CHAPTER 3

STUDIES ON YTTRIUM AND
LANTHANIDE COMPLEXES OF
4-N-(2'-FURFURYLIDENE)AMINOANTIPYRINE
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The present chapter deals with the synthesis and characterization of complexes of perchlorates, nitrates and iodides of yttrium and lanthanides with the Schiff base 4-N-(2'-furfurylidene)aminoantipyrine (FAA).

Fig. 3.1 4-N-(2'-furfurylidene)aminoantipyrine (FAA), where $\Phi$ is $C_6H_5$

Details of the reagents used, their purities and the method of preparation of the ligands are given in Chapter 2. The Schiff base is expected to behave as a neutral tridentate ligand coordinating through the carbonyl oxygen, the azomethine nitrogen and the furan ring oxygen. The tridentate coordination of the ligand with the metal can produce two five membered ring systems.
which would be expected to impart reasonable stability to the resulting complex.

EXPERIMENTAL

3.1 Preparation of Complexes

3.1.1 Yttrium and lanthanide perchlorate complexes of FAA

The ligand (3.2 mmol) in ethylacetate (100 mL) and the metal perchlorate (1 mmol) in ethyl acetate (10 mL) were mixed. The mixture was refluxed for about 3 h on a waterbath. The precipitated solid complex was washed several times with fresh quantity of hot ethyl acetate to remove any excess ligand. Finally it was washed with hot benzene and dried under vacuum over $P_4O_{10}$.

3.1.2 Yttrium and lanthanide nitrate complexes of FAA

The metal nitrate (1 mmol) in ethyl acetate (10 mL) was added drop by drop to a hot solution of the Schiff base (1.2 mmol) in ethyl acetate (50 mL). The mixture was refluxed for 3 h on a waterbath. The red brown product formed was washed several times with hot ethyl acetate to remove the excess ligand. The complex was recrystallized by dissolving it in the minimum amount of ethyl acetate and stirring with ether. It was dried under vacuum over $P_4O_{10}$.
3.1.3 Yttrium and lanthanide iodide complexes of FAA

The ligand (3.2 mmol) in acetonitrile (100 mL) and the metal iodide (1 mmol) in minimum amount of methanol were mixed. The resulting solution was refluxed for 3 h, concentrated to a pasty mass which was washed several times with hot benzene to remove the excess ligand. The separated complex was recrystallized by dissolving it in the minimum quantity of methanol and stirring with solvent ether. It was dried under vacuum over $\text{P}_4\text{O}_{10}$.

The procedural details of the analysis and physicochemical studies of the complexes were given in Chapter 2.

3.2 Results and Discussion

The elemental analyses data (Tables 3.1 to 3.3) of the thirty complexes suggests that they can be represented by the general formulae.

$$\text{Ln(FAA)}_3(\text{ClO}_4)_3$$
$$\text{Ln(FAA)(NO}_3)_3$$ and
$$\text{Ln(FAA)}_3\text{I}_3$$

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

All these complexes are dark brown nonhygroscopic solids which are soluble in acetonitrile, acetone, methanol.
and nitrobenzene but insoluble in benzene, toluene, chloroform, carbon tetrachloride and ethyl acetate.

3.2.1 Electrolytic conductance

The electrolytic conductance data of perchlorate, nitrate and iodide complexes of FAA in acetonitrile, DMF, methanol and nitrobenzene are presented in Tables 3.4 to 3.6. The molar conductance values of all the three series of complexes are in the range expected for a 1:1 electrolytic systems.\textsuperscript{113} Hence the complexes may be formulated as

\[[\text{Ln}(\text{FAA})_3(\text{ClO}_4)_2](\text{ClO}_4)\]
\[[\text{Ln}(\text{FAA})(\text{NO}_3)_2](\text{NO}_3)\] and
\[[\text{Ln}(\text{FAA})_3\text{I}_2]\text{I}\]

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

Comparatively higher values of conductance are observed in methanol in the above three series of complexes which may be attributed to the partial displacement of the coordinated anion by the solvent molecules.\textsuperscript{113,134}

3.2.2 Magnetic susceptibility

The values of magnetic data of the above thirty complexes are given in the Tables 3.4 to 3.7.
magnetic moments were measured at room temperature and the
data indicate that, except yttrium and lanthanum
complexes, all are paramagnetic. The observed magnetic
moments are in agreement with the van Vleck values\(^{116}\)
which indicate that the 4f-electrons, well shielded by the
5s\(^2\)5p\(^6\) octet, play only a small role in bonding.

