CHAPTER 4

STUDIES ON RARE EARTH COMPLEXES OF N,N'-BIS(4-ANTIPYRYLMETHYLDENE)ETHYLENEDIAMINE

This chapter deals with the synthesis and characterisation of thirty complexes derived from the rare earth perchlorates, nitrates and iodides with an antipyrine derivative, which is a Schiff base, viz., N,N'-bis(4-antipyrylmethylidene)ethylenediamine (BAME).

The term 'Schiff base' is normally used to represent the class of compounds bearing the azomethine group, \(-\text{CH}=\text{N}\)-, which is generally formed by the condensation of a primary amine with a compound having an active carbonyl group.\(^{169}\) Basically the possession of a potential N-donor site and the ease of its preparation make these compounds a very important class of ligands in coordination chemistry. Regarding Schiff base complexes, the first successful attempt was made by H. Schiff in 1869 using the ligand prepared by the reaction between salicylaldehyde and aniline, with copper. Later, a very large number of Schiff base complexes of both transition metals and lanthanides have been synthesised and characterised.\(^{170}\) Such a Schiff base, N,N'-bis(4-antipyrylmethylidene)ethylenediamine (BAME), obtained by the condensation between 4-formyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one and ethylenediamine, is used in the present investigation. BAME has two identical
carbonyl groups and two identical azomethine groups in such a way that the Schiff base is capable of forming two five-membered rings and one six-membered ring incorporating the metal ion. Thus, a tetradentate behaviour is expected. But, the possibility of non-participation of either of the two groups cannot be ruled out.

![Diagram](https://via.placeholder.com/150)

Figure 4.1  
N,N'-Bis(4-antipyrylmethylidene)ethylenediamine (BAME)

EXPERIMENTAL

4.1  Preparation of the Complexes

4.1.1  Rare earth perchlorate complexes of BAME

One mmol (0.5 g) of the rare earth perchlorate was dissolved in 10 mL of methanol and it was added to the boiling solution of the Schiff base, obtained by dissolving 2.2 mmol (1.0 g) of BAME in 50 mL of methanol taken in a 100 mL R. B. flask kept on a boiling water bath. The mixture was refluxed further for a period of about 20 min. The resulting solution was filtered and the volume of the filtrate was reduced to half and then cooled. The complex so precipitated
was washed several times with hot methanol to remove the excess ligand, if any.
It was then dried under vacuum over phosphorus(V)oxide.

The formation of rare earth perchlorate complexes of BAME may be represented as:

$$\text{Ln(ClO}_4)_3 + 2\text{BAME} \rightarrow \text{Ln(BAME)}_2(\text{ClO}_4)_3$$

where, \( \text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er} \).

### 4.1.2 Rare earth nitrate complexes

One mmol (0.4 g) of the rare earth nitrate was dissolved in 10 mL of acetonitrile and it was added to the boiling solution of the ligand, obtained by dissolving 2.2 mmol (1.0 g) of BAME in 30 mL of acetonitrile taken in a 100 mL R. B. flask kept on a boiling water bath. The resulting solution was refluxed further for about six hours, cooled, filtered and the filtrate was concentrated. The viscous mass so obtained was then washed several times with hot benzene to remove the excess ligand. The solid complex separated was recrystallised by stirring vigorously a saturated solution of the complex in acetonitrile with a few drops of benzene. It was filtered and dried under vacuum over phosphorus(V)oxide.

The formation of rare earth nitrate complexes of BAME may be represented as:

$$\text{Ln(NO}_3)_3 + 2\text{BAME} \rightarrow \text{Ln(BAME)}_2(\text{NO}_3)_3$$

where, \( \text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er} \).
4.1.3 Rare earth iodide complexes

One mmol (0.5 g) of the rare earth iodide was dissolved in 10 mL of methanol and it was added to the boiling solution of the Schiff base, prepared by dissolving 3.2 mmol (1.5 g) of BAME in 60 mL of acetonitrile taken in a 100 mL R. B. flask kept on a water bath. The resulting solution was refluxed further for about seven hours. It was then filtered and the filtrate was concentrated to get a viscous mass which was then washed repeatedly with hot benzene to remove the excess ligand. The solid complex separated was recrystallised by stirring vigorously a saturated solution of the complex in acetonitrile with a few drops of benzene. It was filtered and dried under vacuum over phosphorus(V)oxide.

