chapter-I
CHAPTER I

INTRODUCTION

Abstract

1.1 General

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1.3 Earlier work

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References
An up-to-date review of Juglones - a typical class of ligands has been done as a prerequisite to the present work. Lawsone and juglone being parent compounds of the Juglone series, their chemistry is reviewed with special reference to (i) structural aspects (ii) chelating ability and (iii) analytical and antimicrobial properties of the ligands and their metal chelates. Coordination chemistry of rare earth metal chelates, especially Ho(III), Er(III) and Yb(III), has been reviewed with reference to "oxygen-oxygen donor system". A summary of the earlier work on lanthanide metal chelates of Juglones and the object of present work are also given.
1.1 GENERAL

1.1.1 Juglones - a typical class of ligands

The term 'JUGLONE' has been specially assigned to a typical class of ligands which include all the hydroxy derivatives of 1,4-naphthoquinone \([\text{I}]\), in which the hydroxy group is situated at the ortho (i.e. C-2 or C-3) or peri (i.e. C-5 or C-8) position to one of the carbonyl groups\(^1-3\). The origin of this term actually lies in the name of naturally occurring compound traditionally known as 'Juglone'. It is basically 5-hydroxy-1,4-naphthoquinone\(\text{[III]}\) which was isolated first from the plants of Juglans species.

![1,4-Naphthoquinone](image)

An equally important isomer of juglone is lawsone (2-hydroxy-1,4-naphthoquinone) \([\text{II}]\). It was traditionally called as 'isojuglone' indicating that juglone was the first recognized compound of this series.
This simple isomeric-pair 'Juglone-Lawsone' attracted the attention of our 'Research Group' about twenty years ago mainly due to the following reasons:

1. The other members of this class of ligands can be derived by replacing one of the hydrogen, either in benzenoid or quinonoid ring, by substituents such as \( \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{Cl}, \text{Br}, \text{I}, \text{NH}_2 \) etc. By substituting the group such as above in the lawsone and juglone, isomeric pairs of substituted lawsone and juglone are formed.

2. The more common members that are naturally occurring which are well characterized are given below:

\[
\text{Lawsone} \ [\text{II}] \quad \text{Juglone} \ [\text{III}] \\
\left(\text{C}_{10}\text{H}_6\text{O}_3\right) \quad \left(\text{C}_{10}\text{H}_6\text{O}_3\right)
\]

\[
\text{Phthiocol} \ [\text{IV}] \quad \text{Plumbagin} \ [\text{V}] \\
\left(\text{C}_{11}\text{H}_8\text{O}_3\right) \quad \left(\text{C}_{11}\text{H}_8\text{O}_3\right)
\]
Some of these naturally occurring isomeric Juglones and their derivatives are synthesised in laboratory by our research group using established synthetic methods. A list of such derivatives, which are widely used by our research group as ligands in the formation of metal chelates is given in Table 1.1.
<table>
<thead>
<tr>
<th>Ligand</th>
<th>Rare earth metal ions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Lawsone</td>
<td>La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III)</td>
<td>T-2</td>
</tr>
<tr>
<td></td>
<td>Eu(III), Tb(III)</td>
<td>T-13</td>
</tr>
<tr>
<td>2. Juglone</td>
<td>La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III)</td>
<td>T-7</td>
</tr>
<tr>
<td></td>
<td>Eu(III), Tb(III)</td>
<td>T-13</td>
</tr>
<tr>
<td>3. Phthiocol</td>
<td>La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III)</td>
<td>T-3</td>
</tr>
<tr>
<td></td>
<td>Eu(III), Tb(III)</td>
<td>T-12</td>
</tr>
<tr>
<td>4. Plumbagin</td>
<td>La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III)</td>
<td>T-12</td>
</tr>
<tr>
<td></td>
<td>Eu(III), Tb(III)</td>
<td>T-13</td>
</tr>
<tr>
<td>5. 3-Chloro-lawsone</td>
<td>La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III)</td>
<td>T-4</td>
</tr>
<tr>
<td></td>
<td>Eu(III), Tb(III)</td>
<td>T-13</td>
</tr>
<tr>
<td>6. 3-Chloro-juglone</td>
<td>La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III)</td>
<td>T-7</td>
</tr>
<tr>
<td></td>
<td>Eu(III), Tb(III)</td>
<td>T-13</td>
</tr>
<tr>
<td>7. 3-Chloro-lawsone-monoxime</td>
<td>La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III)</td>
<td>T-10</td>
</tr>
<tr>
<td></td>
<td>Contd..</td>
<td></td>
</tr>
<tr>
<td>Ligand</td>
<td>Rare earth metal ions</td>
<td>Reference</td>
</tr>
<tr>
<td>---------------------------</td>
<td>---------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>8. 3-Bromo-lawsonemonoxime</td>
<td>La(III), Ce(III), Pr(III),</td>
<td>T-10</td>
</tr>
<tr>
<td></td>
<td>Nd(III), Sm(III), Gd(III),</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dy(III)</td>
<td></td>
</tr>
<tr>
<td>9. 3-Iodo-lawsonemonoxime</td>
<td>La(III), Ce(III), Pr(III),</td>
<td>T-10</td>
</tr>
<tr>
<td></td>
<td>Nd(III), Sm(III), Gd(III),</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dy(III)</td>
<td></td>
</tr>
<tr>
<td>10. 1,2-naphthoquinone-1-oxime</td>
<td>La(III), Ce(III), Pr(III),</td>
<td>T-11</td>
</tr>
<tr>
<td></td>
<td>Nd(III), Sm(III), Gd(III),</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dy(III)</td>
<td></td>
</tr>
<tr>
<td>11. 1,2-naphthoquinone-2-oxime</td>
<td>La(III), Ce(III), Pr(III),</td>
<td>T-11</td>
</tr>
<tr>
<td></td>
<td>Nd(III), Sm(III), Gd(III),</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dy(III)</td>
<td></td>
</tr>
<tr>
<td>12. 1,2-naphthoquinone-dioxime</td>
<td>La(III), Ce(III), Pr(III),</td>
<td>T-11</td>
</tr>
<tr>
<td></td>
<td>Nd(III), Sm(III), Gd(III),</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dy(III)</td>
<td></td>
</tr>
</tbody>
</table>
These ligands as well as their metal chelates are structurally characterized by using different techniques such as elemental analysis, thermogravimetry, electronic absorption spectroscopy, infrared spectroscopy, magnetic susceptibility etc. The studies of these ligands and their metal chelates are carried out from their analytical, biological, antimicrobial, industrial and medicinal point of view.

1.1.2 Lawsone and its characteristic aspects

Lawsone (2-hydroxy-1,4-naphthoquinone) \([\text{II}]\) is well-known as the 'active constituent' of the Indian medicinal plant - *Lawsonia alba* which is commonly known as Henna, its vernacular name being 'Indian Mehendi'. It is also the principal colouring matter of this plant.

