Chapter-6

Complexes of ruthenium (III) chloride with thiocarbohydrazones.

Carbohydrazide and its thioanalog are surprisingly late arrivals on the chemical scene, considering their closer relationship with urea, the compound most directly associated with the foundation of organic chemistry. Having continued investigation on nitrogenous compounds like, hydrazide, hydrazoic acid etc over a number of years. Curtius\(^1\) described in 1894 and more fully in 1895 the results of the hydrazinolysis of derivatives of carbonic acid. The same paper also described the condensation of \(\text{CS}_2\) with hydrazine to give the hydrazine salt of dithiocarbamic acid (i.e., \(\text{NH}_2\text{NHCSSH, NH}_2\text{NH}_2\)), but stopped short of the hydrazinolysis stage. It was not until 1908 that R.stolle\(^2\), formerly Curtius assistant, completed this series of reactions and so discovered thiocarbohydrazide.

Over the years, interest in the chemistry of carbohydrazide and thiocarbohydrazide, through first sporadic, has steadily increased; earlier major studies were undertaken by Wilson and his coworkers at Glasgow, and by Guha and his coworkers at Dacca university, India. More recently, advances have been reported from numerous laboratories; they include the more notable contributions of Audrieth, who carefully reinvestigated and improved thiocarbohydrazide synthesis, of sandstorm at Lund, and of Beyer and his coworkers at Rostock, whose main interest were the use of these nitrogenous compounds in heterocyclic synthesis\(^3\).

\[
\begin{array}{c}
S \\
\text{H}_2\text{NNHCNHNH}_2 \\
1 2 3 4 5
\end{array}
\]

Carbohydrazide and thiocarbohydrazide are hydrazine derivatives of carbonic and thiocarbonic acids, respectively. Thio (carbohydrazide) is seen to be the final member of the structural sequence thio(urea), thio(semicarbazide) and (thio)carbohydrazide,
and to have, moreover, close links with (thio)carbamic and (thio)carbazic acids, as well as with the aminoguanidines.

The compounds containing thione (\( >C = S \)) and thiol (\( >C - SH \)) groups occupy an important position among organic reagents, as they possess many applications in industry, \(^4\) in medicine \(^7\)\(^-\)\(^10\) and in analytical chemistry. \(^11\)\(^-\)\(^13\) Thiocarbohydrazones belong to this class of organic compounds. Thiocarbohydrazones are Schiff base ligands derived from the condensation of thiocarbohydrazide and aldehyde or ketone. Thiocarbohydrazide is known for wide spectrum biological activities such as anticancer, \(^14\) antibacterial, \(^15\) antifungal \(^16\) and anticonvulsant. \(^17\) It is also useful in analytical chemistry for identification and estimation of both organic and inorganic compounds. \(^18\)\(^-\)\(^21\)

Thiocarbohydrazide precipitates aldehydes and ketones quantitatively giving derivatives having sharp melting points, which are suitable for identification purposes and in gravimetric procedures. With certain ions viz, \( U^{6+} \), \( Mo^{4+} \), \( Ni^{2+} \), \( Bi^{3+} \) and \( Cu^{2+} \) thiocarbohydrazide forms characteristic precipitate for which gravimetric curves have been constructed \(^18\)\(^,\)\(^20\).

The IR spectra of thiocarbohydrazide and its complexes with several metals (Zn, Cd, Hg, Co, Ni and Pd) have been studied by Burns, by carrying out a normal coordinate analysis of the free ligand \(^22\). The x-ray crystallographic studies \(^23\)\(^-\)\(^25\) has identified the three typed of coordination of thiocarbohydrazide to the metal as shown below (Fig-1,a-c).

![Chemical Structures](image)

**Fig-1** (a) (b) (c)
Singh et al.\textsuperscript{26} and Srivastava et al.\textsuperscript{27} have synthesized Mn (II), Cu (II), Zn (II), Pd (II), Pt (II) and Sn (IV) complexes with thiocarbohydrazones and concluded that the ligand can act as pentadentate, tetradentate or tridentate. The coordination behaviour of these ligands depends upon the nature of the metal ion, the reaction conditions and the pH of the medium.

Kulakarni et al. have reported the square planar Ni (II) complexes with thiocarbohydrazones derived from substituted salicylaldehyde and thiocarbohydrazide. Further these complexes have been used to prepare bimetallic complexes with Sn (IV)\textsuperscript{29} (Fig-2) and Cu (II)\textsuperscript{30}, by the same authors.

