CHAPTER 4

STUDIES ON YTTRIUM AND LANTHANIDE COMPLEXES OF 4-N-(2'-THIENYLIDENE)AMINOANTIPYRINE
The present chapter deals with the synthesis and characterization of ten new complexes of yttrium and lanthanide perchlorates with the Schiff base 4-N-(2'-thienyldiene)aminoantipyrine (abbreviated as TAA). The methods of preparation and purification of the ligand are discussed in Chapter 2.

Fig. 4.1 4-N(2'-thienyldiene)aminoantipyrine (TAA), where Φ is \( \text{C}_6\text{H}_5 \)

The Schiff base TAA is expected to behave as a neutral tridentate ligand coordinating through the carbonyl oxygen, azomethine nitrogen and thiophene ring sulphur. The tridentate coordination of the ligand to the metal ion can produce two five membered rings which can impart extra stability to the resulting complex.
4.1 Preparation of Complexes

The metal perchlorate (1 mmol) in ethyl acetate (10 mL) was added dropwise to a solution of the ligand (3.2 mmol) in ethyl acetate (100 mL). The resulting solution was refluxed for 3 h on a waterbath. The solution was first turned yellow, then brown and finally the solid complex was precipitated. It was washed several times with hot benzene to remove any excess ligand and finally dried in vacuum over P₄O₁₀.

The complexes of the nitrates and iodides of yttrium and lanthanides could not be isolated because of the extremely hygroscopic nature of the complexes.

Analysis and the physicochemical studies of the complexes are discussed in Chapter 3.

4.2 Results and Discussion

The elemental analyses data (Table 4.1) of the present complexes suggest that they can be represented by the general formulae Ln(TAA)₃(ClO₄)₃ (where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er). The complexes are deep reddish brown hygroscopic solids which are soluble in acetonitrile, acetone, methanol and nitrobenzene but insoluble in benzene, toluene and hexane.
4.2.1 Electrolytic conductance

The electrolytic conductance data of the perchlorate complexes of TAA in nitrobenzene, acetonitrile, methanol and DMF are presented in Table 4.2. These molar conductance values in nitrobenzene, acetonitrile and DMF are in the range expected for a 1:2 electrolytic system.\textsuperscript{113} Slightly higher values of conductivity are observed in methanol which is probably attributed to the partial displacement of coordinated perchlorate ion by the solvent molecule.\textsuperscript{113,134} Thus, the formulae of the complexes may be written as \([\text{Ln(TAA)}_3(\text{ClO}_4)](\text{ClO}_4)_2\) where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er.

4.2.2 Magnetic susceptibility

Even though the nature of the complexes are reddish brown crystalline solids, they are hygroscopic. The attempts to measure the magnetic susceptibilities were not successful in the case of yttrium and lanthanide perchlorate complexes of TAA.

4.2.3 Infrared spectra

The important infrared bands of TAA and their complexes together with the tentative assignments are presented in the Table 4.3.
The ligand TAA shows a strong IR band at 1660 cm$^{-1}$ which is assigned to the stretching vibration of ring carbonyl group. In the complexes this band is shifted to about 1620 cm$^{-1}$ indicating the coordination of carbonyl oxygen.$^{90,92}$ TAA shows a strong band around 1580 cm$^{-1}$ which is assigned to the $\nu_{C=N}$ mode of the azomethine group. This band is shifted to about 1565 cm$^{-1}$ in the complexes. This fall in absorption frequency of about 15 cm$^{-1}$ shows the coordination of azomethine nitrogen.$^{90}$ The thiophene $C_{\text{ring}}$-$C_{\text{exo}}$ stretching at 955 cm$^{-1}$ in the ligand is shifted to about 940 cm$^{-1}$ in the complexes.$^{138}$ Also the ring stretching band at 1430 cm$^{-1}$ and the C-H bending at 1218 cm$^{-1}$ due to thiophene in the ligand are shifted to 1400 cm$^{-1}$ and 1180 cm$^{-1}$ respectively in the complexes.$^{148}$ These results indicate the coordination of thiophene sulphur in the complexes. Thus TAA acts as a tridentate ligand coordinating through the carbonyl oxygen, azomethine nitrogen and the thiophene sulphur resulting in the formation of two five-membered rings.

