Studies on Iron(III), Cobalt(II), Nickel(II) and Copper(II) complexes of N,N’-Bis (4-antipyrylmethylidene)ethylenediamine
The synthesis and characterisation of the complexes of iron(III), cobalt(II), nickel(II) and copper(II) with the Schiff base N,N'-Bis(4-antipyrylmethylene)ethylenediamine (BAME) [Fig. (3.1)] are presented in this chapter.

![Fig. 3.1 N,N'-Bis(4-antipyrylmethylene)ethylenediamine](image)

The ligand N,N'-Bis(4-antipyrylmethylene)ethylenediamine (BAME) has two identical carbonyl groups and two identical azomethine groups in such a way that two six membered rings and one five membered ring can be formed incorporating the metal ion. Thus a tetradentate behavior is expected. But the possibility of non-participation of either of the two groups cannot be ruled out.

**Experimental**

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

Iron(III) Complexes

Perchlorate, Nitrate, Thiocyanate and Bromide Complexes

A quantity of one mmol of Fe(ClO₄)₂·6H₂O, Fe(SCN)₂·6H₂O or FeBr₃·6H₂O in ethyl acetate (10 mL) or Fe(NO₃)₃·6H₂O in methanol (10 mL) was added to a boiling suspension of 2.2 mmol of BAME 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 acetonitrile and dried under vacuum over phosphorus(V) oxide.

Chloride Complex

A quantity of one mmol of FeCl₃·6H₂O in acetone (10 mL) was added to a boiling suspension of 2.2 mmol of BAME in acetone (100 mL). The mixture was refluxed for about 3 h on a steam bath and 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, Nitrate, Chloride, Bromide and Iodide Complexes

A quantity of one mmol of Co(ClO₄)₂·6H₂O, Co(NO₃)₂·6H₂O or CoCl₂·6H₂O in methanol (10 mL) or CoBr₂·6H₂O or CoI₂·6H₂O in
ethyl acetate (10 mL) was added to a boiling suspension of 2.2 mmol of BAME 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 then recrystallised from acetonitrile 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 (10 mL) was added to a boiling suspension of 2.2 mmol of BAME in ethyl acetate (100 mL). This 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 and Bromide Complexes**

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

**Copper(II) Complexes**

**Perchlorate Complexes**

A quantity of one mmol of Cu(ClO$_4$)$_2$, $6\text{H}_2\text{O}$ in methanol (10 mL) was added to a boiling solution of 2.2 mmol of the ligand in methanol (100 mL). The resulting solution was refluxed for about 2 h on a steam bath. The complex, which precipitated on cooling, was filtered and washed several times with hot benzene to remove the excess ligand. It was then recrystallised from acetonitrile and dried under vacuum over phosphorus(V) oxide.

**Nitrate and Bromide Complexes**

A quantity of one mmol of Cu(NO$_3$)$_2$, $6\text{H}_2\text{O}$ in methanol (10 mL) was added to a boiling suspension of 2.2 mmol of BAME in ethyl acetate (100 mL). The resulting solution was refluxed for about 2 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 acetonitrile and dried under vacuum over phosphorus(V)oxide.

Chloride Complex

A quantity of one mmol of CuCl$_2$.2H$_2$O in acetone (10 mL) was added to a boiling solution of 2.2 mmol of BAME in acetone (50 mL). The mixture was refluxed for about 3 h on a steam bath. 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.

3.2 Results and Discussion

3.2.1 Appearance and Solubility of the Complexes

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

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

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

3.2.2 Elemental Analyses

The newly prepared 19 complexes were subjected to elemental analyses. The values are given in Tables 3.1 to 3.4. The data suggest that the complexes can be formulated as follows.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(BAME)₂X₃</td>
<td>X = ClO₄, NO₃, SCN, Cl or Br</td>
</tr>
<tr>
<td>Co(BAME)₂X₂</td>
<td>X = ClO₄, NO₃, Cl, Br or I</td>
</tr>
<tr>
<td>Ni(BAME)₂X₂</td>
<td>X = ClO₄, NO₃, Cl, Br or I</td>
</tr>
<tr>
<td>Cu(BAME)₂X₂</td>
<td>X = ClO₄, NO₃, Cl, or Br</td>
</tr>
</tbody>
</table>

3.2.3 Electrical Conductance

The molar conductance values of the iron(III), cobalt(II), nickel(II) and copper(II) complexes of BAME were measured in acetonitrile, DMF and nitrobenzene. The values are given in Tables 3.5 to 3.8.
Iron(III) Complexes