![Fig-2](image)

Pandey\textsuperscript{31} reported the condensation reactions of 2,6-diacetylpyridine with thiocarbohydrazide in EtOH in the presence of sodium acetate to give acyclic ligand (Fig-3). This ligand reacts with lanthanum salt in 1:1 molar ratio to form ring-opened complexes, which on condensation with 2,6-diacetylpyridine resulted in the formation of macrocyclic complexes of the ligand type shown in (Fig-4).

![Fig-3](image) ![Fig-4](image)
In the same year Sengupta et al.\textsuperscript{32} reported praseodymium (III) complexes of macrocyclic ligand derived from the condensation reaction of diacetylbenzil with thiocarbihydradize in EtOH in presence of dil HCl. Oxovanadium (IV) complexes of thiocarbohydrazide was reported by Pandey\textsuperscript{33} in which thiokeo sulphur is shown to be coordinated to the metal ion.

Gowda et al.\textsuperscript{34} reported the kinetics of oxidation of thiocarbohydrazide and metal complexes by n-bromosuccinimide both in presence and absence of added bromide in aq. HClO\textsubscript{4} medium. Kulakarni and Patil\textsuperscript{35} have synthesized oxovanadium (IV) and dioxouranium (VI) complexes with thiocarbohydrazones. Cowley et al.\textsuperscript{36} have reported the synthesis and characterization of molybdenum (VI) complex with 1.5-bis(salicylidene) thiocarbohydrazide using [MoO\textsubscript{2}(acac)\textsubscript{2}] in MeOH. Chabanur et al.\textsuperscript{37} reported Nb (VI) complexes of the type [NbCl\textsubscript{3}L] (where LH\textsubscript{3}, thiocarbhydroazone derived from condensation thiocarbohydrazide with 5-CH\textsubscript{3}, 5-Cl, 5-Br, 3-OCH\textsubscript{3}, substituted salicylaldehyde and 2-hydrox-o-1-naphthaldehyde). The ligands and complexes were characterized on the basis of elemental analysis, conductivity measurements, IR, UV-Vis, \textsuperscript{1}H NMR and thermal studies. The ligands behave as dibasic tetradeatate ONNO donors.

Yang Xinping and coworkers\textsuperscript{38} have reported the synthesis and characterization of lead (II) complexes of bis-(o-formyl phenoxy) acetic acid hydrazones. These Schiff base ligands bis-(o-formyl phenoxy) acetic acid thiocarbohydrazones, mono o-(formyl phenoxy) acetic acid thiocarbohydrazones and bis-(o-formyl phenoxy) acetic acid hydrazones were prepared by condensation of bis-(o-formyl phenoxy) acetic acid with thiocarbohydrazide and hydrazine hydrate. These ligands and Pb(II) complexes were characterized by elemental analysis, TG, IR, UV-Vis, \textsuperscript{1}H NMR spectral methods. They reported 1:1 (M:L) stiochiometry for isolated complexes and the ligands behave as dibasic quadridentate and dibasic bidentate manner.

From our laboratory A.D.Naik et al.\textsuperscript{39} have synthesized the following macrocyclic and macrocyclic compartmental ligands (\textbf{Fig-5}) and their Co(II). Ni(II),
Cu(II) and Zn(II) complexes and characterized on the basis of elemental, conductivity, magnetic, IR, UV-Vis, FAB mass and ESR spectral studies.

Fig - 5
Bimetallic core is versatile as the active site of many metalloenzymes and play essential role in biological systems by the interplay of a pair of metal ions. Synthetic simple binuclear complexes are important to understand the mutual influences of two metal centres on structural, electronic, magnetic and electrochemical properties of such bimetallic cores. Compartmental macrocyclic ligands having two phenolic oxygens as endogeneous bridges have been developed for this purpose, because they bind two metal centres in close proximity relevant to the active sites of bimetallic enzymes. Recent x-ray crystallographic studies have indicated that most biometallic, biosites are asymmetric with respect to the donor atoms about the metal centres, the nature of the metal ions, the coordination number, and the geometric arrangement of the donor atoms\textsuperscript{40-42}.

Thus the design of the side-off compartmental ligand and asymmetric and symmetric macrocyclic ligands capable of providing a discrete homo/hetero binuclear core and symmetric and symmetric and asymmetric binuclear core is of particular interest.

One of the objects of studying the complexes of thiocarbohydrazones was to investigate whether coordination to metal ion occurs through the sulphur or advantage is taken of the available nitrogen donors to form a coordination sheath consisting of only nitrogen atoms.