Due to its importance in medicinal\(^{15,16}\) and synthetic chemistry particularly as a dye stuff and in textile industry in the earlier period, much attention was paid to isolate this material from natural source *Lawsonia alba*.\(^{17}\) Accordingly its separation from the plant material has been described in detail in Indian\(^{17}\) as well as foreign literature\(^{18}\) and is readily available for reference\(^{18}\). Now-a-days lawsone is not extracted from the plant material for commercial purpose because it is synthetically prepared\(^{18}\) and readily available in enough quantities in pure form. Therefore, for the present work, commercial
sample is being used in our laboratory for elucidating structural, coordination, analytical and biological aspects of lawsone.

(a) **Structural aspect**

Molecular structure of lawsone has been investigated extensively from all possible angles as it is very important compound from structural, medicinal and coordination point of view. Lot of information on the structural investigation is available and it has been collected and summarized by Padhye, as given in Table 1.2.

On the basis of all available literature data and the experimental results obtained by the techniques such as near infrared and infrared spectra, electronic spectra in various organic solvents, PMR spectroscopy, adsorption chromatography, electronic dipole moments, and apparent dissociation constants at various ionic strengths. Padhye has concluded that structural and coordination characteristics of lawsone are strongly influenced by the hydrogen bonding in solid as well as in solution state. By carrying out intensive experimental work, he has shown that there must be some significant intermolecular hydrogen bonding \( [X] \) in lawsone in the solid state as well as in the solution state at higher
<table>
<thead>
<tr>
<th>Property</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical characteristics</td>
<td>Yellow needles (with reddish shades)</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in ethanol, chloroform, acetone</td>
</tr>
<tr>
<td>Melting point ( °C )</td>
<td>190</td>
</tr>
<tr>
<td>Rf value (TLC) (with solvent)</td>
<td>Benzene (0.00); Chloroform (0.12); Dioxane (0.28).</td>
</tr>
<tr>
<td>Source</td>
<td>Lawsonia alba (Indian Mehendi)</td>
</tr>
<tr>
<td>Dissociation constant</td>
<td>pK = 4.01</td>
</tr>
<tr>
<td>Dipole moment (μ RT) BM</td>
<td>Carbon tetrachloride (0.0); Benzene (2.18); dioxane (7.73).</td>
</tr>
<tr>
<td>Absorption maxima (in nm)</td>
<td>Ethanol (243, 248, 273, 278, 330)</td>
</tr>
<tr>
<td></td>
<td>Dioxane (242.5, 248, 274, 330)</td>
</tr>
<tr>
<td></td>
<td>n-hexane(240, 246, 270, 278, 330)</td>
</tr>
<tr>
<td></td>
<td>Chloroform (244.5, 251, 274.5, 282, 334.5)</td>
</tr>
<tr>
<td>Infrared spectra (Nujol mull)(in cm⁻¹)</td>
<td>ν(O-H) : 3150</td>
</tr>
<tr>
<td></td>
<td>ν(C=O) chelated : 1630</td>
</tr>
<tr>
<td></td>
<td>ν(C=O) free : 1660</td>
</tr>
<tr>
<td></td>
<td>ν(C-O) : 1210</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>Carbon tetrachloride (2.212); benzene (2.262); dioxane (2.218)</td>
</tr>
<tr>
<td>Oxidation-reduction Potential</td>
<td>E₀ = 0.330 - 0.485</td>
</tr>
<tr>
<td>PMR spectra 27,28 (in V)</td>
<td>H-3 (6.36), H-6 (7.75), H-8 (8.09)</td>
</tr>
<tr>
<td>in CDCl₃ (δ values)</td>
<td>H-5 (8.09), H-7 (7.75), OH (7.41)</td>
</tr>
</tbody>
</table>
concentration (provided that solvent-solute interaction is negligible) while weak but appreciable intramolecular hydrogen bonding [XI] in solution is expected at low concentration.

![Chemical structure of lawsone]

- **Intermolecular hydrogen bonding in lawsone [X]**
- **Intramolecular hydrogen bonding in lawsone [XI]**

(b) **Coordination characteristics**

The extensive study done by Masoud et al., Bottei and Mc Echern, Delima et al. indicated that lawsone has excellent chelating ability. The chelate formation with Fe(II) (pale red), Ni(II) (dark red), Cu(II) (orange red), Pb(II) (orange red), Ag(I) (red), Sn(II) (brown) and Al(III) (orange) was reported long back. Therefore, it was visualised that lawsone should be regarded as a versatile ligand and it should be exploited for research purpose. From this point...
of view, an exhaustive study by our research group has shown that lawsone, as a powerful ligand, can interact and form a number of complexes with most of metals from the periodic table. The most interesting aspect of the lawsone and its derivatives is the formation of 'five membered' \([\text{XII}]\) ring through the hydrogen bonding or by the chelate formation with the metal ion.

\[
\text{[XII]}
\]

\[
\text{[XIII]}
\]

It is still more interesting that juglone (5-hydroxy-1,4-naphthoquinone) can form 'six-membered' \([\text{XIII}]\) ring in similar way. This has generated two series of isomeric pairs which lead to a characteristic isomerism which may be referred to as ring isomerism.

Systematic study on isomeric Juglonates was done by Joshi \(^2\) and it was followed by Kelkar \(^4\), Kulkarni \(^7\) and Kadam \(^8\).
(c) **Analytical aspect**

Padhye has studied the colour reactions of lawsone with some metal ions such as Hg(II), Co(II), Al(III), Pd(II), Pt(II), Au(III), Th(IV) in various solvent systems like water, water-ethanol and water-acetone. By careful examination of colour reactions of lawsone with these metal ions, it was found that most of the reactions are nonselective and nonsensitive and hence lawsone was found to be unsuitable reagent for spectrophotometric estimation and complexometric titration as a metallochromic indicator.

Lawsone was studied in our laboratory by Kulkarni in order to find its applicability as an analytical reagent. By careful study in this context, he concluded that sodium salt of lawsone can be used as a gravimetric reagent for estimation of Co(II) and Cu(II) in aqueous medium. He also suggested that 3-substituted halo derivatives of sodium salt of lawsone can be used as the gravimetric reagent if the necessary conditions are maintained.

(d) **Biological activity**

The biological study of Cu(II) salts of lawsone and its C-3 substituted derivatives such as 3-chloro, 3-bromo and 3-methyl lawsone has been done by Mirua. To study some
structure-activity relationship more extensive work was done by Kelkar$^T-4$ and Kulkarni$^T-7$ using 3-substituted derivatives of lawsone and their metal chelates.

1.1.3 Juglone and its characteristic aspects

Juglone is naturally occurring compound largely present in the green parts—particularly in green shells of the walnut. Combes$^{30}$ isolated juglone from walnut in 1907. Juglone can be synthesised more easily on laboratory scale. Padhye$^{T-1}$ and Kulkarni$^{T-7}$ reviewed the methods of synthesis of juglone and established the conditions for better yield. Purity of juglone is checked by various physical and chemical properties.

