorate, Bromide and Iodide Complexes

A quantity of one mmol of Co(ClO$_4$)$_2$, CoBr$_2$, CoI$_2$ or CoI$_2$ in ethyl acetate (10 mL) was added to a boiling suspension of 2.2 mmol of BAMH in ethyl acetate (100 mL). The mixture was
refluxed for about 3 h on a steam bath. The complexes, which precipitated on cooling, were filtered and washed several times with hot benzene to remove the excess ligand. These were recrystallised from methanol and dried under vacuum over phosphorus(V)oxide.

Nitrate Complex

A quantity of one mmol of Co(NO$_3$)$_2$. 6H$_2$O in methanol (10 mL) was added to a boiling suspension of 2.2 mmol of BAMH in ethyl acetate (100 mL). The mixture was refluxed for about 3 h on a steam bath. The resulting solution was concentrated and cooled. The complex, which precipitated on cooling, was filtered and washed several times with hot benzene to remove the excess ligand. It was recrystallised from acetonitrile and dried under vacuum over phosphorus(V)oxide.

Chloride Complex

A quantity of one mmol of CoCl$_2$. 6H$_2$O in acetone (10 mL) was added to a boiling suspension of 2.2 mmol of BAMH in acetone (100 mL). The mixture was refluxed for about 3 h. The complex, which precipitated on cooling, was filtered and washed several times with hot benzene to remove the excess ligand. It was recrystallised from methanol and dried under vacuum over phosphorus(V)oxide.

Nickel(II) Complexes

Perchlorate and Iodide Complexes

A quantity of one mmol of Ni(ClO$_4$)$_2$. 6H$_2$O or NiI$_2$. 6H$_2$O in ethyl acetate was added to a boiling suspension of 2.2 mmol BAMH in ethyl acetate (100 mL). The mixture was refluxed for about 4 h on a steam bath.
The complexes, which precipitated on cooling, were filtered and washed several times with hot benzene to remove the excess ligand. These were recrystallised from methanol and dried under vacuum over phosphorus(V)oxide.

**Chloride Complex**

A quantity of one mmol of NiCl₂. 6H₂O in methanol (10 mL) was added to a boiling suspension of 2.2 mmol of BAMH in ethyl acetate (100 mL). The mixture was refluxed for about 3 h on a steambath. The complex, which precipitated on cooling, was filtered and washed several times with hot benzene to remove the excess ligand. It was recrystallised from acetonitrile and dried under vacuum over phosphorus(V)oxide.

**Bromide and Nitrate Complexes**

A quantity of one mmol of NiBr₂. 6H₂O or Ni(NO₃)₂. 6H₂O in acetone (10 mL) was added to a boiling suspension of 2.2 mmol BAMH in acetone (100 mL). The mixture was refluxed for about 3 h on a steam bath. The resulting solution was concentrated and cooled. The complexes, which precipitated on cooling, were filtered and washed several times with hot benzene to remove the excess ligand. It was recrystallised from methanol and dried under vacuum over phosphorus(V)oxide.

**Copper(II) Complexes**

**Perchlorate Complex**

A quantity of one mmol of Cu(ClO₄)₂. 6H₂O in ethyl acetate (10 mL) was added to a boiling suspension of 2.2 mmol of BAMH in
ethyl acetate (100 mL). The mixture was refluxed for about 2 h on a steambath. The complex, which precipitated on cooling, was filtered and washed several times with hot benzene to remove the excess ligand. It was recrystallised from methanol and dried under vacuum over phosphorus(V)oxide.

**Nitrate and Chloride Complexes**

A quantity of one mmol of Cu(NO$_3$)$_2$.3H$_2$O or CuCl$_2$.2H$_2$O in acetone (10 mL) was added to a boiling suspension of 2.2 mmol of BAMH in acetone (100 mL) for copper nitrate or 1.1 mmol of BAMH in acetone (100 mL) for copper chloride. The mixture was refluxed for about 2 h on a steambath. The precipitated complexes were filtered and washed several times with hot benzene to remove the excess ligand. These were recrystallised from methanol and dried under vacuum over phosphorus(V)oxide.