Thiocarbohydrazide in the present investigation was used as diamine with 3-acetyl coumarin, salicylaldehyde or substituted salicylaldehyde, 2-hydroxy 1-naphthaldehyde and 2,6-diformyl-p-cresol to construct a compartmental mononuclear and binucleating ligand, hoping that the toxophoric functional group (\(\text{C} = \text{S}\)) will away from the coordinating site so that these functional groups could provide “points of attachment”, a system which mimic certain classes of biological systems\textsuperscript{43} (similar to Jager macrocycle) and such groups could be toxic to microbes when used as drugs.
EXPERIMENTAL

In this part of the chapter, methods of synthesis of ligands and their complexes, Elemental analysis and physico-chemical method employed are discussed. Salicylaldehyde, 3-methoxysalicylaldehyde, 2-hydroxy-1-napthaldehyde and other chemical used for the preparation of ligands were of reagent grade. Purified solvents were used for the synthesis of ligands and complexes.

I. Synthesis of ligands

1. Synthesis of thiocarbohydrazide

The reaction of hydrazine with CS$_2$ (Eq-1) is no doubt the cheapest and most useful method for the preparation of thiocarbohydrazide in quantity. The isolation and subsequent decomposition of the intermediate hydrazinium dithiocarbazinate may be disposed with direct interaction of carbon disulphide and three molar excess of aqueous hydrazine hydrate at the boiling point and periodic removal of thiocarbohydrazide gave approximately 60% yield of products.

$$\text{CS}_2 + 2 \text{NH}_2\text{NH}_2 \rightarrow [\text{NH}_2\text{NHCSSH NH}_2 \text{ NH}_2] \rightarrow \text{NH}_2\text{NHCS NHNH}_2 + \text{H}_2\text{S}$$-[1]

Thiocarbohydrazide is a white crystalline solid, melting with decomposition at 168°C. It may be recrystallized from water. Thiocarbohydrazide incorporating both acidic and basic functions in its structure it is amphoteric, being soluble in both dil bases and acids.

$$\text{H}_2\text{NNHC NHNH}_2 \leftrightarrow \text{H}_2\text{NNC NHNH}_2$$

Condensation with carbonyl compounds

Both hydrazine groups of thiocarbohydrazide display normal reactivity towards carbonyl compounds and give rise to a large variety of crystalline mono- and
dihydrazones. In general, the di addition products are formed so rapidly that the mono-adducts are only obtainable under specially controlled conditions.

Thiocarbohydrazide reacts readily with two molar proportions of baldheaded or ketenes to yield thiocarbohydrazones. The dihydrazones derived from acetone, acetophenone and dibenzyl ketone are formed only after prolonged boiling using an excess of ketone.

2. Synthesis of 3-acetyl coumarin

3-acetyl coumarin was prepared by knoevengel’s method as described in chapter III.

3. Synthesis of 2, 6-diformyl-p-cresol

2, 6-diformyl-p-cresol was prepared by Denton method with slight modification as described in chapter II.

4. Synthesis of bis-3-acetylcoumarin thiocarbohydrazone

Thiocarbohydrazide 2.12g (0.02mol) and 3-acetyl coumarin 7.5g (0.04 mol) were taken in 80 ml of ethyl alcohol containing 1 ml of acetic acid. The mixture was refluxed on a water bath for two hours. The slightly yellowish coloured crystalline mass was separated on cooling, which is filtered and washed with ethyl alcohol. The yield was almost quantitative. Thiocarbohydrazone was purified by crystallization from ethyl alcohol. M.p. 218-223°C.

5. Synthesis of bis-salicylaldehyde or substituted salicylaldehyde thiocarbohydrazone and Bis (2-hydroxy-1-naphthalidene) thiocarbohydrazone

Thiocarbohydrazide (0.02 mol) and salicylaldehyde or substituted salicylaldehyde or 2-hydroxy naphthaldehyde (0.04mol) were taken in 80 ml of methanol. The mixture was refluxed on a water bath for two hours. The slightly yellowish coloured crystalline mass was separated on cooling, which is filtered and washed with ethyl alcohol. The yield was almost quantitative. Thiocarbohydrazone was purified by crystallization from ethyl alcohol.
6. Preparation of 2, 6-diformyl-p-cresol bis (thiocarbohydrazone)