(a) Structural aspect

The name 'juglone' has its origin in its natural occurrence in the Juglandaceae which is found in Juglans regia, Juglans nigra, Juglans cinera etc. Juglone is important in biological and coordination chemistry as compared to lawsone. Apart from its common features with lawsone it has additional merits from analytical as well as biological point of view and, therefore, it possesses more attraction in juglone series for research purpose. All the previous work on the molecular structure has been reviewed by Padhye$^{T-1}$ along with lawsone. The available data of juglone is summarized in Table 1.3.
**Table 1.3: The available data for juglone**

<table>
<thead>
<tr>
<th>Property</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical characteristics</td>
<td>Yellowish-red needles</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in chloroform, sparingly soluble in ethanol, ether, acetic acid, insoluble in water.</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>153</td>
</tr>
<tr>
<td>Rf value (TLC)</td>
<td>n-hexane (0.0), Dioxane (0.08), Ethanol (0.62), Acetone (0.75)</td>
</tr>
<tr>
<td>Source</td>
<td><em>Juglans regia, Juglans nigra</em></td>
</tr>
<tr>
<td>Dissociation constant</td>
<td>pH = 1.01 (Ionic strength 0.1)</td>
</tr>
<tr>
<td>Dipole moment (μ RT) BM</td>
<td>Carbon tetrachloride (1.18), Benzene (1.30), Dioxane (1.32)</td>
</tr>
<tr>
<td>Absorption maxima (in nm)</td>
<td>n-heptane (300, 412.7), Ethanol (249, 425), Dioxane (248, 412), Chloroform (251,422)</td>
</tr>
<tr>
<td>Infrared spectra (Nujol mull) (in cm⁻¹)</td>
<td>( \nu (0-H) ) : 3072   ( \nu (C=O) ) chelated : 1644   ( \nu (C=O) ) free : 1664   ( \nu (C-O) ) : 1227</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>Carbon tetrachloride (( \varepsilon = 2.218 )); Benzene (( \varepsilon = 2.21 )); Dioxane (( \varepsilon = 2.24 ))</td>
</tr>
<tr>
<td>Oxidation-reduction Potential (in V)</td>
<td>( E_0 = 0.450 ) (Alcohol)   ( E_0 = 0.448 ) (1.0 N HCl)</td>
</tr>
<tr>
<td>PMR spectra (in CDCl₃) (δ values)</td>
<td>H-2, H-3, H-6, H-7, H-8, OH   6.97 6.97 7.75 7.60 7.70 12.30</td>
</tr>
</tbody>
</table>
Juglone \([\text{III}]\) is also a typical and attracting ligand which is expected to possess powerful chelating ability which may be employed for the preparation and detailed investigation of metal chelates involving six membered ring. Its analytical utility may be appreciably enhanced through appropriate substitution at C-2 and C-3 positions. The presence of hydrogen bonding in juglone also plays an important role in its chemical and biological activity. Therefore, elucidation of the nature of hydrogen bonding and its importance in governing the characteristics was the object behind the study of its molecular structure.

\[
\text{[XIV]}
\]

The experimental evidences in connection with the structural investigations of juglone, which mainly include near infrared spectra in carbon tetrachloride (or chloroform); solvent effect on the electronic spectra studied by using different organic solvents of varying polarity, chromatographic investigations in various donor/acceptor solvent and proton magnetic spectroscopy is clearly in favour of the conclusion
that there is powerful intramolecular hydrogen bonding both in solution state as well as in solid state. Deuteration study using infrared spectroscopy and nuclear magnetic resonance spectroscopy has given the confirmatory evidence for the strong intramolecular hydrogen bonding [XIV].

(b) **Coordination characteristics**

Although juglone possesses strong chelating ability as compared to its isomer lawsone, comparatively much less research work has been done on metal chelates of juglone and its C-2 and C-3 derivatives. When we tried to find the reason behind this rather unexpected situation it seemed that most probably the main limitation behind the inability of carrying out extensive work on coordination aspect of juglone derivatives might be the unavailability of these derivatives on commercial scale in fairly pure state. They are costly and the yields are also less.

However, Joshi has done a systematic and detail work on the transition metal juglonates along with corresponding metal lawsonates by selecting a group of five bivalent metal ions which includes Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) and this work latter on was extended by Kulkarni to rare earth metal ions namely La(III), Ce(III), Pr(III), Nd(III), Gd(III), Sm(III) and Dy(III). Kulkarni has also studied structural and coordination aspects of some juglone derivatives.
(c) **Biological activity**

Juglone being an important derivative of 1,4-naphthoquinone, its biological aspects were recognized long ago. Thus Brissemoret et al.\(^{32}\) as well as Fieser\(^{33}\) and his coworkers have reported their results on biological and physiological activity of juglone. Apart from this earlier work certain characteristic properties of juglone were also recognized which include sneezing and coughing action if inhaled, purgative action etc. Some pharmacological investigations were also reported. Juglone was shown to increase the respiration rate of rabbits and also oxidize the ascorbic acid\(^{34}\). Similarly it is known to activate the sperm of sea urchins and also to possess a feeble antihaemorrhagic activity.

(d) **Analytical aspect**\(^{35}\)

It is observed that juglone and its C-2 substituted and C-3 substituted derivatives are better analytical reagents as compared to lawsone and its derivatives. Thus useful metallochromic reactions of juglone and its derivatives are possible with many transition as well as nontransition metals and some of these can be employed for the analytical purpose and some work in this direction has been done by Kelkar\(^{T-4}\), Patil\(^{T-5}\) and Kulkarni\(^{T-7}\). These workers have established the
experimental conditions for the colorimetric estimation of some metal ions, and these are published in literature. The main advantage of the colour reactions of juglone and its derivatives is the formation of sufficiently stable colours with lower limits of estimation. Mixed solvent systems such as water-ethanol and water-acetone are found to be more advisable for better sensitivity and accuracy. Juglone is also shown to be an useful metallochromic indicator in complexometric titration with EDTA and Joshi has done detailed work in this field.

1.1.4 Phthiocol and its characteristic aspect

The naturally occurring alkyl derivatives, which also are well-known for their structural, coordination and biological characteristics are mainly 3-alkyllawsones only. These include phthiocol, lapachol, isolapachol and lomatol.[XV]

Naturally occurring 3-alkyllawsones [XV]

- R : -CH\(_3\) (Phthiocol)
- R : -CH\(_2\)-CH = C (CH\(_3\))\(_2\) (Lapachol)
- R : -CH =CH (CH\(_3\))\(_2\) (Isolapachol)
- R : -CH =CH (CH\(_3\))\(_2\).CH\(_2\)OH (Lomatol)
In the series of 3-alkyllawsone, phthiocol (2-hydroxy-3-methyl-1,4-naphthoquinone) is the simplest member possessing certain merits like its resemblance with vitamin K in certain respect; its superiority as a better ligand over lawsone itself and its ready availability by synthetic method

Phthiocol occurs in trace amount in lipic isolated from the human Tubercle bacillus in wax fractions, along with lawsone and in cultures of Mycobacterium tuberculosis, Tirturus cristatus and Corynebacterium diphtherie.