The observed magnetic moments of all these complexes,
except those of Sm and Eu, are found to agree well with
Hund’s theoretical values\(^{135}\) for the first spin-orbit
coupling model. The experimental magnetic moments of the
Sm complexes are almost double the expected theoretical
Hund’s value.\(^{135}\)

3.2.3 Infrared spectra

The important infrared bands of FAA and their
complexes together with the tentative assignments are
presented in the Tables 3.8 to 3.10.

The IR spectrum of the ligand FAA indicates a strong
band at 1645 cm\(^{-1}\) which is assigned to the stretching
vibration of carbonyl group. In the complexes of FAA this
band is shifted to 1618 cm\(^{-1}\) indicating the coordination
of the carbonyl oxygen.\(^{90,92}\) FAA shows strong band around
1590 cm\(^{-1}\) which is assigned to the \(V_{C=N}\) mode of the
azomethine group. This band is shifted to about 1575-
1580 cm\(^{-1}\) in the complexes which shows the coordination of azomethine nitrogen.\(^{90}\) The \(\nu_{C-H}\) band of the furan ring at 880 cm\(^{-1}\) is shifted to 825 cm\(^{-1}\) in all the complexes. The antisymmetric bands due to \(\nu_a(C-O-C)\) observed at 1215 and 1132 cm\(^{-1}\) in the ligand are lowered to 1180 and 1110 cm\(^{-1}\) respectively in the complexes.\(^{136,137}\) Also the \(\nu_{C-H}\) (out of plane bend) band observed at 820 cm\(^{-1}\) in FAA is shifted to 800 cm\(^{-1}\) in the complexes. All these results indicate the coordination of the furan oxygen to the metal ion in the complexes.\(^{136,138,139}\)

Thus FAA acts as a neutral tridentate ligand coordinating through the carbonyl oxygen, the azomethine nitrogen and the oxygen of the furan ring resulting in the formation of two five-membered rings.

**Perchlorate complexes**

The infrared spectra of the complexes show the doubly split strong band with band maxima at about 1142 and 1120 cm\(^{-1}\) (\(\nu_4\) vibrations \(C_{3v}\)), a medium band at 928 cm\(^{-1}\) (\(\nu_2\) vibration \(C_{3v}\)) and a medium band at 630 cm\(^{-1}\) (\(\nu_5\) vibration \(C_{3v}\)) characteristic of monodentately coordinated perchlorate group. The complexes also show a strong band at 1080 cm\(^{-1}\) and a medium band at 626 cm\(^{-1}\) which are attributed to the \(\nu_3\) and \(\nu_4\) vibrations (Td) of the ionic perchlorate group.\(^{123,124,127}\) The above results
indicate that two of the perchlorate ions are coordinated to the respective metal ion which is in conformity with conductance data.

The new bands observed in the complexes at about 550, 475 and 410 cm⁻¹ are attributed to the $V_{\text{M-O}}$ (carbonyl), $V_{\text{M-O}}$(furan) and $V_{\text{M-N}}$ vibrations respectively.⁶⁹,¹³⁹,¹⁴⁰

On the basis of the above observations the perchlorate complexes may be represented by the formula $[\text{Ln(FAA)}_3(\text{ClO}_4)_2]\text{ClO}_4$ and a coordination number of eleven may be assigned to the metal ion in these complexes.