The formation of rare earth iodide complexes of BAME may be represented as:

$$\text{LnI}_3 + 3\text{BAME} \rightarrow \text{Ln(BAME)}_3\text{I}_3$$

where, \(\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er.}\)

RESULTS AND DISCUSSION

4.2 Analyses and Physicochemical Studies

The details of the different kinds of analyses and physicochemical studies employed in the present investigation are described in Chapter 2.
4.2.1 Appearance and solubility of the complexes

The rare earth perchlorate complexes of BAME are coloured yellow and are non-hygroscopic solids. They are readily soluble in acetone, acetonitrile, DMF, DMSO and nitrobenzene but partially soluble in chloroform and insoluble in benzene, carbon tetrachloride, ethanol, methanol and toluene.

The rare earth nitrate complexes of BAME are yellowish, non-hygroscopic solids. They are soluble in acetone, acetonitrile, DMF, DMSO, ethanol, methanol and nitrobenzene but insoluble in benzene, carbon tetrachloride, chloroform and toluene.

The rare earth iodide complexes of BAME are yellow, non-hygroscopic solids. They are soluble in acetone, acetonitrile, chloroform, DMF, DMSO, ethanol, methanol and nitrobenzene but insoluble in benzene, carbon tetrachloride and toluene.

4.2.2 Elemental analyses

The thirty newly prepared rare earth complexes were analysed for the percentage of metal,\textsuperscript{130} perchlorate,\textsuperscript{131} iodide,\textsuperscript{132} carbon, hydrogen and nitrogen in accordance with the system under investigation. The results obtained are given in Tables 4.1-4.3.

The analytical data suggest that the perchlorate and nitrate complexes have the same stoichiometric composition. These may be formulated as \( \text{Ln}(\text{BAME})_2\text{X}_3 \), where \( \text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er} \); and
The iodide complexes may be represented by the general formula $\text{Ln(BAME)}_3\text{I}_3$, where, $\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er}$.

### 4.2.3 Electrical conductance

The molar conductance data of the rare earth perchlorate, nitrate and iodide complexes of BAME in three non-aqueous solvents, viz., nitrobenzene, acetonitrile and DMF are given in Tables 4.4–4.6.

**Perchlorate complexes**

The molar conductance values of the rare earth perchlorate complexes of BAME in nitrobenzene, acetonitrile and DMF are in the range suggested for 1:2 electrolytes, but in certain cases, the molar conductance values in acetonitrile and DMF are slightly higher than that of the values expected for 1:2 electrolytes. This deviation may be due to the partial displacement of the coordinated perchlorate group by the solvent molecule.

Thus, the complexes may be formulated as:

$$[\text{Ln(BAME)}_2(\text{ClO}_4)](\text{ClO}_4)_2$$

where, $\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er}$.

**Nitrate complexes**

The observed molar conductance values of the rare earth nitrate complexes of BAME in nitrobenzene, acetonitrile and DMF are in agreement
with the values corresponding to 1:2 electrolytes. Thus, the nitrate complexes of BAME may be represented as:

$$[\text{Ln}(	ext{BAME})_2(\text{NO}_3)_2](\text{NO}_3)_2$$

where, $\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er.}$

**Iodide complexes**

The molar conductance values of the rare earth iodide complexes of BAME in nitrobenzene, acetonitrile and DMF agree with the values proposed for 1:2 electrolytes. The slightly higher values observed in certain cases may be due to the partial displacement of the coordinated iodide ion by solvent molecule. Thus, the complexes may be formulated as:

$$[\text{Ln}(	ext{BAME})_3\text{I}]_2$$

where, $\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er.}$

### 4.2.4 Infrared spectra

The infrared spectrum of the free ligand shows the bands characteristic of both carbonyl and azomethine groups at 1648 and 1594 cm$^{-1}$ respectively. But, in their complexes the band at 1594 cm$^{-1}$ characteristic of the azomethine group is totally shifted to around 1605 cm$^{-1}$ indicating that both azomethine nitrogen atoms are coordinated to the rare earth ion. But, the band corresponding to the carbonyl group remains practically unchanged around 1649 cm$^{-1}$ in these complexes suggesting that the carbonyl oxygens are not coordinated to the
metal ion in these complexes. 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 five-membered rings incorporating the rare earth ion adds considerable stability to these complexes.