The molar conductance values of iron(III) complexes of BAME (10⁻³M solution) in acetonitrile, DMF and nitrobenzene fall in the range suggested for 1:2 electrolytes for perchlorate and nitrate complexes.¹⁴⁴ The thiocyanate, chloride and bromide complexes behave as 1:1 electrolytes. Thus the complexes may be formulated as \([\text{Fe(BAME)}_2\text{X}_2]X\) \((X = \text{ClO}_4\) or \(\text{NO}_3)\) and \([\text{Fe(BAME)}_2\text{X}_2]X\) \((X = \text{SCN}, \text{Cl} \text{or Br})\).

Cobalt(II) Complexes

The molar conductance values of the complexes of BAME (10⁻³M solution) in acetonitrile, DMF and nitrobenzene indicate 1:2 electrolytic behaviour.¹⁴⁴ Thus the complexes may be formulated as \([\text{Co(BAME)}_2\text{X}_2]X\) \((X = \text{ClO}_4, \text{NO}_3, \text{Cl}, \text{Br} \text{or I})\).

Nickel(II) Complexes

The molar conductance values of the complexes of BAME (10⁻³M solutions) in acetonitrile, DMF and nitrobenzene fall in the range suggested for 1:2 electrolytes.¹⁴⁴ Thus the complexes may be formulated as \([\text{Ni(BAME)}_2\text{X}_2]X\) \((X = \text{ClO}_4, \text{NO}_3, \text{Cl}, \text{Br} \text{or I})\).

Copper(II) Complexes

The molar conductance values of the complexes of BAME (10⁻³M solution) in acetonitrile, DMF and nitrobenzene indicate 1:2 electrolytic behaviour.¹⁴⁴ Thus the complexes may be formulated as \([\text{Cu(BAME)}_2\text{X}_2]X\) \((X = \text{ClO}_4, \text{NO}_3, \text{Cl} \text{or Br})\).
3.2.4 Infrared Spectra

The important infrared spectral bands of BAME and its complexes together with the tentative assignments are given in Tables 3.9 to 3.12.

The infrared spectrum of the ligand shows the bands characteristic of the carbonyl and azomethine groups at 1650 and 1594 cm\(^{-1}\) respectively.\(^{138}\)

In complexes the band at 1594 cm\(^{-1}\) characteristic of azomethine group is totally shifted to region 1604-1612 cm\(^{-1}\) indicating that both the azomethine nitrogens are coordinated to the metal ion.\(^{171}\) But the band corresponding to the carbonyl group remains practically unaltered in these complexes indicating the non-coordination of carbonyl oxygen\(^{143}\) to the metal ion. Thus the Schiff base BAME acts as a neutral bidentate ligand coordinating through both the azomethine nitrogens leaving the two carbonyl oxygens uncoordinated. The formation of the five membered ring incorporating the metal ion adds considerable stability to these complexes.

Iron(III) Complexes

The bands at 1650 and 1594 cm\(^{-1}\) of BAME are attributable to the stretching vibrations of the carbonyl and azomethine groups respectively.\(^{138}\) In the complexes the band at 1594 cm\(^{-1}\) is blue-shifted to the 1607-1612 cm\(^{-1}\) region indicating the coordination of both the azomethine nitrogens. But the band at 1650 cm\(^{-1}\) remains practically
unaltered suggesting the non-coordination of both the carbonyl oxygens in these complexes.\textsuperscript{138}

In the perchlorate complex, the triply split band with maxima at 1142, 1110 and 1024 cm\textsuperscript{-1} are due to $\nu_8$, $\nu_6$ and $\nu_1$, vibrations respectively of the perchlorate ion of C$_{2v}$ symmetry. This indicates that at least one of the perchlorate ions may be coordinated in a bidentate fashion. The band at 1089 cm\textsuperscript{-1} is assigned to $\nu_3$ vibrations of the uncoordinated perchlorate of T$_d$ symmetry. The vibrational frequencies observed at 942 and 636 cm\textsuperscript{-1} corresponding to $\nu_2$ and $\nu_3$ vibrations of perchlorate ion of C$_{2v}$ symmetry and the band at 627 cm\textsuperscript{-1} due to the $\nu_4$ vibration of the uncoordinated perchlorate, which are not present in the spectrum of the free ligand, support the coexistence of both uncoordinated and bidentately coordinated perchlorate ions in this complex.\textsuperscript{138}