**Bromide Complex**

A quantity of one mmol of CuBr$_2$.4H$_2$O in acetonitrile (10 mL) was added to a boiling solution of 2.2 mmol of BAMH in acetonitrile. The mixture was refluxed for about 2 h on a steambath. The complex, which precipitated on cooling, was filtered and washed several times with hot benzene to remove the excess ligand. It was recrystallised from methanol and dried under vacuum over phosphorus(V)oxide.

**Analyses and Physicochemical Studies of the Complexes**

The procedural details of the analyses and physicochemical studies of the complexes are given in Chapter 2.
4.2 Results and Discussion

4.2.1 Appearance and Solubility of the Complexes

The iron(III) complexes are brown non-hygroscopic solids. These are soluble in DMF, ethanol, methanol, and nitrobenzene but insoluble in benzene, chloroform, ethyl acetate and toluene.

The cobalt(II) complexes are yellowish brown in colour except the chloride complex which is rose red in colour. All of these are non-hygroscopic and soluble in acetonitrile, DMF, ethanol, methanol and nitrobenzene but insoluble in benzene, chloroform, ethyl acetate and toluene.

The nickel(II) complexes are light green in colour and are non-hygroscopic solids. These are soluble in acetonitrile, DMF, ethanol, methanol and nitrobenzene but insoluble in benzene, chloroform, ethyl acetate and toluene.

The copper(II) complexes are light yellow in colour except the bromide complex which is brown in colour. These are non-hygroscopic and are soluble in DMF, ethanol, methanol and nitrobenzene but insoluble in benzene, chloroform, ethyl acetate and toluene.

4.2.2 Elemental Analyses

The 19 newly prepared complexes were subjected to elemental analyses. The results obtained are given in Tables 4.1 to 4.4.
The analytical data suggest that the complexes may be formulated as follows.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(BAMH)$_2$X$_3$</td>
<td>$X = \text{ClO}_4, \text{NO}_3, \text{SCN}, \text{Cl}, \text{or Br}$</td>
</tr>
<tr>
<td>Co(BAMH)$_2$X$_2$</td>
<td>$X = \text{ClO}_4, \text{NO}_3, \text{Cl}, \text{Br or I}$</td>
</tr>
<tr>
<td>Ni(BAMH)$_2$X$_2$</td>
<td>$X = \text{ClO}_4, \text{NO}_3, \text{Cl}, \text{Br or I}$</td>
</tr>
<tr>
<td>Cu(BAMH)$_2$X$_2$</td>
<td>$X = \text{ClO}_4, \text{NO}_3 \text{ or Br}$</td>
</tr>
<tr>
<td>Cu(BAMH)Cl$_2$</td>
<td></td>
</tr>
</tbody>
</table>

4.2.3 Electrical Conductance

The molar conductance data of iron(III), cobalt(II), nickel(II) and copper(II) complexes of BAMH in a set of three different non-aqueous solvents from among acetonitrile, DMF, methanol and nitrobenzene are given in Tables 4.5 to 4.8.

Iron(III) Complexes

The molar conductance values of the perchlorate and nitrate complexes of BAMH ($10^{-3}$M solutions) in DMF, methanol and nitrobenzene fall in the range expected for 1:2 electrolytes, while for the chloride, bromide and thiocyanate complexes 1:1 electrolytic behaviour is observed. Thus the complexes may be formulated as [Fe(BAMH)$_2$(ClO$_4$)](ClO$_4$)$_2$, [Fe(BAMH)$_2$(NO$_3$)](NO$_3$)$_2$, and [Fe(BAMH)$_2$X$_2$]X (where $X = \text{SCN}, \text{Cl or Br}$).
Cobalt(II) Complexes

The molar conductance values of the cobalt(II) complexes of BAMH (10^{-3} M solution) in acetonitrile, DMF and nitrobenzene fall in the range expected for 1:2 electrolytes.\textsuperscript{144} Thus the complexes may be formulated as [Co(BAMH)\textsubscript{2}]X\textsubscript{2} (where X = ClO\textsubscript{4}, NO\textsubscript{3}, Cl, Br or I).