The important infrared spectral bands of the Schiff base and its complexes together with the tentative assignments are given in Tables 4.7-4.9.

**Perchlorate complexes**

The infrared band at 1594 cm\(^{-1}\) corresponding to the azomethine group of BAME is totally shifted to around 1605 cm\(^{-1}\) in the rare earth perchlorate complexes indicating that both azomethine nitrogens are coordinated\(^{68,126}\) to the rare earth ion, while the band due to the ring carbonyl group remains practically unchanged at around 1649 cm\(^{-1}\) indicating that the carbonyl oxygens are not coordinated\(^{68,133}\) to the metal ion. The triply split band maxima observed at around 1145, 1100 and 1020 cm\(^{-1}\) are due to the \(v_8\), \(v_6\) and \(v_1\) vibrations respectively of the perchlorate group of \(C_{2v}\) symmetry which indicate that the perchlorate groups must be coordinated\(^{137,138}\) in a bidentate fashion. But, the band at around 1089 cm\(^{-1}\) is assigned to the \(v_3\) vibration of the ionic perchlorate of \(Td\) symmetry. Thus, the presence of both ionic and bidentately coordinated perchlorate groups is indicated in these complexes. The vibrational frequencies observed\(^{137,138}\) around 942 and 636 cm\(^{-1}\) corresponding to the \(v_2\) and \(v_3\) vibrations respectively of the perchlorate (\(C_{2v}\)) group, and the band at 624 cm\(^{-1}\) due to the \(v_4\) vibration of the ionic perchlorate, which are not present in the
spectrum of the free ligand, also support the coexistence of both ionic and bidentately coordinated perchlorate groups in these complexes. Besides, the broad band observed at 381 cm\(^{-1}\) due to the stretching vibration\(^{21,147}\) of the Ln-N bond supports the coordination of azomethine nitrogen in these complexes. The weak band observed at around 465 cm\(^{-1}\) is attributed to the Ln-O stretching vibration.\(^{64,145-147}\) Since the oxygen atoms of BAME are in the uncoordinated state, the \(v_{\text{Ln-O}}\) band is attributed to the coordination of the perchlorate oxygen. These spectral observations, which are in conformity with the molar conductance data, indicate that one of the perchlorate ions is coordinated to the metal ion in a bidentate fashion while the other two perchlorates remain as counter ions.

Thus, a coordination number of six is assigned to the metal ion in the rare earth perchlorate complexes of BAME.

**Nitrate complexes**

The infrared band observed at 1594 cm\(^{-1}\) corresponding to the azomethine group of BAME is totally shifted to around 1604 cm\(^{-1}\) in the rare earth nitrate complexes indicating that both of the azomethine nitrogens are coordinated\(^{68}\) to the rare earth ion, while the band corresponding to the ring carbonyl group remains practically unchanged at about 1649 cm\(^{-1}\) indicating that the carbonyl oxygens are not coordinated\(^{68,133}\) to the metal ion. Besides, the complexes show characteristic vibrational frequencies of both ionic and
coordinated nitrate groups. A very strong band observed around 1384 cm\(^{-1}\) indicates the presence of ionic nitrate group\(^{121,142}\) and it is due to the \(v_3\) vibration of the nitrate group of \(D_{3h}\) symmetry. This is supported by another band of medium intensity observed around 820 cm\(^{-1}\) due to the \(v_2\) vibration\(^{100,142}\) of the ionic nitrate. The presence of coordinated nitrate group is indicated by the bands observed around 1438 and 1250 cm\(^{-1}\) due to the \(v_4\) and \(v_1\) vibrations respectively of the nitrate group of \(C_{2v}\) symmetry.\(^{142}\) A medium band observed around 1054 cm\(^{-1}\) due to the \(v_2\) vibration\(^{143}\) of the nitrate group (\(C_{2v}\)) stands as additional evidence for the presence of coordinated nitrate ion. The difference in wave numbers between the two highest frequency bands (\(v_4-v_1\)) of the \(C_{2v}\) nitrate is about 192 cm\(^{-1}\), which indicates that the coordinated nitrate ion is bidentate.\(^{142}\) Another broad band observed\(^{21,147}\) around 380 cm\(^{-1}\) due to \(v_{Ln-N}\) supports the coordination of azomethine nitrogen in these complexes. Besides, the weak band observed at around 464 cm\(^{-1}\) due to the Ln–O stretching vibration\(^{64,145-147}\) provides an additional evidence for the coordination of nitrate oxygen in these complexes, because the carbonyl oxygen atoms of the ligand BAME are not coordinated to the metal ion. These results, which are in conformity with the conductance data, indicate that one of the nitrate ions is coordinated in a bidentate fashion while the other two nitrates remain as counter ions.