In the nitrate complex, two strong bands at 1475 and 1280 cm\textsuperscript{-1} are attributable to $\nu_4$ and $\nu_1$ stretching vibrations respectively of the coordinated nitrate ion of C$_{2v}$ symmetry. Since $\nu_4$-$\nu_1$ is 195 cm\textsuperscript{-1}, the nitrate ion is bidentately coordinated.\textsuperscript{172} A very strong band at 1380 cm\textsuperscript{-1} and a medium intensity band at 824 cm\textsuperscript{-1} are due to $\nu_3$ and $\nu_2$ vibrations respectively of the uncoordinated nitrate ion of D$_{3h}$ symmetry.\textsuperscript{173}

In the thiocyanate complex, a sharp band at 2053 cm\textsuperscript{-1} is attributable to N-coordinated thiocyanate ion.\textsuperscript{117} This is supported by the presence of a medium intensity band at 478 cm\textsuperscript{-1} and a weak band at 852 cm\textsuperscript{-1}. 
In the spectrum of halide complexes, Fe-Cl and Fe-Br stretching vibrations are observed at 310 and 289 cm\(^{-1}\) which are absent in the ligand spectrum.\(^{117}\)

Furthermore, the Fe-N stretching vibration is observed at about 450 cm\(^{-1}\) in all these complexes.\(^{117}\)

The above spectral observations along 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 strong bands observed at 1650 and 1594 cm\(^{-1}\) in BAME are attributed to the stretching vibrations of the carbonyl and azomethine groups respectively.\(^{138}\) In the present complexes the \(\nu(C=\!N)\) band is blue-shifted to the region 1606-1610 cm\(^{-1}\) indicating the coordination of both the azomethine nitrogens. But the band at 1650 cm\(^{-1}\) remains practically unaltered suggesting the non-coordination of both the carbonyl oxygens in these complexes.\(^{138}\)

In the perchlorate complex an intense unsplit band at 1087 cm\(^{-1}\) and a medium intensity band at 623 cm\(^{-1}\) are attributed to the \(v_3\) and \(v_4\) vibrations respectively of the uncoordinated perchlorate ion of \(T_d\) symmetry.\(^{117,174}\)
In the nitrate complex the strong band at 1381 cm\(^{-1}\) and a medium intensity band at 828 cm\(^{-1}\) are attributed to \(v_3\) and \(v_2\) vibrations respectively of ionic nitrate of \(D_{3h}\) symmetry.\(^{147,175}\)

Co-N stretching vibration is observed at about 450 cm\(^{-1}\) in the complexes which is absent in the ligand.\(^{105}\)

The above spectral observations along with the conductance data indicate that both the anions remain uncoordinated in all these complexes.

**Nickel(II) Complexes**

The bands at 1650 and 1594 cm\(^{-1}\) in the ligand are attributable to the stretching vibrations of carbonyl and azomethine groups respectively.\(^{138}\) In the present complexes, the band at 1594 cm\(^{-1}\) is blue-shifted to the region 1606-1610 cm\(^{-1}\) indicating the coordination of both the azomethine nitrogens. But the band at 1650 cm\(^{-1}\) remains practically unaltered suggesting the non-coordination of both the carbonyl oxygens in the complexes.\(^{138}\)

The perchlorate complex shows an intense unsplit band at 1088 cm\(^{-1}\) attributable to \(v_3\) vibration of uncoordinated perchlorate ion of \(T_d\) symmetry.\(^{174}\) Further the medium intensity band at 623 cm\(^{-1}\) is due to \(v_4\) vibration of perchlorate ion of \(T_d\) symmetry.\(^{174}\)

In the nitrate complex, the strong band at 1382 cm\(^{-1}\) and a medium intensity band at 830 cm\(^{-1}\) are attributed to \(v_3\) and \(v_2\) vibrations
of uncoordinated nitrate of $D_{3h}$ symmetry. Furthermore, the Ni-N stretching vibration is observed at about 445 cm$^{-1}$.

These results along with the conductance data indicate that both the anions remain as counter anions in these complexes.