Nickel(II) Complexes

The molar conductance values of the nickel(II) complexes of BAMH (10^{-3} M solution) in acetonitrile, DMF and nitrobenzene are in the range suggested for non-electrolytes\textsuperscript{144} except for the perchlorate and nitrate complexes which show 1:1 electrolytic behaviour.\textsuperscript{144}

Copper(II) Complexes

The molar conductance values of the copper(II) complexes of BAMH (10^{-3} M solution) in DMF, methanol and nitrobenzene fall in the range expected for 1:2 electrolytes except the chloride and bromide complexes which show non-electrolytic behaviour.\textsuperscript{144} Thus the complexes may be formulated as [Cu(BAMH)\textsubscript{2}]X\textsubscript{2} (where X = ClO\textsubscript{4} or NO\textsubscript{3}), [Cu(BAMH)Cl\textsubscript{2}] and [Cu(BAMH)\textsubscript{2}Br\textsubscript{2}].

4.2.4 Infrared Spectra

The important infrared spectral data of BAMH and their complexes together with the tentative assignments are presented in Tables 4.9 to 4.12.

The infrared spectrum of the free ligand BAMH shows bands at 3270, 1674, 1630, 1571 and 998 cm\textsuperscript{-1}. The band at 3270 cm\textsuperscript{-1} is attributed to N-H stretching vibrations.\textsuperscript{187} The bands at 1674 and 1630 cm\textsuperscript{-1} are attributed to the
stretching vibrations of the carbonyl groups of the pyrazolone ring and benzoyl moiety\textsuperscript{188,189} respectively. The strong band at 1571 cm\textsuperscript{-1} and a weak band at 998 cm\textsuperscript{-1} are due to C=N and N=N stretching vibrations respectively.\textsuperscript{115,187}

**Iron(III) Complexes**

The infrared spectral bands at 1674 cm\textsuperscript{-1} characteristic of \(\nu(C=O)\) of the pyrazolone ring of BAMH is shifted to the region 1639-1642 cm\textsuperscript{-1} in the complexes indicating the coordination of carbonyl oxygen.\textsuperscript{188} The band corresponding to \(\nu(C=O)\) of benzoyl moiety remain practically unaltered in all the complexes at about 1628 cm\textsuperscript{-1} indicating the non-coordination of benzoyl oxygen.\textsuperscript{190} The strong band observed at 1571 cm\textsuperscript{-1} in BAMH attributed to C=N stretching vibration is shifted to the range 1550-1560 cm\textsuperscript{-1} indicating the coordination of the azomethine nitrogen in the complexes.\textsuperscript{138,188} The shift of \(\nu(N-N)\) band at 998 cm\textsuperscript{-1} of BAMH to higher frequencies (1008-1010 cm\textsuperscript{-1}) in the complexes further supports coordination through the azomethine nitrogen.\textsuperscript{187}

The triply split band with maxima observed at around 1144, 1112 and 1018 cm\textsuperscript{-1} due to the \(\nu_8, \nu_6\) and \(\nu_1\) vibrations respectively of the perchlorate ion of \(C_2v\) symmetry indicate that the perchlorate ion may be coordinated in a bidentate fashion.\textsuperscript{156,158} But the band at 1090 cm\textsuperscript{-1} is attributed to the \(\nu_3\) vibration of the uncoordinated perchlorate of \(T_d\) symmetry. Thus the presence of both uncoordinated and bidentately coordinated perchlorate ions is observed in the perchlorate complex. The band observed around 940 and 632 cm\textsuperscript{-1} corresponding to the
\( \nu_2 \) and \( \nu_3 \) vibrations respectively of the coordinated perchlorate (C\(_{2v}\)) ion and the band at 624 cm\(^{-1}\) due to the \( \nu_4 \) vibration of the uncoordinated perchlorate (T\(_6\)), which are not present in the spectrum of the free ligand, also support the coexistence of both uncoordinated and bidentately coordinated perchlorate ions in the complex.\(^{156,158}\)