**Nitrate complexes**

The IR spectra of the nitrate complexes show four additional bands, which are not present in the spectrum of the ligand. These four bands appear at 1520, 1380, 1310 and 1040 cm⁻¹, which are assigned to the $V_4$ (coordinated), $V_3$ (uncoordinated), $V_1$ (coordinated) and $V_2$ (coordinated) vibrations, respectively, of the nitrate ion.¹²³,¹²⁷

The $V_4$ and $V_1$ modes are the split bands of the $V_3$ mode of free nitrate ion and these corresponds to the coordinated nitrate ion. Since the magnitude of splitting, i.e., $V_4 - V_1$ is about 210 cm⁻¹, the nitrate ion is coordinated to the metal ion in a bidentate fashion.¹²⁹,¹⁴¹,¹⁴² The coexistence of the $V_3$ band at
1380 cm⁻¹ with the split $V_4$ and $V_1$ bands in the spectra of the complexes indicates that all the nitrate ions are not coordinated which is in conformity with the conductance data.

The Ln-O (carbonyl), Ln-O (furan) and Ln-N stretching vibrations are observed at about 550, 460 and 418 cm⁻¹ in the spectra of the complex.\textsuperscript{69,139,140}

In the light of the above evidence, the complexes may be represented by the general formula \(\text{[Ln(PAA)(NO}_3\text{)]}_2\text{NO}_3\). A coordination number of seven may be assigned to the metal ion in these complexes.

**Iodide complexes**

The far infrared spectra of the iodide complexes of FAA show a band at 154 cm⁻¹, which is not present in the spectrum of the ligand. This corresponds to the Ln-I stretching band. This result indicates the coordination of two iodide ions to the metal ion,\textsuperscript{126,143-145} which is in conformity with the conductance data.

The Ln-O (carbonyl), Ln-O (furan) and Ln-N stretching vibrations are observed at about 565, 470, 420 cm⁻¹ respectively in these complexes.\textsuperscript{69,139,140}
Thus the complexes may be represented as \([\text{Ln}(\text{FAA})_3\text{I}_2]\). A coordination number of eleven may be assigned to the metal ion in these complexes.

3.2.4 Proton NMR spectra

The proton NMR spectrum of the ligand FAA shows the azomethine proton resonance at about 7.70 \(\delta\) with respect to TMS. It is shifted to 8.16 \(\delta\) in the case of yttrium perchlorate complex and to 8.03 \(\delta\) in the case of lanthanum perchlorate complex, indicating the coordination of azomethine nitrogen\(^{146}\) (Table 3.13). The azomethine proton resonance occurs at 8.18 and 8.16 \(\delta\) respectively, in yttrium nitrate and lanthanum nitrate complexes (Table 3.14). The azomethine proton resonance is observed at 8.20 and 8.18 \(\delta\) respectively, in yttrium iodide and lanthanum iodide complexes (Table 3.15). The other relevant bands\(^{147}\) observed in the case of ligand and complexes are as follows: phenyl multiplet at 7.33 \(\delta\) and furan proton at 6.53 \(\delta\), \(-\text{C-CH}_3\) at 2.42 \(\delta\) and \(-\text{N-CH}_3\) at 3.17 \(\delta\).

3.2.5 Electronic spectra

The electronic spectra of the free ligand and the complexes were recorded in the solution and in the solid state. Acetonitrile was used as the solvent for the
solution state spectral analyses. For the solid state spectral analyses, a paste of the substance in Nujol was used. Both the solution and the solid state spectra are almost identical, suggesting the same nature of the complexes in these media.

The electronic spectra of the ligand and the complexes in acetonitrile as well as in solid state do not give much structural details. The ligand FAA has the following absorption maxima in acetonitrile: one \( n \rightarrow \pi^* \) transition at 29.49 kK and two \( \pi \rightarrow \pi^* \) transition at 38.76 and 47.85 kK respectively. The intense bands at 29.45 and 38.76 kK may be attributed to the transition of C=O and -N=C- groups of the ligand.

In the perchlorate complexes the \( n \rightarrow \pi^* \) transition is almost unchanged and the high energy \( \pi \rightarrow \pi^* \) transition is not observable. The low energy \( \pi \rightarrow \pi^* \) transition is blue-shifted to the region 32.8-34.84 kK (Table 3.10a).