Thus, a coordination number of six is assigned to the metal ion in the rare earth nitrate complexes of BAME.
iodide complexes

The infrared band at 1594 cm\(^{-1}\) corresponding to the azomethine group of BAME is totally shifted to around 1605 cm\(^{-1}\) in the rare earth iodide complexes, indicating that both of the azomethine nitrogens are coordinated\(^{68}\) to the rare earth ion, while the band corresponding to the ring carbonyl group remains practically unchanged at around 1650 cm\(^{-1}\) indicating that the carbonyl oxygens are not coordinated\(^{68,133}\) to the metal ion. In addition to this, a band is observed around 182 cm\(^{-1}\) in the far infrared region of these complexes, which is not present in the free ligand. This band is attributed to the Ln-I stretching vibration\(^{126,140}\) which suggests that at least one of the iodides must be in the coordinated state. The \(\nu_{\text{Ln-N}}\) vibration observed\(^{21,147}\) as a broad band around 381 cm\(^{-1}\) in these complexes also supports the coordination of azomethine nitrogens. These spectral observations, which are in conformity with the conductance data, indicate that one of the iodide ions is coordinated while the other two iodides remain as counter ions.

Thus, a coordination number of seven is assigned to the metal ions in the rare earth iodide complexes of BAME.

4.2.5 Proton NMR spectra

The proton NMR spectrum of the Schiff base, BAME, shows the resonance signal corresponding to the azomethine proton at \(\delta 8.21\) ppm as a singlet with respect to TMS. But in the complexes of yttrium and lanthanum, this
signal is found to be shifted to high fields with respect to TMS indicating that the nitrogen atoms of both the azomethine groups are coordinated\textsuperscript{153} to the rare earth ion in these complexes. The other signals corresponding to the phenyl, =N–CH\textsubscript{2}–, –N–CH\textsubscript{3} and =C–CH\textsubscript{3} are obtained in the region \(\delta\) 7.46–7.29 ppm (multiplet), \(\delta\) 3.60 ppm (singlet), \(\delta\) 3.29 ppm (singlet) and \(\delta\) 2.53 ppm (singlet) respectively in the spectrum of the free ligand.

The important proton NMR signals of BAME and its yttrium and lanthanum complexes with the tentative assignments are given in Tables 4.10-4.12.

\textit{Perchlorate complexes of yttrium and lanthanum}

The resonance signal corresponding to the azomethine proton of BAME is observed at \(\delta\) 8.21 ppm as a singlet with respect to TMS. But, in the perchlorate complexes of Y and La, it is observed at \(\delta\) 7.89 and 7.87 ppm respectively, indicating that both the azomethine nitrogens are coordinated\textsuperscript{153} to the rare earth ion. The other signals are found in the region \(\delta\) 7.55–7.14 ppm as a multiplet, \(\delta\) 3.52 ppm as a singlet, \(\delta\) 3.34 ppm as a singlet and \(\delta\) 2.48 ppm as a singlet with respect to TMS corresponding to the phenyl, =N–CH\textsubscript{2}–, –N–CH\textsubscript{3} and =C–CH\textsubscript{3} groups respectively.

\textit{Nitrate complexes of yttrium and lanthanum}

The resonance signal corresponding to the azomethine proton of BAME is observed at \(\delta\) 8.21 ppm as a singlet with respect to TMS. But, in the nitrate
complexes of Y and La, it is observed at δ 7.85 and 7.80 ppm respectively, indicating that both the azomethine nitrogens are coordinated\textsuperscript{153} to the rare earth ion. The other signals are found in the region δ 7.56–7.14 ppm as a multiplet, δ 3.54 ppm as a singlet, δ 3.34 ppm as a singlet and δ 2.50 ppm as a singlet with respect to TMS corresponding to the phenyl, =N–CH\textsubscript{2}–, =N–CH\textsubscript{3} and =C–CH\textsubscript{3} groups respectively.