Several methods of synthesis for phthiocol are known amongst which one suggested by Fieser using 2-methyl-1,4-naphthoquinone, is most convenient and has been followed in our laboratory.

(a) Structural aspect

The molecular structure of phthiocol has been elucidated by Padhye in greater details using various techniques such as nuclear magnetic resonance spectroscopy, electric dipole moment study, dissociation constants at different ionic strengths, near infrared and infrared spectroscopy and electronic spectra in different organic solvents. On the basis of all investigations it was concluded by Padhye that most probably a hydroxyl
group is either weakly 'bonded' (involved in weak inter-molecular hydrogen bonding) or 'free' in phthiocol in the solution state as well as in the solid state. However, such intermolecular hydrogen bonding resulting the formation of dimeric species cannot be predominant in donor solvent such as dioxane, dimethyl formamide (DMF) or dimethyl sulphoxide (DMSO) and in such cases one may expect the solvent-solute interaction to some significant extent as has been actually observed in dioxane. It has been also found that phthiocol is dimeric in carbon tetrachloride solution just like that of lawsone. The relevant structural information has been summarized in Table 1.4.

(b) **Coordination aspects**

Although precipitation reaction with silver (I) and barium (II) were reported by Madinaveitia and Buu-Hoi respectively, Geyer and Smith were the first to prepare few of its transition metal chelates in 1941. No structural characterization of the metal phthiocolates was, however, made by these workers who examined their solubilities in different solvents, the drying temperatures and the absorption spectra in n-butyl alcohol. de Lima and coworkers reviewed some studies in 1971 to include Mossbauer spectral investigations of ferrous and ferric phthiocolates and assigned
**Table 1.4**: The available data for phthiocol $^T_1$

<table>
<thead>
<tr>
<th>Property</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical characteristics</td>
<td>Bright-yellow to orange yellow prisms</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in ethanol, chloroform, acetone, methanol and DMSO</td>
</tr>
<tr>
<td>Melting point ($^\circ$C)</td>
<td>173</td>
</tr>
<tr>
<td>Rf value (TLC) (with solvent)</td>
<td>Benzene (0.05), Chloroform (0.13), Acetone (0.19)</td>
</tr>
<tr>
<td>Source</td>
<td>Lipid isolated from human <em>tubercle bacillus</em></td>
</tr>
<tr>
<td></td>
<td>In <em>Lawsonia alba</em> along with lawsone</td>
</tr>
<tr>
<td></td>
<td>Culture of mycobacterium tuberculosis</td>
</tr>
<tr>
<td>Dissociation constant</td>
<td>$pK = 5.4$</td>
</tr>
<tr>
<td>Dipole moment ($\mu RT$ EM)</td>
<td>Benzene (2.01), Dioxane (7.54)</td>
</tr>
<tr>
<td>Absorption maxima (in nm)</td>
<td>Ethanol (250, 281, 331, 385), Dioxane (250, 275, 330, 380)</td>
</tr>
<tr>
<td>Infrared spectra (Nujol mull) (in cm$^{-1}$)</td>
<td>$\nu$(O-H) : 3334</td>
</tr>
<tr>
<td></td>
<td>$\nu$(C=O) free : 1660</td>
</tr>
<tr>
<td></td>
<td>$\nu$(C=O) chelated : 1645</td>
</tr>
<tr>
<td></td>
<td>$\delta$(CH$_3$) : 1355</td>
</tr>
<tr>
<td></td>
<td>$\delta$(OH) : 1310</td>
</tr>
<tr>
<td></td>
<td>$\nu$(C-CH$_3$) : 1182</td>
</tr>
<tr>
<td>Oxidation-reduction Potential (in V)</td>
<td>$\varphi_o = 0.299$</td>
</tr>
<tr>
<td>PMR spectra (in CDCl$_3$) $^\delta$ values</td>
<td>H-5, H-6, H-7, H-8, CH$_3$, OH</td>
</tr>
<tr>
<td></td>
<td>8.09 7.73 7.73 8.09 2.10 11.72</td>
</tr>
</tbody>
</table>
tetrahedral, distorted octahedral and planar geometries for the Fe(II), Fe(III) and Pd(II) phthiocolates respectively.

Data on formation constants of few transition metal phthiocolates is due to Kido et al\textsuperscript{43} and Purdy et al\textsuperscript{44}.

Rane\textsuperscript{T-3} prepared coordination compounds of phthiocol to study the effect of metal substitution on its chelating properties.

(c) **Analytical aspect**

Phthiocol itself is not a suitable metallochromic indicator but its oxime has been found to be more useful for analytical purpose\textsuperscript{T-3,T-7}.

(d) **Biological activity**

The antibacterial and antifungal activity of phthiocol in vitro was investigated by Padhye\textsuperscript{T-1}. The results show that phthiocol possesses:

(i) greater inhibitory action against *E. coli* in acidic medium and would be useful in the treatment of infection of the upper intestinal tract;

(ii) antimicrobial activity against *Bacillus subtilis* in both acidic as well as basic medium\textsuperscript{45-47}. Phthiocol is also said to potentiate the action of certain antibacterial and antifungal chemotherapeutic agents\textsuperscript{47-50}.
1.1.5 Plumbagin and its characteristics aspects

Plumbagin (5-hydroxy-2-methyl-1,4-naphthoquinone) which is naturally occurring is isolated from the roots of Plumbago zeylanica (called as Chitrak). Plumbagin occurs in the families Plumbaginaceae, Droseraceae and Ebenaceae. The synthetic reports on plumbagin are not numerous, and usually involve a multistep procedure. Bendz and Lindberg's route via chlorojuglone seems reasonable as does the one step synthesis starting with menadione with comparatively lower yields.

(a) Structural aspects

Different methods are employed for the characterization of plumbagin which include colour reactions, chromatography, electronic absorption spectroscopy, infrared spectroscopy, luminescence spectroscopy, NMR, EPR spectra and mass spectra by M. Kirzenhaus has reviewed. Due to the importance of plumbagin in structural, synthetic, coordination and medicinal chemistry, its molecular structure has been studied in detail.