In the nitrate complex, a very strong band observed at 1383 cm\(^{-1}\) due to the \( \nu_3 \) vibration of the D\(_{3h}\) symmetry indicates the presence of uncoordinated nitrate ion.\(^{143,173,191}\) This is supported by the presence of another band of medium intensity at 821 cm\(^{-1}\) due to the \( \nu_2 \) vibration of the uncoordinated nitrate ion.\(^{192}\) The presence of coordinated nitrate ion with C\(_{2v}\) symmetry is indicated by the bands observed at around 1440 and 1244 cm\(^{-1}\) due to \( \nu_4 \) and \( \nu_1 \) vibrations respectively.\(^{173}\) A medium intensity band observed around 1052 cm\(^{-1}\) due to \( \nu_2 \) vibration of the nitrate (C\(_{2v}\)) ion stands as an additional evidence for the coordination of nitrate ion.\(^{160}\) Since the difference between the two frequencies, \((\nu_4 - \nu_1)\) is 196 cm\(^{-1}\) the coordinated nitrate ion is bidentate.\(^{160}\)

In the thiocyanate complex, a sharp band at 2054 cm\(^{-1}\) is attributable to N-coordinated thiocyanate ion. The presence of bands at 854 and 472 cm\(^{-1}\) stands as an additional evidence for N-coordinated thiocyanate ion.\(^{157,193}\)

In the far infrared spectra of chloride and bromide complexes, Fe-Cl and Fe-Br stretching vibrations are observed at 310 and 285 cm\(^{-1}\), respectively\(^{157}\) which are not present in the spectrum of the free ligand. Further \( \nu(\text{Fe-O}) \) and \( \nu(\text{Fe-N}) \) stretching vibrations are observed at about
550 and 455 cm\(^{-1}\) respectively in all these complexes.\(^{105}\) These results which are in agreement with the conductance data, indicate that one of the perchlorate and nitrate ions as well as two of the thiocyanate, chloride and bromide ions are coordinated to the metal ion in these complexes.

**Cobalt(II) Complexes**

The infrared spectral bands at 1674 cm\(^{-1}\) characteristic of \(\nu(C=O)\) of the pyrazolone ring are shifted to the region 1640-1658 cm\(^{-1}\) in the complexes indicating the coordination of carbonyl oxygen.\(^{188}\) The band at 1630 cm\(^{-1}\) corresponding to \(\nu(C=O)\) of benzoyl moiety is shifted to the region 1598 --1612 cm\(^{-1}\) indicating the coordination of benzoyl oxygen in these complexes.\(^{188}\) The strong band observed at 1571 cm\(^{-1}\) in the ligand attributed to C=N stretching vibration is shifted to 1550-1560 cm\(^{-1}\) indicating the coordination of the azomethine nitrogen in the complexes.\(^{188}\) The \(\nu(N-N)\) band at 998 cm\(^{-1}\) in the ligand which is shifted to higher frequencies (1008-1012 cm\(^{-1}\)) in the complexes further supports the coordination through the azomethine nitrogen.\(^{187}\)

In the perchlorate complex, the band observed at 1089 cm\(^{-1}\) is assigned to \(\nu_3\) vibration of uncoordinated perchlorate ion of \(T_d\) symmetry.\(^{158}\) This is further supported by the presence of another strong band at 624 cm\(^{-1}\) due to \(\nu_4\) vibration of the perchlorate ion\(^{158}\) of \(T_d\) symmetry.

In the nitrate complex, the strong band observed at 1384 cm\(^{-1}\) is attributed to the \(\nu_3\) vibration of uncoordinated nitrate ion of \(D_{3h}\)
symmetry. This is further supported by the presence of another medium intensity band at 825 cm$^{-1}$ due to the $v_2$ vibration of nitrate ion of $D_{3h}$ symmetry.\textsuperscript{173}

Further Co-O and Co-N stretching vibrations are observed at about 555 and 450 cm$^{-1}$ respectively in all of these complexes.\textsuperscript{105} The above spectral observations along with the conductance data indicate that the perchlorate, nitrate and halide ions remain as uncoordinated in all the complexes.