\textit{Iodide complexes of yttrium and lanthanum}

The resonance signal corresponding to the azomethine proton of BAME is observed at δ 8.21 ppm as a singlet with respect to TMS. But, in the iodide complexes of Y and La, it is observed at δ 7.84 and 7.82 ppm respectively, indicating that both the azomethine nitrogens are coordinated\textsuperscript{153} to the rare earth ion. The other signals are found in the region δ 7.54–7.28 ppm as a multiplet, δ 3.56 ppm as a singlet, δ 3.36 ppm as a singlet and δ 2.52 ppm as a singlet with respect to TMS corresponding to the phenyl, =N–CH\textsubscript{2}–, =N–CH\textsubscript{3} and =C–CH\textsubscript{3} groups respectively.

\subsection*{4.2.6 Electronic spectra}

The electronic spectrum of BAME shows two maxima at 24.81 kK and 40.00 kK corresponding to n → π\textsuperscript{*} and π → π\textsuperscript{*} transitions respectively. But, in the spectra of the complexes these transitions are found to be slightly shifted.
The important electronic spectral bands of BAME and its rare earth complexes with the tentative assignments along with the calculated covalency parameters are presented in Tables 4.13-4.15.

Perchlorate complexes

In the spectra of the perchlorate complexes, both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands are found to be blue shifted and appeared in the region 26.38-25.44 kK and 41.84-40.16 kK respectively compared with that of BAME. The f-f bands are observed only in the complexes of Pr, Nd, Sm, Ho and Er and are found to be slightly red shifted with respect to the corresponding aquo ions. The observed shift is a reflection of the 'nephelauxetic effect'. The interelectronic repulsion parameter ($\beta$), the percentage covalency ($\delta$), the bonding parameter ($b^{1/2}$) and the covalency angular overlap parameter ($\eta$) are calculated. It is found that the values of $\beta$ are less than unity and those of $b^{1/2}$ and $\eta$ are positive. This result suggests some covalent character of the metal-ligand bond. But, the covalent character of Ln-ligand bond is weak as indicated by the values of $\delta$, which are less than 1.5. Further, the hypersensitive bands obtained in the spectra of Nd, Ho and Er complexes have striking resemblance with that of the six-coordinated complexes reported earlier. Since Nd, Ho and Er perchlorate complexes of BAME are isomorphous with the remaining perchlorate complexes of BAME, the same coordination number of six may be proposed to
other metal ions also in these complexes. Besides, the nature of electronic spectra both in solid and solution states remains identical in all the complexes suggesting that these complexes retain the same structure in both of these media.

**Nitrate complexes**

The n → π* band is found to be red shifted in the spectra of the nitrate complexes and appeared in the region 24.75–24.15 kK, while the π → π* is observed as blue shifted to the region 42.01–40.65 kK. The f–f bands are observed only in the complexes of Pr, Nd, Sm, Ho and Er and are found to be slightly red shifted with respect to the corresponding aquo ions. The values of covalency parameters, β, δ, b½ and η are calculated. The values of β are less than unity and that of η and b½ are positive, suggesting some covalent character of the metal–ligand bond, but it is weak as indicated by the values of δ, which are less than 1.5. Further, the hypersensitive bands observed in the complexes of Nd, Ho and Er have close resemblance with that of the six-coordinated complexes reported earlier. Hence, a coordination number of six is assigned to the metal ion in these complexes. Since Nd, Ho and Er nitrate complexes of BAME are isomorphous with the remaining nitrate complexes of BAME, the same coordination number may be assigned to the other rare earth ions also in these complexes. Besides, the electronic spectra of the nitrate complexes, both in solid and solution states have identical nature and hence,
it may be inferred that these complexes maintain the same structure in both of these media.