The structural investigations carried out by Padhye T-1 using infrared spectroscopy, indicated that a strong intramolecular hydrogen bonding is favoured in plumbagin, which forms highly stable six membered ring. The available data is summarized in Table 1.5.
Table 1.5 : The available data for plumbagin

<table>
<thead>
<tr>
<th>Property</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical characteristics</td>
<td>Orange needles (with reddish shade)</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in ethanol, chloroform, acetone, methanol and DMSO</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>76</td>
</tr>
<tr>
<td>Rf value (TLC) (with solvent)</td>
<td>Benzene (0.26), Chloroform (0.37) Acetone (0.76)</td>
</tr>
<tr>
<td>Source</td>
<td>Roots and leaves of <em>Plumbago pulchella</em> Boiss, Roots of <em>Plumbago zeylanica</em></td>
</tr>
<tr>
<td>Dissociation constant</td>
<td>pK = 9.6</td>
</tr>
<tr>
<td>Dipole moment (µ RT) BM</td>
<td>Benzene (0.59), Dioxane (1.18)</td>
</tr>
<tr>
<td>Absorption maxima (in nm)</td>
<td>Ethanol (252, 266, 420) Dioxane (274, 570)</td>
</tr>
<tr>
<td>Infrared spectra (Nujol mull) (in cm⁻¹)</td>
<td>$\nu$(O-H) overlapped with $\nu$(C-H) of Nujol</td>
</tr>
<tr>
<td></td>
<td>$\nu$(C=O) free : 1655</td>
</tr>
<tr>
<td></td>
<td>$\nu$(C=O) chelated : 1630</td>
</tr>
<tr>
<td></td>
<td>$\delta$(CH₃) : 1360</td>
</tr>
<tr>
<td></td>
<td>$\delta$(OH) : 1290</td>
</tr>
<tr>
<td></td>
<td>$\nu$(C-CH₃) : 1165</td>
</tr>
<tr>
<td></td>
<td>$\nu$(OH) stretch : 1235</td>
</tr>
<tr>
<td>Oxidation-reduction Potential (in V)</td>
<td>$E_0 = 0.381$</td>
</tr>
<tr>
<td>PMR spectra (in CDCl₃) δ values</td>
<td>H-3, H-6, H-7, H-8, CH₃, OH</td>
</tr>
<tr>
<td></td>
<td>6.84, 7.70, 7.34, 7.62, 2.20, 11.8</td>
</tr>
</tbody>
</table>
(b) **Coordination aspects**

Plumbagin has strong chelating ability with transition and nontransition metals. In our laboratory Padhye\(^{1}\) and Rane\(^{3}\) carried out work on coordination characteristic on plumbagin which includes study of metal plumbaginates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II), and this work was extended to rare earth elements such as La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III). The coordination chemistry of the lanthanide elements is rapidly growing up in recent years and extensive work is appearing in current literature.

(c) **Analytical aspect**

Plumbagin has strong chelating ability and its chelates are expected to show useful analytical applications\(^{58,59}\). The precipitation reaction of plumbagin with Cu(II) has been mentioned by some workers\(^{2}\) without any structural investigations. The study done by Padhye,\(^{1}\) Rane,\(^{3}\) Chali\(^{60}\) and John\(^{61}\) indicate that plumbagin is a good analytical reagent for quantitative analysis.

(d) **Biological activity**

Plumbagin is well known for its biological activity\(^{8,62}\). Its physiological activity on the nervous system has been
examined by Lal. Plumbagin has an odour and affects the mucous membrane as does menadione. It stains the skin and produces blisters. In Malaya chewing plumbago roots is said to be effective for abortion. Plumbagin exhibits antifeedant activity, antifertility activity, anticancer and antitumour activity. There have been large number of studies including those from our laboratories devoted to the antimicrobial properties of plumbagin. Chalgeri has studied the antimicrobial activities of metal chelates of plumbagin with Co(II), Ni(II), Cu(II), Al(III), Fe(III), Zn(IV), Th(IV) and UO₂(II) against selected microorganisms and compared the results with antimicrobial activity of plumbagin.

1.1.6 Characteristic aspects of 3-chlorolawsone and 3-chlorojuglone

3-chlorolawsone and 3-chlorojuglone are the simplest 3-haloderivatives of lawsone and juglone respectively. In lawsone and juglone, substitution of halo group at C-3 position affects chelating ability, analytical utility and other features. Therefore, these derivatives are expected to be more useful from biological and analytical point of view.

(a) Structural aspect

In our laboratory a detailed and systematic work on the molecular structure of 3-chlorolawsone and 3-chlorojuglone
was carried out by Kelkar\textsuperscript{T-4} on the basis of infrared\textsuperscript{20}, near infrared spectroscopy\textsuperscript{26,27}, electronic absorption spectroscopy, PMR study, dissociation constants and adsorption chromatography in different solvents\textsuperscript{23}. The relevant structural informations is summarized in Tables 1.6 and 1.7.

On the basis of experimental evidences obtained by using modern techniques mentioned above, Kelkar\textsuperscript{T-4} has come to the conclusion that there is significant and remarkable effect on the hydrogen bonding due to halo substituent at C-3 position. The weak intramolecular hydrogen bonding in lawsone becomes still weaker in 3-chlorolawsone due to presence of electron withdrawing chloro group.

![3-Chlorolawsone](image)

This may be probably due to the rearrangement of electron density through the mesomeric and inductive effect such that a still weaker intramolecular hydrogen bonding between hydrogen
<table>
<thead>
<tr>
<th>Property</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical characteristics</td>
<td>Yellow needles</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in ethanol, chloroform, acetone</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>213</td>
</tr>
<tr>
<td>Rf value (TLC) (with solvent)</td>
<td>Benzene (0.04), Dioxane (0.56) Chloroform (0.06), acetone (0.32)</td>
</tr>
<tr>
<td>Source</td>
<td>Synthetic</td>
</tr>
<tr>
<td>Dissociation constant</td>
<td>pK = 2.17</td>
</tr>
<tr>
<td>Absorption maxima (in nm)</td>
<td>n-Heptane (237, 245, 251, 275, 278, 331, 380) Dioxane (246, 251, 278, 314, 332, 385)</td>
</tr>
<tr>
<td>Infrared spectra</td>
<td>$\nu$ (O-H) : 3260 $\nu$ (C=O) free : 1656 $\nu$ (C=O) chelated : 1623 $\nu$ (C-Cl) : 638 $\delta$ (O-H) in plane of phenol : 1340</td>
</tr>
<tr>
<td>PMR spectra (in CDCl$_3$) $\delta$ values</td>
<td>H-2, H-5, H-6, H-7, OH 7.20* 8.19, 7.80, 7.80, 8.19</td>
</tr>
</tbody>
</table>

* Overlapped with CDCl$_3$
<table>
<thead>
<tr>
<th>Property</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical characteristics</td>
<td>Orange needles</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in ethanol, chloroform, acetone and DMSO</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>166</td>
</tr>
<tr>
<td>Rf value (TLC) (with solvent)</td>
<td>Benzene (0.54) water (0.27)</td>
</tr>
<tr>
<td>Source</td>
<td>Synthetic</td>
</tr>
<tr>
<td>Dissociation constant</td>
<td>pK = 7.66</td>
</tr>
<tr>
<td>Absorption maxima (in nm)</td>
<td>Chloroform (275, 436), Methanol (272, 428), DMF (273, 427), Acetone (271, 428).</td>
</tr>
<tr>
<td>Infrared spectra (Nujol mull) (in cm⁻¹)</td>
<td>( \nu(\text{OH}) ) : 3070 ( \nu(\text{C}=\text{O}) ) free : 1650 ( \nu(\text{C}=\text{O}) ) chelated : 1600 ( \nu(\text{C}-\text{Cl}) ) : 634</td>
</tr>
<tr>
<td>PMR spectra (in CDCl₃) δ values</td>
<td>H-2, H-6, H-7, H-8, OH 7.36, 7.36, 7.75, 7.75, 11.71</td>
</tr>
</tbody>
</table>
and chlorine might have been formed as shown in above $^{[XVI]}$. Such weaker intramolecular hydrogen bonding in 3-chlorolawsone was also indirectly supported by its higher melting point (213 °C) compared to that of lawsone (190 °C).