**Nickel(II) Complexes**

The infrared spectral band at 1674 cm$^{-1}$ characteristic of $v$(C=O) of the pyrazolone ring which is shifted to the region 1640- 1657 cm$^{-1}$ in the complexes indicate that the carbonyl oxygen is coordinated.\textsuperscript{188} The band corresponding to $v$(C=O) of benzoyl moiety remain practically unaltered in all the complexes at about 1625 cm$^{-1}$, indicating the non-coordination of benzoyl oxygen in these complexes.\textsuperscript{190} The strong band observed at 1571 cm$^{-1}$ in the ligand attributed to C=N stretching vibration is shifted to 1551-1558 cm$^{-1}$ in the complexes, indicating the coordination of azomethine nitrogen.\textsuperscript{188} The $v$(N-N) band in the ligand at 998 cm$^{-1}$ shifted to higher frequencies (1008-1010 cm$^{-1}$) in the complexes further supports the coordination through the azomethine nitrogen.\textsuperscript{187}

In the perchlorate complex the triply split band with maxima observed at 1142, 1110 and 1020 cm$^{-1}$ are due to $v_8$, $v_6$ and $v_1$ vibrations respectively of the perchlorate ion of $C_{2v}$ symmetry, indicating the coordination of perchlorate ion in a bidentate fashion.\textsuperscript{156,158}
But the band observed at 1089 cm\(^{-1}\) is assigned to the \(v_3\) vibration of uncoordinated perchlorate ion of \(T_d\) symmetry.\(^{158}\) In addition, the vibrational frequencies observed at 940 and 636 cm\(^{-1}\) corresponding to \(v_2\) and \(v_3\) vibrations of the perchlorate ion of \(C_{2v}\) symmetry and the band at 625 cm\(^{-1}\) due to the \(v_4\) vibration of the perchlorate ion of \(T_d\) symmetry also support the coexistence of both bidentately coordinated and uncoordinated perchlorate ions in this complex.

In the nitrate complex characteristic vibrational frequencies of both ionic and coordinated nitrate ions are observed. A very strong band observed at 1384 cm\(^{-1}\) due to the \(v_3\) vibration of the nitrate ion of \(D_{3h}\) symmetry indicates the presence of uncoordinated nitrate ion.\(^{173}\) This is supported by another band of medium intensity observed at 830 cm\(^{-1}\). The presence of coordinated nitrate ion is indicated by the bands observed around 1440 and 1247 cm\(^{-1}\) due to the \(v_4\) and \(v_1\) vibration respectively of the nitrate of \(C_{2v}\) symmetry.\(^{173}\) A medium intensity band observed around 1052 cm\(^{-1}\) due to the \(v_2\) vibration of the nitrate ion (\(C_{2v}\)) stands as an additional evidence for the presence of coordinated nitrate ion. The difference between the two highest frequency bands, \((v_4-v_1)\), of the nitrate ion of \(C_{2v}\) symmetry is 193 cm\(^{-1}\) which indicates that the coordinated nitrate ion is bidentate.\(^{173}\)

In the far infrared spectrum of the chloride, bromide and iodide complexes, Ni-Cl, Ni-Br and Ni-I stretching vibrations occur at 240, 165 and 125 cm\(^{-1}\) respectively which are not present in the spectrum of the free ligand.\(^{157}\)
Further $v$(Ni-O) and $v$(Ni-N) stretching vibrations are observed at about 550 and 450 cm$^{-1}$ respectively in all the complexes.$^{105,157}$ The above results along with the conductance data confirm that one of the perchlorate and nitrate ions as well as two of the chloride, bromide and iodide ions are coordinated to the metal ion in these complexes.

**Copper(II) Complexes**

The infrared spectral band at 1674 cm$^{-1}$ characteristic of $v$(C=O) of the pyrazolone ring shifted to the region 1642-1654 cm$^{-1}$ in the complexes indicate that the carbonyl oxygen is coordinated.$^{188}$ The band corresponding to $v$(C=O) of benzoyl moiety remain practically unaltered in all the complexes at about 1630 cm$^{-1}$ indicating the non-coordination of benzoyl oxygen in these complexes.$^{197}$ The strong band observed at 1571 cm$^{-1}$ in the ligand attributed to C=N stretching vibration is shifted to 1551-1560 cm$^{-1}$ region indicating the coordination of azomethine nitrogen in the complexes.$^{188}$ The $v$(N-N) band at 998 cm$^{-1}$ in the ligand, shifted to higher frequency (1007-1010 cm$^{-1}$) in the complexes, further supports the coordination through the azomethine nitrogen.$^{187}$