**Copper(II) Complexes**

The bands observed at 1650 and 1594 cm$^{-1}$ in BAME are attributed to the stretching vibrations of the carbonyl and azomethine groups respectively. In the present complexes the $v(C=N)$ band is found to be shifted to the 1604-1608 cm$^{-1}$ region indicating the coordination of both the azomethine nitrogens. But the band at 1650 cm$^{-1}$ remains practically unaltered suggesting the non-coordination of both the carbonyl oxygens in these complexes.

In the perchlorate complex, an intense unsplit band at 1094 cm$^{-1}$ and a medium intensity band at 624 cm$^{-1}$ are attributed to the $v_3$ and $v_4$ vibrations respectively of uncoordinated perchlorate ion of $T_d$ symmetry.

In the nitrate complex, the strong band at 1383 cm$^{-1}$ and a medium intensity band at 833 cm$^{-1}$ are attributed to the $v_3$ and $v_2$ vibrations of uncoordinated nitrate ion of $D_{3h}$ symmetry.

Furthermore, the Cu-N stretching vibration is observed at about 450 cm$^{-1}$ in the complexes.
The above spectral observations along with the conductance data indicate that both the anions remain uncoordinated in all of these complexes.

### 3.2.5 Electronic Spectral Studies

The electronic spectrum of BAME shows two bands with maxima at 25,000 and 40,322 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 bands of the complexes of BAME with tentative assignments are presented in Tables 3.13 to 3.16.

**Iron(III) Complexes**

In iron(III) complexes \(n \rightarrow \pi^*\) transitions are red-shifted to the region 24,390-24,875 cm\(^{-1}\) while \(\pi \rightarrow \pi^*\) transitions are blue-shifted to the region 40,485-40,983 cm\(^{-1}\). The band in the region 20,533-21,978 cm\(^{-1}\) of the complexes is attributed to \(^6A_{1g} \rightarrow ^4T_{1g}\) transition which is consistent with octahedral geometry\(^{50,164}\) around the iron(III) ion. An intense absorption band in the 33,222-33,898 cm\(^{-1}\) region may be due to a charge transfer process.

**Cobalt(II) Complexes**

In cobalt(II) complexes both \(n \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) transitions are found to be red-shifted to the regions 23,584-24,875 cm\(^{-1}\) and 38,759-39,525 cm\(^{-1}\) respectively when compared to that of BAME. The absorption band observed in the region 18,518-19,920 cm\(^{-1}\) may be assigned to \(^4A_2(F) \rightarrow ^4T_{1g}(P)\) transitions. A low energy band in the region
6,756-7,092 cm\(^{-1}\) is attributable to \(^4\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!
3.2.6 Magnetic Behaviour

The magnetic susceptibility measurements were done as described in Chapter 2. The molar magnetic moments of the complexes are given in Tables 3.13 to 3.16.

Iron(III) Complexes

The molar magnetic moment values of the iron(III) complexes lie in the range 5.71-5.96 BM suggesting high spin octahedral configuration around the iron(III) ion.\textsuperscript{24,178}

Cobalt(II) Complexes

The molar magnetic moment values of the cobalt(II) complexes vary in the range 4.52-4.84 BM suggesting tetrahedral configuration around the cobalt(II) ion.\textsuperscript{179} The observed values are higher than the spin only value (3.87 BM). This may be due to incomplete quenching of orbital magnetic moment by the surrounding ligand.\textsuperscript{180}

Nickel(II) Complexes

The molar magnetic moment values of the nickel(II) complexes lie in the range 3.32-3.79 BM suggesting tetrahedral configuration around the nickel(II) ion.\textsuperscript{181}

Copper(II) Complexes

The molar magnetic moment values of the copper(II) complexes vary in the range 1.80-1.84 BM. This indicates that the
complexes are monomeric in nature and that any metal-metal interaction is absent in these complexes\textsuperscript{182}.

3.2.7 EPR Spectra

The X-band EPR spectra of the complexes are recorded in 1:1 methanol-toluene mixture at liquid nitrogen temperature (Fig. 3.2). All the complexes have a well resolved $g_{\perp}$ and a broadened $g_{\parallel}$ region. In all of the spectra no superhyperfine splitting from the ligand part is observed.