Electronic absorption spectra in the region 200-200 nm in different organic solvents were also studied to examine the effect of C-3 halo substituent and polarity of solvent on the electronic energy levels of the parent compound i.e. lawsone. The substitution at C-3 position in quinonoid ring affects energy levels of benzene ring as well as quinone ring. It may be due to steric distortion of the quinonoid ring.

Apart from the ultraviolet spectra Kadam$^{7-8}$ has recorded solid state infrared spectra of 3-chlorolawsone in nujol mull. The infrared spectra of 3-chlorojuglone have been studied by Kelkar$^{7-4}$ to study the effect of C-3 substitution on O-H stretching, C=O stretching, C-O stretching and C-X stretching frequencies directly involve in the chelate formation. Near infrared spectra in chloroform were also recorded in order to throw more light on the nature of hydrogen bonding. The infrared spectral study has shown that the carbonyl and hydroxyl group play an important role in the coordination and structural characteristics of 3-halolawsone and 3-halojuglone.
Kelkar has also studied adsorption chromatography in different organic solvents, nuclear magnetic resonance spectra and apparent ionisation constants to elucidate structural aspect. NMR signals of the OH proton shows upfield shifts up to 7.2 and masked by CDCl3 peak indicating that the hydroxyl O-H is involved in the hydrogen bonding. It is strongly supported by the ionization constant data.

(b) Coordination aspect

A detailed and systematic survey of 3-chlorolawsone and 3-chlorojuglone reveals that very few coordination compounds of 3-chlorolawsone and 3-chlorojuglone have been reported. These reports do not involve any major study besides the synthesis and elemental analysis. The available work, however, is summarized below:

Metal chelates of 3-chlorolawsone with Ba(II) and Ag(I) have been examined by several coworkers in order to study their temperatures. Aizenberg et al have studied stability constant of Co(II) and Ni(II) chelates of 3-chlorojuglone.

Kelkar has synthesised 3-chlorolawsonates of La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) and their infrared and thermogravimetric study was done in order to elucidate their molecular structure. In addition to this
Kelkar has also done comparative structural studies of transition metal chelates of juglone and its 3-halo derivatives.

Kulkarni\textsuperscript{T-7} has synthesised 3-chlorolawsonates of Zn(II), Cd(II), Hg(II) and Pb(II) and investigated their structure on the basis of elemental analysis, infrared spectra in nujol mull and thermogravimetry. Kulkarni has also done the comparative structural studies of rare earth chelates of juglone and 3-chlorojuglone and studies of transition metal chelates of 2,3-dichlorojuglone.

Kelkar\textsuperscript{T-4} has done detailed and systematic study of these ligands and their transition metal chelates with Fe(II), Co(II), Ni(II) and Cu(II) with reference to infrared spectra, thermogravimetry, magnetic susceptibility measurements and solid state electronic spectra to investigate molecular structures of the chelates.

By careful analysis of infrared spectra, Kelkar observed that there is shift in the peak position as well as intensity of the O-H stretching frequency, C=O stretching frequency, C-O and C-X stretching frequencies after chelation.

Rawal has synthesized the alkaline earth metal chelates of 3-halolawsone and molecular structure of chelates
was studied with the help of elemental analysis, thermogravimetry, infrared spectra and electronic absorption spectra in various organic solvents having different polarity. All these chelates possess attractive colours with different shades having molecular composition $ML_2\cdot2H_2O$ with an exception of Be(II) chelates are anhydrous with $ML_2$ composition. The hydrated chelates were assigned trans-octahedral geometry while the anhydrous Be(II) chelates were assumed to be tetrahedral.

(c) **Analytical aspect**

Kelkar\textsuperscript{7-4} was the first to study systematically the detail colour reactions of 3-halolawsones with metal ions with a view to test the utility of 3-chlorolawson as the colorimetric reagent and metallochromic indicator. However, he observed that these derivatives are not effective colour-forming reagents as compared to similar type of ligands used as metallochromic indicators. This is mainly because there was no appreciable difference in colour between the reagent and chelate at the optimum pH. Therefore, it was concluded that in aqueous medium, 3-chlorolawson was of no use for analytical purpose.

Kelkar\textsuperscript{7-4} has also studied the utility of 3-halo derivatives of juglone in the analytical estimations of
various metal ions by examining colour reactions. On the basis of this study, spectrophotometric methods are established using 3-halojuglone as the analytical reagent. Aizenberg et al. have studied analytical reactions of 3-chlorojuglone with Be(II), Th(IV), Ni(II), Al(III), Zr(IV) and Fe(III) along with juglone and its other derivatives.

As compared to juglones, 3-halojuglones have been found to be more sensitive. However, halojuglonates have less stability than juglonates.

(d) Biological activity

According to biological point of view, 3-halosalons have been known to show remarkable antimicrobial activities. 3-Chlorosalone and 3-bromosalone have been reported to exhibit antivitamin K activity. In addition to this 3-chlorosalone and its Cu(II) chelates were known to have disinfectant and fungicidal properties. Apart from these, antibacterial and antifungal activity of 3-halosalones and their cobalt (II), nickel (II), copper (II), calcium (II) and magnesium (II) chelates are reported by Kulkarni. In comparison with 3-chlorosalone and 3-bromosalone, 3-iodosalone did not show any remarkable antimicrobial activity.

In our laboratory Kulkarni has studied antimicrobial activity of 3-chlorojuglone and its chelates with
Co(II), Ni(II) and Cu(II) by disc assay method. Ambrogi et al. have explained the antibacterial and antifungal properties of some of the substituted naphthoquinones including some halo derivatives on the basis of cell respiration inhibition than the antivitamin activity. Vishnyakova et al. have attributed antifungal activity to the halo derivatives of juglone.

1.2 COORDINATION CHEMISTRY OF Ho(III), Er(III) AND Yb(III)

Since 1950 and at an ever-increasing pace during last 20 years, the picture of lanthanide chemistry has become much broader and clearer. The use of anhydrous conditions and of variety of ligands has led to an extensive nitrogen ligand chemistry, a great extension of oxygen ligand chemistry, the discovery of reactive organolanthanide complexes. There have been other important advances also, including syntheses of macrocyclic complexes and cryptates, investigations of electronic spectra in terms of crystal field effects and the introduction of lanthanide NMR shift reagents.