In the perchlorate complex, the band observed at 1086 cm$^{-1}$ is assigned to the $v_3$ vibration of uncoordinated perchlorate ion of $T_d$ symmetry.$^{158}$ This is also supported by the presence of a medium intensity band at 624 cm$^{-1}$ due to the $v_4$ vibration of perchlorate ion of $T_d$ symmetry.$^{158}$

In the nitrate complex a strong band at 1378 cm$^{-1}$ is assigned to $v_3$ vibration of uncoordinated nitrate ion of $D_{3h}$ symmetry.$^{173}$ This is
further supported by the presence of a medium intensity band at 821 cm\(^{-1}\) due to \(v_2\) vibration of nitrate\(^{173}\) ion of \(D_{3h}\) symmetry.

In the far infrared spectrum of the chloride and bromide complexes Cu-Cl and Cu-Br stretching vibrations occur at 310 and 292 cm\(^{-1}\) respectively\(^{157}\) but these are not present in the spectrum of the ligand.

Further \(v(Cu-O)\) and \(v(Cu-N)\) stretching vibrations are observed at about 550 and 460 cm\(^{-1}\) respectively in all these complexes.\(^{105,157}\) The above observations along with the conductance data confirm that the perchlorate and nitrate ions remain as uncoordinated in these complexes while the chloride and bromide ions are coordinated to the metal ion.

4.2.5 Electronic Spectral Studies

The electronic spectrum of BAMH shows two bands with maxima at 23,866 and 41,153 cm\(^{-1}\) corresponding to \(n \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) transitions respectively. But in the spectra of the complexes, these transitions are found to be slightly shifted. The important electronic spectral data of the complexes of BAMH with tentative assignments are presented in Tables 4.13 to 4.16.

Iron(III) Complexes

In iron(III) complexes \(n \rightarrow \pi^*\) bands are found to be blue-shifted to the region 23,952-24,630 cm\(^{-1}\) while \(\pi \rightarrow \pi^*\) bands are red-shifted to the region 39,370-40,983 cm\(^{-1}\) respectively when compared to that of BAMH. The spectra of all the complexes exhibit a band in the region 19,230-20,080 cm\(^{-1}\) corresponding to \(^6\)A\(_{1g}\) \(\rightarrow\) \(^4\)T\(_{1g}\) transition consistent
with octahedral iron(III) complexes. A strong band observed in the region 33,112-33,783 cm\(^{-1}\) may be due to a charge transfer process.

### Cobalt(II) Complexes

In cobalt(II) complexes \(\pi \rightarrow \pi^*\) bands are found to be blue-shifted to the region 25,062-25,641 cm\(^{-1}\) while \(\pi \rightarrow \pi^*\) bands are red-shifted to the region 40,485-40,816 cm\(^{-1}\) respectively when compared to that of BAMH. The band observed in the regions 19,607-20,833 cm\(^{-1}\) and 13,774-15,873 cm\(^{-1}\) may be attributed to \(^{4}T_{1g}(F) \rightarrow ^{4}T_{1g}(P)\) and \(^{4}T_{1g}(F) \rightarrow ^{4}A_{2g}(F)\) transitions respectively supporting octahedral geometry around the metal ion in these complexes. A low energy band observed in the region 9,216-9,523 cm\(^{-1}\) may be attributed to \(^{4}T_{1g}(F) \rightarrow ^{4}T_{2g}(F)\) transition consistent with octahedral configuration in all these complexes. The strong band observed in the 33,333-33,557 cm\(^{-1}\) region may be due to a charge transfer process.

### Nickel(II) Complexes

In nickel(II) complexes \(\pi \rightarrow \pi^*\) bands are found to be blue-shifted to the region 24,510-25,839 cm\(^{-1}\) while \(\pi \rightarrow \pi^*\) bands are found to be red-shifted to the region 40,160-41,052 cm\(^{-1}\) respectively when compared to that of BAMH. The band observed in the regions 21,551-21,978 cm\(^{-1}\) and 15,527-16,891 cm\(^{-1}\) are attributed to \(^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(P)\) and \(^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(F)\) transitions respectively consistent with octahedral geometry around nickel(II) in these complexes. In addition to this a low energy band in the region 9,191-9,541 cm\(^{-1}\) attributable to \(^{3}A_{2g}(F) \rightarrow ^{3}T_{2g}(F)\) transition further support octahedral geometry around
nickel(II) in these complexes. An intense absorption band in the region 32,573-33,898 cm\(^{-1}\) may be due to a charge transfer process.

