Preface

A remarkable development in the coordination chemistry of rare earths has been observed only after 1940 and now it becomes relevant in a wide range of chemical, biological, industrial and applied problems.\textsuperscript{1,2} The rare earth complexes are mainly derived from the tripositive ions and a majority of them are synthesised from either neutral or anionic oxygen donor ligands, even though complexes derived from ligands having nitrogen donor sites are known. The ability of rare earths to form complexes helps much in the separation of lanthanides which is a very difficult problem even now. Besides, certain rare earth complexes find application as antiknock additives and NMR shift reagents. Thus, the increasing demand in the application side makes the investigation on rare earth complexes worth and interesting.

Antipyrine and its derivatives, being potential oxygen donor ligands, are capable of forming stable complexes with rare earth ions. Moreover, antipyrine is well-known for its antipyretic activity since a long time. Hence, the derivatives of it and the complexes derived from them may also have some biochemical applications. This possibility makes the investigation on rare earth complexes of antipyrine derivatives more relevant.
Schiff bases, the compounds containing the azomethine group (-CH=N-) form another class of compounds which plays an important role in the development of coordination chemistry. The complexes of Schiff bases are found to possess considerable stability and a number of such complexes with tripositive rare earths as the central ions are known. In addition to this, a number of Schiff bases especially those derived from antipyrine are shown to have antibacterial and antiinflammatory properties\(^3\,^5\) and it would be expected, and observed in some cases, that these properties may vary on complexation with metal ions. This fact makes the present investigation much more important and meaningful.

The present study includes the preparation and characterisation of sixty rare earth complexes derived from two antipyrine derivatives among which one is a Schiff base. The ligands used are:

(i) 4-Formyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one, or 4-Antipyrine carboxaldehyde

(abbreviated as FDPP)
(ii) \( N,N'\)-Bis(4-antipyrylmethylidene)ethylenediamine

(abbreviated as BAME)

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

FDPP possesses two carbonyl oxygen atoms while BAME contains two carbonyl oxygens and two azomethine nitrogens as potential donor sites. Therefore, these ligands would be expected to form stable complexes with rare earth salts.

The rare earths selected for the present investigation are:

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

The newly prepared complexes have been subjected to the physicochemical methods such as elemental analyses, molar conductance in non-aqueous solvents, infrared, proton NMR and electronic spectra as well as thermogravimetry.

The ligands being antipyrine derivatives, these complexes would be expected to be of physiological importance and we hope these complexes may become important probes for biochemical studies.
The work incorporated with this thesis has been under publication as detailed below:

1. Yttrium and lanthanide perchlorate complexes of 4-formyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one,

2. Yttrium and lanthanide perchlorate complexes of N,N'-bis(4-antipyrylmethylidene)ethylenediamine,

3. Rare earth nitrate complexes of 4-formyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (under publication).

4. Rare earth iodide complexes of 4-formyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (under publication).

5. Rare earth nitrate complexes of N,N'-bis(4-antipyrylmethylidene)ethylenediamine (under publication).

6. Rare earth iodide complexes of N,N'-bis(4-antipyrylmethylidene)ethylenediamine (under publication).

7. Thermal studies of the rare earth nitrate complexes of 4-formyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (under publication).

8. Thermal studies of the rare earth perchlorate complexes of N,N'-bis(4-antipyrylmethylidene)ethylenediamine (under publication).