![EPR spectra of copper(II) complexes of BAME](image)

Fig. 3.2. EPR spectra of copper(II) complexes of BAME

- $A = [\text{Cu(BAME)}_2](\text{ClO}_4)_2$
- $B = [\text{Cu(BAME)}_2](\text{NO}_3)_2$
- $C = [\text{Cu(BAME)}_2]\text{Cl}_2$
- $D = [\text{Cu(BAME)}_2]\text{Br}_2$. 
The various spin Hamiltonian parameters computed are presented in Table 3.1. The trend $g_{\|} > g_{\perp} > 2.0023$ indicates that the unpaired electron is most likely in the $d_{x^2-y^2}$ orbital. The covalency parameter $\alpha^2$ is calculated using Kivelson and Neiman equation:

$$\alpha_{Cu}^2 = -\left( A_{\|} / 0.36 \right) + (g_{\|} - 2.002) + \frac{3}{7} (g_{\perp} - 2.002) + 0.04$$

The values are given in Table 3.17

The values of $\alpha^2$ lie in the range 0.74 to 0.76. This indicates fairly covalent nature in the metal-ligand bonding. Further the shape of the EPR spectra indicates that the geometry around copper(II) ion is square planar as is evident from the less intense peaks on the low-field side and high-intense peaks on the high-field side.

### 3.3 Summary and Conclusion

**Iron(III) Complexes**

The iron(III) complexes of BAME of the compositions $[\text{Fe(BAME)}_2X]X_2$ ($X = \text{ClO}_4$ or $\text{NO}_3$) and $[\text{Fe(BAME)}X_2]X$ ($X = \text{SCN}, \text{Cl}$ or $\text{Br}$) have been synthesised and characterised by elemental analyses, electrical conductance in non-aqueous solvents, infrared and electronic spectra as well as magnetic susceptibility measurements. In these complexes BAME acts as a neutral bidentate ligand coordinating through both the azomethine nitrogen atoms. In the perchlorate and nitrate complexes one of the anions is coordinated bidentately while in the thiocyanate, chloride and bromide complexes, two of the anions are
coordinated to the metal ion. A high spin octahedral geometry is assigned around the iron(III) in all of these complexes.

Based on the above observations the following tentative structures may be assigned to the complexes.
Cobalt(II) Complexes

The cobalt(II) complexes of BAME of the composition \([\text{Co(BAME)}_2]\)\(X_2\) (\(X = \text{ClO}_4, \text{NO}_3, \text{Cl, Br or I}\)) have been synthesised and characterised by elemental analyses, electrical conductance in non-aqueous solvents, infrared and electronic spectra as well as magnetic susceptibility measurements. In these complexes BAME acts as a neutral bidentate ligand coordinating through both the azomethine nitrogens and both the anions remain uncoordinated. A tetrahedral geometry around the cobalt(II) may be assigned in all these complexes.
Based on the results of the present study, the following tentative structure shown in Fig. 3.4 may be assigned to the complexes.

\[(X = \text{ClO}_4, \text{NO}_3, \text{Cl}, \text{Br or I})\]

**Fig. 3.4 Tentative structure of cobalt(II) complexes of BAME**

**Nickel(II) Complexes**

The nickel(II) complexes of BAME of the composition \([\text{Ni(BAME)}_2]X_2\) (\(X = \text{ClO}_4, \text{NO}_3, \text{Cl}, \text{Br or I}\)) have been synthesised and characterised by elemental analyses, electrical conductance in non-aqueous solvents, infrared and electronic spectra as well as magnetic
susceptibility measurements. In these complexes BAME acts as a neutral bidentate ligand coordinating through both the azomethine nitrogens and both the anions remain uncoordinated. A tetrahedral geometry around the nickel(II) may be assigned in all of these complexes.

Based on the above observations, the following tentative structure shown in Fig 3.5 may be assigned to the complexes.

\( (X = \text{ClO}_4, \text{NO}_3, \text{Cl}, \text{Br or I}) \)

Fig. 3.5 Tentative structure of nickel(II) complexes of BAME
Copper(II) Complexes

The copper(II) complexes of BAME of the composition [Cu(BAME)$_2$]X$_2$ (X = ClO$_4$, NO$_3$, Cl or Br) have been synthesised and characterised by elemental analyses, electrical conductance in non-aqueous solvents, infrared, electronic and EPR spectra as well as magnetic susceptibility measurements. In these complexes BAME acts as a neutral bidentate ligand coordinating through both the azomethine nitrogens. Both the anions remain uncoordinated generating a square planar geometry around the copper(II) in all of these complexes.

Based on the results of the present study the structure shown in Fig. 3.6 may be assigned to the complexes.

![Tentative structure of copper(II) complexes of BAME](image)

Fig. 3.6 Tentative structure of copper(II) complexes of BAME