**Copper(II) Complexes**

In copper(II) complexes \(n \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) bands are found to be red-shifted to the regions 22,123-22,471 cm\(^{-1}\) and 39,682-40,816 cm\(^{-1}\) respectively when compared to that of BAMH. The band observed in the region 13,477-13,820 cm\(^{-1}\) is attributed to \(^2\)B\(_{1g}\) \(\rightarrow \) \(^2\)A\(_{1g}\) transition consistent with square planar\(^{196}\) geometry around the copper(II) in all the complexes except the bromide complex. The broad band at 19,608 cm\(^{-1}\) in the bromide complex indicates tetragonal configuration around the copper(II) ion.\(^{186,197}\) The electronic spectra of all the complexes exhibit an intense absorption band in the region 33,222-33,444 cm\(^{-1}\) which may be due to a charge transfer process.

**4.2.6 Magnetic Behaviour**

The magnetic susceptibility measurements were done as described in Chapter 2. The effective magnetic moments of the complexes are presented in Tables 4.13 to 4.16.

**Iron(III) Complexes**

The magnetic moments of the iron(III) complexes of BAMH are found to be in the range 5.61 to 6.05 BM. This suggests a high spin octahedral configuration around the metal ion.\(^{24,194}\)

**Cobalt(II) Complexes**

The observed magnetic moment values of the complexes are in the range 4.84 – 5.02 BM. In an octahedral field, the ground state is
triply degenerate which would cause an orbital angular momentum contribution to the magnetic moment. The moments therefore would lie between the limits of 3.88 and 5.20 BM depending upon the extent of orbital angular momentum contribution. The magnetic moments of the present complexes are very close to those expected for a high spin octahedral geometry.198

**Nickel(II) Complexes**

The magnetic moments of the complexes are in the range 2.98-3.30 BM. The typical octahedral nickel(II) complexes have magnetic moments between 2.90-3.40 BM depending on the magnitude of the orbital contribution.24 The results indicate that these complexes probably have octahedral geometry.199

**Copper(II) Complexes**

The magnetic moments of copper(II) complexes vary in the range 1.61-2.01 BM. This clearly indicates that the complexes except the chloride complex are monomeric in nature and any metal-metal interaction is absent.186 The magnetic moment of the chloride complex is slightly lower than that expected which may be due to metal-metal interaction.200

4.2.7 **EPR Spectra**

The X-band EPR spectra of the copper(II) complexes were recorded in 1:1 methanol-toluene mixture at liquid nitrogen temperature using DPPH free radical as the ‘g’ marker (Fig. 4.2). All the complexes have a well-resolved $g_\parallel$ and a broadened $g_\perp$ region. In
all the spectra no superhyperfine splitting from the ligand part is observed.

![EPR Spectra](image)

**Fig. 4.2 EPR Spectra of copper(II) complexes of BAMH**

\[
A = [\text{Cu}(\text{BAMH})\text{ClO}_4], \quad B = [\text{Cu}(\text{BAMH})\text{NO}_3], \\
C = [\text{Cu}(\text{BAMH})\text{Cl}_2], \quad D = [\text{Cu}(\text{BAMH})\text{Br}_2]
\]

The various spin Hamiltonian parameters computed are presented in Table 4.17. The trend \(g_1 > g > 2.0023\) indicates that the unpaired electron is most likely in the \(d_{x^2-y^2}\) orbital.\(^8^3\) The covalency parameter \(\alpha^2\) is found to be in the range 0.75 to 0.76 indicating the fairly covalent nature in the metal-ligand bonding.\(^8^6\) Further the shape of the EPR spectra indicates that the geometry around the copper(II) ion is square planar in the perchlorate, nitrate and chloride complexes and an elongated octahedron in
the bromide complex as is evident from the less intense low field side and high intense high field side.201

4.3 Summary and Conclusion

The iron(III), cobalt(II), nickel(II) and copper(II) complexes of N-Benzoyl-N'(4-antipyrlymethylidene)hydrazine have been synthesised and characterised by elemental analyses, molar conductance, infrared and electronic spectra as well as magnetic susceptibility measurements. The copper(II) complexes were also characterised by EPR spectral analyses.