The complexes show the doubly split strong band with band maxima at about 1140 and 1118 cm$^{-1}$ ($\nu_4$ vibrations $C_3\!\!\!\!\!\!\!\!\!_V$) respectively, a medium band at 920 cm$^{-1}$ ($\nu_2$ vibration $C_3\!\!\!\!\!\!\!\!\!_V$) and a medium band at 630 cm$^{-1}$ ($\nu_5$ vibration $C_3\!\!\!\!\!\!\!\!\!_V$) which are characteristic of monodentately coordinated perchlorate group. The complexes
also show a strong band at 1080 cm\(^{-1}\) and a medium band at 635 cm\(^{-1}\) which are attributed to the \(v_3\) and \(v_4\) vibrations (Td) of the ionic perchlorate group.\(^{123,124,127}\) This indicates that one of the perchlorate ions is coordinated to the metal ion which is in conformity with the conductance data.

The new bands observed in the complexes at about 410, 550 and 340 cm\(^{-1}\) are attributed to \(v_{M-N}\), \(v_{M-O}\) and \(v_{M-S}\) vibrations respectively.\(^{69,140,149}\)

A coordination number of ten may be assigned to the metal ion in the present complexes of TAA.

4.2.4 Proton NMR Spectra

The proton NMR spectrum of the ligand TAA shows the azomethine proton resonance at about 8.03 \(\delta\) with respect to TMS. It is shifted to 8.12 \(\delta\) in yttrium perchlorate complex and to 8.16 \(\delta\) in lanthanum perchlorate complex indicating the coordination of azomethine nitrogen.\(^{146}\) The spectrum of the free ligand and the complexes give the following bands: phenyl multiplet along with the thiophene \(\alpha,\beta\)-hydrogen bands at 7.06 and 7.36 \(\delta\), \(-CN\) at 2.4 \(\delta\) and \(-N-CH_3\) at 3.2 \(\delta\) (Table 4.5).
4.2.5 Electronic spectra

The ligands as well as the complexes are intensely coloured and so many of the useful bands are masked. The electronic spectra of the ligand and the complexes in acetonitrile and in solid state do not give much structural details. The ligand TAA have the following absorption maxima in acetonitrile: one $n \rightarrow \pi^*$ transition at 25.06 kK and one $\pi \rightarrow \pi^*$ transition at 30.67 kK. The intense bands at 25.06 and 30.63 kK may be attributed to the transitions of C=O and -N=C- groups of the ligand (Table 4.4).

In the complexes the $n \rightarrow \pi^*$ transition is slightly red-shifted to about 28.73 kK and the $\pi \rightarrow \pi^*$ transition is red-shifted to about 34.97 kK.

The complexes are intensely coloured and most of the absorption bands due to f-f transitions are masked in the complexes by the charge transfer transition spreading over the visible region. Hence, electronic spectral studies are not very helpful in the interpretation of f-f transitions in the present complexes.

4.3 Summary and Conclusion

The perchlorate complexes of yttrium and lanthanides with a Schiff base TAA have been synthesized and
characterized by elemental analyses, molar conductance as well as infrared, proton NMR and electronic spectra.

The conductance studies of the complexes in nitrobenzene, methanol, DMF and acetonitrile suggest their 1:2 electrolytic behaviour. Thus, the complexes may be represented as \([\text{Ln(TAA)}_3(\text{ClO}_4)](\text{ClO}_4)_2\) where \(\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er}\). The IR spectra indicate that TAA acts as a neutral tridentate ligand and that only one of the perchlorate ions is coordinated monodentately to the metal ion.

A coordination number of ten may be assigned to the metal ion in these complexes. A tentative structure of the present complexes may be as shown in Figure 4.2.

![Tentative structure of lanthanide perchlorate complexes of TAA](image)

where \(X = \text{ClO}_4^-\) and \(\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er}\).

Figure 4.2 Tentative structure of lanthanide perchlorate complexes of TAA.