To a hot ethanolic solution of 2, 6-diformyl-p-cresol (1.64g, 0.01 mol) was added drop wise hot suspensions of thiocarbohydrazide (2.12 gm, 0.02 mol) also in ethanol, with stirring. Pale yellow precipitate that separated was refluxed for 1 hr, filtered, washed with ethanol and dried, Yield 85%. (Chart-1)
<table>
<thead>
<tr>
<th>Code</th>
<th>Ligand</th>
<th>Colour</th>
<th>M.p</th>
</tr>
</thead>
<tbody>
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<td>Bis 3-acetycoumarin thiocarbohydrazone</td>
<td>Yellow</td>
<td>&gt;270</td>
</tr>
<tr>
<td>L₂H₂</td>
<td>Bis(Salicylidine) thiocarbohydrazide</td>
<td>Yellow</td>
<td>192-193</td>
</tr>
<tr>
<td>L₃H₂</td>
<td>Bis(3-methoxy salicylidine)thiocacbohydrazone</td>
<td>Yellow</td>
<td>198-200</td>
</tr>
<tr>
<td>L₄H₂</td>
<td>Bis(2-hydroxy-1-naphthalidene)thiocarbohydrazone</td>
<td>Yellow</td>
<td>&gt;250</td>
</tr>
<tr>
<td>L₅H₃</td>
<td>2,6-diformyl-p-cresol bis thiocarbohydrazone</td>
<td>Yellow</td>
<td>&gt;270</td>
</tr>
</tbody>
</table>

(Chart-1)

**II. Synthesis of complexes**

*Complexes of L₁, L₂H₂, L₃H₂ and L₄H₂ (C1-C4)*

To an ethanolic solution of ligand (0.003 mol), ruthenium (III) chloride (0.003 mol) in the same solvent was added. The resulting mixture was refluxed on a water bath for two hours, and cooled. Thus obtained complex was filtered at suction and washed with ethanol and dried in vaccum over P₂O₅. M.p>250⁰c, yield 65%.

*Complex of 2, 6-diformyl-p-cresol bis thiocarbohydrazone (C5)*

To an ethanolic solution of 2, 6-diformyl-p-cresol bis thiocarbohydrazone (0.001 mol) ruthenium (III) chloride (0.002 mol) also in ethanol was added with stirring. Complex that separated immediately were refluxed for 3-4 hr, filtered, washed with ethanol and dried, M.p >250⁰c, Yield 75%.

*Results and Discussion*

All the complexes are non hygroscopic. Complex (C1-C4) contains 1:1 metal to ligand ratio, where as Complex (C5) contain 2:1 metal to ligand ratio. Complex (C1), Complex (C2-4) and Complex (C5) are formed by the loss of zero, two and three proton respectively. They are insoluble in water, ethanol, methanol, but soluble in DMF, DMSO and MeCN. Analytical and physical data are presented in Table-1. colours of the complexes are pale black to dark brown. Melting points of the complexes are above 250⁰c.
Molar conductivity measurements

Molar conductivity of all the complexes was measured in DMF solution at 10^{-3} M concentration. The observed molar conductance values (12-17 mho cm^2 mol^{-1}) (Table-1) suggest that, the complexes are non electrolytes^{48}.

Magnetic measurements

The magnetic susceptibilities of the complexes, recorded at room temperature (Table-1). The magnetic moments of complexes (C1-C4) are 1.79- 1.84BM and complex (C5) has 1.89 BM/ Ru (III) ion. These values are within the range of (1.73-2.2BM) expected for Ru (III) ion in an octahedral field.

Electronic spectra

Electronic spectral data are summarized in Table-2. the representative electronic spectra are reproduced in Fig-6a-d. All the ligands show band at 260-270, 312-335 and 370-380nm. The broad intense band around 260nm is assigned to intra ligand П→П* transition. This band is almost unchanged in the spectra of complexes. The band around 320nm with shoulder on lower energy side is assigned to n→П* transition associated with azomethine linkage.

Infrared spectral study

Infrared spectra of ligands and complexes were scanned in KBr pellet from 4000-400 cm^{-1}. Important bands with assignments are shown in Table-3 and spectra are reproduced in Fig- 7a-j. Comparison of the spectrum of ligand with its complex forms the basis of assignments of the bands.