The most stable oxidation state of the lanthanides in their complexes in all the cases is the $\text{M}^{+3}$ ion, in which all outer electrons reside in 4f shell, in contrast to the metal atom where, in addition to the 4f, the 5d shell may be partially filled.
Ionic radii of the $M^{+3}$ ions range from 1.06 to 0.85Å and which arises only partially in an analogous manner to the corresponding effect in the 3d transition metals. Because of the ligand field, 4f electron interaction is much weaker than in 3d series but is mainly due to 4f-4f interactions. A comparable value for ionic radii is difficult to obtain, as structure and coordination number usually change along the series. The large ionic radii in combination with the electrostatic nature of the metal-ligand bonding of these metals, leads to high coordination number.

Lanthanide coordination geometries are governed purely by minimization of repulsive terms which arise from ligated atom-ligated atom repulsion. Coordination polyhedra are governed by crystal field effects, as in the case of transition metals. Kepert has considered high coordination number stereochemistries, on the basis of a point-charge repulsion model, where the point-charges lie on the surface of a sphere. Coordination number lower than six some times is obtained with bulky ligands. In addition to regular polyhedra namely octahedron and tetrahedron a number of semiregular polyhedra such as dodecahedron, trigonal prism and square antiprism are also obtained.

Richardson et al have discussed lanthanide complexes of the simple parent β-diketone i.e. acetylacetone resulting
in $\text{M(}\text{acac})_3 \cdot x\text{H}_2\text{O}$, where $x = 3$ except of La where $x = 2$. These compounds are partially hydrolyzed to $\left[\text{M(}\text{acac})_2 \cdot (\text{OAC})\right] \cdot n\text{H}_2\text{O}$ or $\left[\text{M(}\text{acac})_2 (\text{OH})\right] \cdot n\text{H}_2\text{O}$. Several X-ray structures of the hydrates have appeared, thus $\left[\text{M(}\text{acac})_3 \cdot (\text{H}_2\text{O})\right] \cdot 96,97$ (M: La, Nd) are eight coordinated as is $\left[\text{Eu(}\text{acac})_3 (\text{H}_2\text{O})\right] \cdot 98$ and $\left[\text{Ho(}\text{acac})_3 (\text{H}_2\text{O})\right] \cdot 99$, while $\left[\text{Yb(}\text{acac})_3 (\text{H}_2\text{O})\right] \cdot 100,101$ shows seven coordination of the smaller Yb$^{+3}$ ion. However, $\left[\text{Gd(}\text{acac})_3 (\text{H}_2\text{O})\right]$ is dimeric, with Gd$^{+3}$ coordinated to six oxygen atoms from the diketone, two form of water molecules and one oxygen atom from diketone which is bidentate towards other Gd$^{+3}$ ion.

The relationship between the repulsion energy and coordination polyhedron of this M(bidentate)$_3$ (monodentate)$_3$ coordination was explored$^{102}$. Solid state studies of adducts where the β-diketone is not very much bulky include the monohydrate $\left[\text{Ho(PhCOCHCOPh)}_3 \cdot \text{H}_2\text{O}\right]$, where X-ray structure$^{103}$ shows a capped octahedron with H$_2$O molecule located on trigonal axis.

![Image of molecule](attachment:image.png)
The dipivaloylmethanates $M\left(\text{Me}_3\text{CCOCHCOCHMe}_2\right)_3$ have been studied by Eisentraut and Sievers\textsuperscript{104} for the first time\textsuperscript{[XVII]} (where $M = \text{La}-\text{Lu}$). They have concluded that the larger lanthanides\textsuperscript{5} do not form monomer\textsuperscript{5} but always form the bridged dimer\textsuperscript{5}. These complexes are remarkably volatile and can be separated by gas chromatography\textsuperscript{105}. Study of X-ray crystal structure\textsuperscript{106,107} of $\text{Pr}_2\left(\text{Me}_3\text{CCOCHCOCHMe}_3\right)_6$ and $\text{Er}\left(\text{Me}_3\text{CCOCHCOCHMe}_3\right)_3$ reveals that the coordination polyhedron of the praseodymium complex is irregular, while the erbium complex shows trigonal prismatic coordination, probably a consequence of the comparatively large ionic radius of $\text{Er}^{3+}$.

Sievers and coworkers\textsuperscript{108} prepared $M(\text{fod})_3 \cdot \text{H}_2\text{O}$ where $\text{fod} : \text{CF}_3\text{CF}_2\text{COCHCOCHMe}_3$ and $M : \text{Y}, \text{La}-\text{Lu}$ using standard methods. The hydrated complexes were converted into $M(\text{fod})_3$ but are rehydrated\textsuperscript{[XVIII]}. 

![diagram](diagram.png)
They are much soluble in benzene and are volatile, volatilizing completely at 260 °C (La) or 180 °C (Lu). It is interesting that in these two last volatility-dependant properties, \( \text{Y(fod)}_3 \) and \( \text{Er} \) has intermediate behaviour between those of the \( \text{Ho} \) complexes.

The lanthanides can complex with the carboxylate anion and a variety of anhydrous and hydrated carboxylates have been described, most of which are hydrated. Preparation of the hydrated solid compounds is usually straightforward from aqueous solution, but long chain aliphatic anhydrous carboxylate may be prepared from organic solvents either directly or by ligand exchange with the acetate. According to X-ray single crystal determination, the structures of hydrated and anhydrous oxalates show chelation of oxalate ion, forming five membered ring with the lanthanide ions in nine coordinated polymeric \( \left[ \text{M(OX)}_3 \cdot \text{H}_2\text{O} \right] \cdot \text{2H}_2\text{O} \), where \( \text{M} = \text{Nd-Tb} \) and \( \text{K}_8 \left[ \text{M}_2(\text{OX})_7 \cdot 14\text{H}_2\text{O} \right] \), where \( \text{M} = \text{Y, Tb, Dy, Er, or Yb} \).

Wang Xiaoling et al. have studied lanthanide chelates of Ho(III), Er(III) and Yb(III) with acetylacetonates in order to study electronic spectra in ultra-violet region. The absorption peak appearing in \( n \rightarrow \pi^* \) and \( n \rightarrow \pi^* \) transition of ligand shifted to blue and red region respectively. Guofa Shi and coworkers have prepared and investigated the
rare earth chelates of Ho(III) and Yb(III) with acetyl-acetonate. Mixed ligand complexes of Ho(III), Er(III) and Yb(III) acetylacetonates are studied by Trikha et al. These complexes were investigated by elemental analysis, infrared spectra, ultraviolet spectra and NMR, suggested as eight coordinated complexes.

Rare earth metal ions show influence on magnetic behaviour at low dimensional system transition at high temperature while some rare earth metal ions get influenced by coupling mechanism.

Liu Zhanmei and et al. have synthesized and characterized the rare earth (La-Iu) complexes of 3-ferrocenylacrylate using spectral and thermal analysis. They conclude that carboxylate group coordinates to rare earth metal ion in bidentate fashion while all the complexes lose water molecular at about 90 °C and decompose at 216 °C. X-ray diffraction study of these chelates show crystalline nature.