Iron(III) Complexes

According to elemental analyses and molar conductance data, the iron(III) complexes may be formulated as [Fe(BAMH)2X]X2 (X = ClO₄ or NO₃) and [Fe(BAMH)₂X₂]X (X = SCN, Cl or Br). The infrared spectra reveals that BAMH acts as a neutral bidentate ligand coordinating through the carbonyl oxygen of antipyrine ring and the azomethine nitrogen in all the complexes. The molar conductance data and infrared spectra indicate that one of the perchlorate and nitrate ions is coordinated bidentately leaving the other two as counter anions while in the thiocyanate, chloride and bromide complexes two of the anions are coordinated. The electronic spectra and magnetic moment data suggest a high spin octahedral geometry around the iron(III) ion in all these complexes. Thus a coordination number of six is assigned to the metal ion in these complexes.
The tentative structures of the complexes are presented in Fig. 4.3.
Cobalt(II) Complexes

According to the elemental analyses and molar conductance data, cobalt(II) complexes may be represented by the general formula [Co(BAMH)$_2$]X$_2$ (X=ClO$_4$, NO$_3$, Cl, Br or I). The infrared spectral data suggests that BAMH acts as a neutral tridentate ligand coordinating through the carbonyl oxygens of the antipyrine ring and the benzoyl group as well as the azomethine nitrogen in all these complexes. The molar conductance data and the infrared spectra indicate that both the anions remain as counter anions in all these complexes. The electronic spectra and magnetic moment data suggest an octahedral geometry around the cobalt(II) ion in these complexes. Thus a coordination number of six is assigned to the metal ion in these complexes. The tentative structures of the complexes are presented in Fig. 4.4.
Nickel(II) Complexes

In accordance with the elemental analyses and molar conductance data, the nickel(II) complexes of BAMH may be formulated as \([\text{Ni(BAMH)}_2(\text{ClO}_4)](\text{ClO}_4), [\text{Ni(BAMH)}_2(\text{NO}_3)](\text{NO}_3)\) or \([\text{Ni(BAMH)}_2X_2] (X=\text{Cl, Br or I})\). The infrared spectra reveal that BAMH acts as a neutral bidentate ligand coordinating through the carbonyl oxygen of the antipyrine ring and the azomethine nitrogen. The molar conductance data and infrared spectra indicate that one of the perchlorate and nitrate ions is coordinated bidentately leaving the other as counter anion. Both of the chloride, bromide or iodide ions are coordinated to the metal.
The tentative structures of the complexes are presented in Fig. 4.5.
Fig. 4.5 Tentative structures of nickel(II) complexes of BAMH

Copper(II) Complexes

The elemental analyses and molar conductance data of the copper(II) complexes of BAMH indicate that these complexes have the general formulae [Cu(BAMH)$_2$]X$_2$, (X = ClO$_4$ or NO$_3$), [Cu(BAMH)$_2$Br$_2$] or [Cu(BAMH)Cl$_2$]. The infrared spectral data indicate that BAMH acts as a neutral bidentate ligand coordinating through the carbonyl oxygen of antipyrine ring and the azomethine nitrogen in all these complexes. The molar conductance data and the infrared spectra reveal that both the perchlorate and nitrate ions remain as counter anions while both the chloride and bromide ions are coordinated to the metal ion in these complexes. From the electronic spectra, a square planar geometry is assigned to the copper(II) ion in the perchlorate,
nitrate and chloride complexes while an octahedral geometry is suggested for the bromide complex. The tentative structures of the complexes are presented in the Fig. 4.6.

\[ X_2 \]

\( (X = \text{ClO}_4 \text{ or } \text{NO}_3) \)
Fig. 4.6 Tentative structures of copper(II) complexes of BAMH