**Iodide complexes**

In the iodide complexes of BAME, the $n \rightarrow \pi^*$ band is observed as red shifted to the region 24.57–24.21 kK, while the $\pi \rightarrow \pi^*$ band is found as blue shifted to the region 41.84–40.16 kK. The f-f bands are observed only in the complexes of Pr, Nd, Sm, Ho and Er and are found to be slightly red shifted with respect to the corresponding aquo ions. The calculated values$^{26,159,168}$ of interelectronic repulsion parameter ($\beta$) are found to be less than unity and those of $b$ and $\eta$ are positive. This result suggests some covalent character of the metal-ligand; but it is weak$^{121}$ as suggested by the values of $\delta$ which are less than 1.5. Further, the nujol mull spectrum of the Nd, Ho and Er complexes show almost similar profile as that of the hypersensitive transitions of the seven-coordinated complexes reported earlier.$^{166,167}$ This result suggests a coordination number of seven to Nd, Ho and Er in these complexes. Since these complexes are isomorphous with the other rare earth iodide complexes of BAME, the same coordination number may be assigned to the other rare earth ions also in these complexes. Besides, the electronic absorption bands are identical both in solid and solution states, which proposes that the complexes retain the same structure in both of these media.
4.3 Summary and Conclusion

The rare earth perchlorate, nitrate and iodide complexes of N,N'-bis(4-antipyrilmethylidene)ethylenediamine (BAME) have been synthesised and characterised by elemental analyses, molar conductance as well as infrared, proton NMR and electronic spectra.

**Perchlorate complexes**

According to the elemental analyses and molar conductance data, the rare earth perchlorate complexes of BAME may be represented by the general formula:

\[ \text{[Ln(BAME)₂(ClO₄)](ClO₄)₂} \]

where, Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er.

The infrared and proton NMR spectra reveal that BAME acts as a neutral bidentate ligand coordinating through both of the azomethine nitrogens. The molar conductance data and infrared spectra indicate that one of the perchlorate ions is coordinated bidentately to the metal ion leaving the other two perchlorates as counter ions. The electronic spectra of the complexes indicate that the metal-ligand bond is weakly covalent.

Thus, a coordination number of six is assigned to the metal ion in these complexes. The tentative structure of the complexes is represented in Figure 4.2.
where, \( Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho \) and Er; \( Ph = -C_6H_5 \)

Figure 4.2  Tentative structure of rare earth perchlorate complexes of BAME.

Nitrate complexes

According to the elemental analyses and molar conductance data, the nitrate complexes may be formulated as:

\[
[\text{Ln(BAME)}_2(\text{NO}_3)](\text{NO}_3)_2
\]

where, \( Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho \) and Er.

The infrared and proton NMR spectra indicate that BAME acts as a neutral bidentate ligand coordinating through both azomethine nitrogens. The molar conductance data and infrared spectra indicate that one of the nitrate ions is coordinated in a bidentate manner leaving the other two nitrates as counter ions. The electronic spectra of the complexes indicate that the metal–ligand bond is weakly covalent in these complexes.
Thus, a coordination number of six is assigned to the rare earth ion in these complexes. The tentative structure of the complexes is represented in the Figure 4.3.

\[
\begin{array}{c}
\text{[H}_3\text{C-}N-\text{CH}_3]_6\text{O}^\text{2-} \\
\text{N-}N-\text{C-}\text{O}^\text{2-} \\
\text{Ph} \\
\text{[H}_3\text{C-}N-\text{CH}_3]_6\text{O}^\text{2-} \\
\text{N-}N-\text{C-}\text{O}^\text{2-} \\
\text{Ph}
\end{array}
\]

\[(\text{NO}_3)_2\]

where, Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er; Ph = -C_6H_5

Figure 4.3 **Tentative structure of rare earth nitrate complexes of BAME.**

iodide complexes

In accordance with the elemental analyses and molar conductance data, the rare earth iodide complexes of BAME may be represented by the general formula:

\[
[\text{Ln}^{\text{III}}\text{(BAME)}_3\text{I}_3]_2
\]

where, Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er.
The infrared and proton NMR spectra show that BAME acts as a neutral bidentate ligand coordinating through both azomethine nitrogens. The molar conductance data and infrared spectra indicate that one of the iodide ions is coordinated to the metal ion leaving the other two iodides as counter ions. The electronic spectra of the complexes indicate weak covalent character of the metal–ligand bond in these complexes.

Thus, a coordination number of seven is assigned to the rare earth ion in these complexes. The tentative structure of the complexes is given in Figure 4.4.

![Tentative structure of rare earth iodide complexes of BAME.](image)

where, \( \text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er; } \quad \text{Ph} = -\text{C}_6\text{H}_5\)

**Figure 4.4** **Tentative structure of rare earth iodide complexes of BAME.**
Chapter 5

THERMAL STUDIES ON LANTHANIDE COMPLEXES OF SOME ANTIPYRINE DERIVATIVES