In the nitrate complexes the \( n \rightarrow \pi^* \) transition remain unchanged or slightly red-shifted to 29.6 kK, the low energy \( \pi \rightarrow \pi^* \) transition is red-shifted to the region 40.16-44.44 kK and the high energy \( \pi \rightarrow \pi^* \) transition is blue-shifted to 43.90-47.10 kK (Table 3.11).
In the case of the iodide complexes the \( n \rightarrow \pi^* \) transition and low energy \( \pi \rightarrow \pi^* \) transitions are blue-shifted to the regions 28.01-29.0 kK and 31.1-36.6 kK respectively and the high energy \( \pi \rightarrow \pi \) band is vanished (Table 3.12).

The compounds are intensely coloured and most of the absorption bands due to \( f-f \) transitions of the lanthanide ions in the visible region are obscured in the complexes by the broad metal-ligand charge transfer transitions spreading over the whole visible region. Hence, the electronic spectra are not very helpful in the investigation of \( f-f \) transitions of the present complexes.

### 3.3 Summary and Conclusion

Thirty new complexes of perchlorates, nitrates and iodides of yttrium and lanthanides with a Schiff base 4-N-(2'-furfurylidene)aminoantipyrine have been isolated and characterized by elemental analyses, molar conductance, magnetic susceptibilities as well as infrared, proton NMR and electronic spectra.

**Perchlorate complexes**

The conductance studies of the perchlorate complexes in nitrobenzene, methanol and acetonitrile indicate their
1:1 electrolytic behaviour. So the perchlorate complexes can be represented as \([\text{Ln(FAA)}_3(\text{ClO}_4)_2](\text{ClO}_4)\), where \(\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er}\).

The IR and proton NMR spectra indicate that the ligand FAA acts as a neutral tridentate one and that two of the perchlorate ions are coordinated monodentately and the third one is ionic. The magnetic moment of the complexes agree well with van Vleck values. A coordination number of eleven may be assigned to the metal ion in these complexes. A tentative structure of the present complexes may be suggested as given in Figure 3.2.

\[
\begin{align*}
\text{H}_3\text{C}\text{N}\text{N}\text{O} & \quad \phi \quad \text{N} \quad \text{O} \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{H}_3\text{C}\text{N}\text{N}\text{O} & \quad \phi \quad \text{N} \quad \text{O} \\
\end{align*}
\]

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

**Fig. 3.2 Tentative structure of lanthanide perchlorate complexes of FAA**
**Nitrate complexes**

The molar conductance values of the nitrate complexes in nitrobenzene, methanol and acetonitrile indicate that the complexes exhibit 1:1 electrolytic behaviour. Therefore, the nitrate complexes can be represented as \([\text{Ln(FAA)(NO}_3)_2(\text{NO}_3)]^+\), where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er. The IR and proton NMR spectra of the complexes show that FAA acts as neutral tridentate ligand and that two of the nitrate ions are bidentately coordinated and the third one ionic. The magnetic moments of the complexes agree well with van Vleck values.

A coordination number of seven may be assigned to the metal ion in the nitrate complexes. With the foregoing evidences the structure of the complexes may be proposed as follows.

\[
\begin{align*}
\begin{array}{c}
\text{Ln}^3+ \\
\text{NO}_3^- \\
\end{array}
\begin{array}{c}
\text{FAA} \\
\text{NO}_3^- \\
\end{array}
\end{align*}
\]

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

**Fig. 3.3** Tentative structure of lanthanide nitrate complexes of FAA.
Iodide complexes

The conductance values of the iodide complexes suggest a 1:1 electrolytic nature. Hence, lanthanide iodide complexes can be represented as \([\text{Ln}(\text{FAA})_3\text{I}_2]\text{I} \), where \(\text{Ln} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er} \). The ligand FAA is neutral tridentate in these complexes. Two of the iodide ions are coordinated to the metal ion and the third one is ionic. The magnetic moments of the complexes agrees well with van Vleck values.

In accordance with the above observations, a coordination number of eleven may be assigned to the lanthanide ion in these complexes. A tentative structure of the complexes may be proposed as in Figure 3.4 below.

![Tentative structure of lanthanide iodide complexes of FAA](image)

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

Fig. 3.4. Tentative structure of lanthanide iodide complexes of FAA

64