The single crystal of some lanthanide carboxylates were characterized by a lack of inversion symmetry, so they could be used for generation of the second harmonic. The single crystals of Nd(III) and Er(III)-trichloroacetate were have chain linking dimeric subunits where the lanthanide ion can occupy different site.
symmetry positions. Spectroscopic properties were related to X-ray crystal data. Probabilities of f-f transitions depending on the orientation of biaxial single crystal were considered

Thermal decomposition of rare earth p-amino-salicylates in air atmosphere were carried out by Brzyska and coworkers and final residues were found to match with \( \text{M}_2\text{O}_3 \) except \( \text{La}(\text{p-aminosalicylate}) \).

Rare earth chelates of ortho-chlorobenzoic acid were synthesized by Ma Jitanfang et al in order to study their thermal decomposition temperatures and crystal structure by X-ray diffraction and concluded that all the chelates were in crystalline form and show infinite chain structures having coordination number of nine.

The lanthanide (III) complexes with pyruvic acid semicarbazone were synthesized and characterized by elemental analysis, IR spectra and thermal analysis. The ligand and its complexes possess scavenger effect on hydroxy (-OH) and \( O_2^- \) radical.

The holmium salicylate has two different structures, one is triclinic dimer with coordination number nine and other is monoclinic with eight coordination number.
Rare earth chelates of Ho, Er, Pr, Sm with cyclopentadienyl and 2-naphthoyltrifluoroacetionate were prepared and investigated by Shen Furen and co-workers. The crystal structure has been studied by single crystal X-ray diffraction. The structural analysis showed that the holmium atom is surrounded by two cyclopentadienyl ligands, two oxygen atoms of the 2-naphthoyltrifluoroacetionate ligands and one oxygen gets solvated.

As a prerequisite to the study of chelates of the rare earth metal ion selected - Ho(III), Er(III) and Yb(III), some general characteristics of them are summarised in Table 1.8.

1.3 EARLIER WORK

Joshi has synthesised and characterised the chelates of lawsone and juglone with transition metal ions - Mn(II), Fe(II), Fe(III), Co(II), Ni(II) and Cu(II), while Rane has studied similar such chelates of phthiocol and plumbagin. Joshi has synthesized and characterised the chelates of lawsone with La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III), while Rane has studied similar such chelates with phthiocol.

Kelkar has done systematic and detailed structural
Table 1.8: Some properties related to coordination chemistry of rare earth metals selected

<table>
<thead>
<tr>
<th>Property</th>
<th>Holmium</th>
<th>Erbium</th>
<th>Ytterbium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Symbol</td>
<td>Ho</td>
<td>Er</td>
<td>Yb</td>
</tr>
<tr>
<td>2. Atomic number</td>
<td>67</td>
<td>68</td>
<td>70</td>
</tr>
<tr>
<td>3. Atomic weight</td>
<td>164.93</td>
<td>167.26</td>
<td>173.04</td>
</tr>
<tr>
<td>4. Electronic configuration : M</td>
<td>[Xe]⁴f¹¹⁵d⁰⁶S²</td>
<td>[Xe]⁴f¹²⁵d⁰⁶S²</td>
<td>[Xe]⁴f¹⁴⁵d⁰⁶S²</td>
</tr>
<tr>
<td>5. Electronic configuration : M⁺³</td>
<td>[Xe]⁴f¹⁰⁵d⁰⁶S⁰</td>
<td>[Xe]⁴f¹¹⁵d⁰⁶S⁰</td>
<td>[Xe]⁴f¹³⁵d⁰⁶S⁰</td>
</tr>
<tr>
<td>6. Unpaired electrons in M⁺³</td>
<td>4</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>7. Common oxidation states</td>
<td>+3</td>
<td>+3</td>
<td>+3</td>
</tr>
<tr>
<td>8. Related coordination number</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>9. Probable geometries</td>
<td>Square</td>
<td>Square</td>
<td>Square</td>
</tr>
<tr>
<td></td>
<td>antiprism</td>
<td>antiprism</td>
<td>antiprism</td>
</tr>
<tr>
<td>10. Ionic radii (Å)</td>
<td>0.894</td>
<td>0.881</td>
<td>0.858</td>
</tr>
<tr>
<td>11. Colour of M⁺³ ions</td>
<td>Pink;</td>
<td>Lilac</td>
<td>Colourless</td>
</tr>
<tr>
<td></td>
<td>Yellow</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[Xe]²⁺: Electronic configuration of Xenon as (at.no. 54)
1⁰S²2⁰S²2P⁶3S²3P²3d¹⁰4S²4P⁶4d¹⁰5S²5P⁶.
study of 3-chlorolawsone and 3-chlorojuglone along with their transition metal chelates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II). He has also synthesised and characterized the chelates of 3-chlorolawsone with the rare earth metal ions La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III).

Literature survey showed that a very limited work has been carried out on antimicrobial studies of Juglones and their metal chelates though these chelates are expected to show useful microbiological, pharmaceutical and medicinal properties. Padhye\textsuperscript{T-1} has studied antimicrobial activity of parent ligands lawsone, juglone, C-3 substituted juglone, phthiocol and plumbagin against selected bacteria and fungi for the first time. This study was followed by Joshi\textsuperscript{T-2} for metal chelates of Fe(II), Co(II), Ni(II), and Cu(II) with lawsone and juglone. The antimicrobial study was further extended by Kulkarni\textsuperscript{T-7} using Co(II), Ni(II) and Cu(II) metal chelates of lawsone, juglone and 3-chlorolawsone. Later on Kulkarni studied antimicrobial activity of lawsone, 3-chlorolawsone monoxime, phthiocol and phthiocoloxime and metal chelates with Zn(II).

This review on earlier work indicates that although a number of metal chelates of Juglones are synthesized in our laboratory, no one, except Padhye\textsuperscript{T-1}, Rane\textsuperscript{T-3} and
Kelkar has made an attempt to explore structurally rare earth metal chelates in detail.

1.4 PRESENT WORK

Lawsone, juglone, phthiocol, plumbagin, 3-chloro-lawsone and 3-chlorojuglone and their chelates with holmium (III), erbium (III) and ytterbium (III) have been studied for the first time. The structures of these chelates are investigated by using techniques such as thermogravimetry, elemental analysis, magnetic susceptibility, infrared spectroscopy in solid state and electronic absorption spectroscopy. The main objectives of the present work are as follows:

(i) To investigate the structural and coordination chemistry of these chelates.

(ii) To study the effect of C-3 substituent on the spectral and magnetic properties.

(iii) To study the effect of metal ion.

(iv) To study the nature of metal-ligand bonding.

(v) Involvement of the participation of 4 'f' orbitals in the bonding etc. of the metal chelates.

The present work also includes the comparative antimicrobial studies of the ligands and their Ho(III), Er(III) and Yb(III) chelates using DMSO as a carrier solvent.
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