Complex of L^1 [bis 3-acetylcoumarin (thiocarbohydrazone)]

The IR spectrum of ligand shows medium intensity absorption band at 3240 cm^{-1}, which is assigned to hydrazine ν (NH) stretching vibration. the band observed at 1710 cm^{-1} in the ligand is assigned to ν (C=O) stretching vibration of coumarin moiety. the bands at 1550, 1240, 1100 and 760 cm^{-1} that are assigned to thiomide-I, thiomide-II, thiomide-III and thiomide-IV vibrations respectively. The ligand
containing HNC=S group can undergo thione – thiol tautomeration, however the appearance of four thiomide bands in the ligand indicates the existence of thione form. The thiomide-IV band has been found to have a maximum \( \nu (C=S) \)\(^{31} \). The ligands show a medium intensity band at 1610 cm\(^{-1} \), which can be assigned to the \( \nu (C = N) \) vibration of azomethine linkage\(^{49} \). The IR spectrum of complex (C1) shows a broad band at 3447 cm\(^{-1} \). This band is assigned to \( \nu (OH) \) of coordinated water. The \( \nu (N-H) \) vibration in the complex is observed at 3250 cm\(^{-1} \). This observation clearly indicates the non-involvement of N-H nitrogen atoms in the coordination. The strong band appearing at 1710 cm\(^{-1} \) appears at the same position in the complex, but much diminished in intensity in the complex. In addition, there is a new band at 1637 cm\(^{-1} \) in the complex. This band may be assigned to the coordinated lactone \( \geqslant C=O \) group. This observation indicates that in the complex oxygen atom of lactone \( C=O \) of one part, coordinates to the metal atom, while other \( C=O \) remains free. The \( \nu (C=N) \) observed at 1610 cm\(^{-1} \) remains unchanged in position in complex. A new band appears in the complex at 1606 cm\(^{-1} \). This observation indicates that only single nitrogen of azomethine linkage is involved in coordination. The \( \nu (C=S) \) observed at 760 cm\(^{-1} \) in the ligand remains at the same position in the complex indicating non-coordination of thiomide sulphur to the metal\(^{31} \). The \( \nu (N-N) \) band assigned at 980 cm\(^{-1} \) in the ligand shifts to the higher frequency 1030 cm\(^{-1} \) in the complex indicating the coordination of azomethine nitrogen atom to the metal\(^{50} \).

**Complexes of \( L^{2-4} \) [Bis(Salicylaldehyde or substituted salicylaldehyde thiocarbohydrazone)]**

The infrared spectrum of ligand shows no characteristic absorption bands assignable to \( \nu (C=O) \) and \( \nu (NH_{2}) \) function confirming the formation of thiocarbohydrazones. The ligand exhibits broad and medium intensity band at 3170-3250 cm\(^{-1} \), which is assigned to the \( \nu (N-H) \) vibration and \( \sim 3050 \) cm\(^{-1} \) due to (C-H) stretching\(^{*CHAB} \) the broad and weak intensity band in the 2720-2800 cm\(^{-1} \) region is assigned to intramolecular hydrogen bonded \( \nu (O-H) \) of phenolic hydroxyl group. The medium intensity band in the 1620-1625 cm\(^{-1} \) region is assigned to \( \nu (C=N) \) of
azomethine nitrogen. Strong band in the region 1275-1295 cm\(^{-1}\) is due to the phenolic (C-O). A medium intensity or strong intensity around 745-770 cm\(^{-1}\) is assigned to \(\nu\) (C=S) vibrations. The bands ~3050 cm\(^{-1}\) due to \(\nu\) (C-H) and 3170-3250 cm\(^{-1}\) due to \(\nu\) (N-H) are observed in the complexes. In case of complexes the band in the 2750-2800 cm\(^{-1}\) region is absent indicating coordination of the phenolic –OH via deprotonation\(^{26, 28, 35}\). The band due to \(\nu\) (C=N) of azomethine shifts to lower frequency in the 1595-1615 cm\(^{-1}\) region, suggesting that both the azomethine nitrogens are coordinated to the metal ion\(^{29, 35}\). In all the complexes the band due to \(\nu\) (C=S) remains almost unchanged, suggesting that the \(\nu\) (C=S) group is not coordinated to the metal ion\(^{26, 28, 30, 35, 51}\). All the complexes exhibit medium or weak intensity band in the 450-495, 365-380 and 325-345 cm\(^{-1}\) region, which was assigned to \(\nu\) (M-N), \(\nu\) (M-O) and \(\nu\) (M-Cl) vibrations.

**Complex of \(L^5\) H\(_3\), 2,6-diformyl-p-cresol bis thiocarboxydrazone**

The possibility of thione – thiol tautomerism (H-N-C=S↔C-N-SH) in the ligand has been ruled out for no bands around 2500-2600 cm\(^{-1}\), characteristics of thiol group, are displayed in the infrared absorption\(^{52-54}\). The \(\nu\) \(\left(^4\text{NH}\right)\) and hydrazine \(\nu\) \(\left(^2\text{NH}\right)\) are observed at 3287 and 3139 cm\(^{-1}\) respectively. Coupled vibration among thiomide bands I \(\beta\) (NH) + \(\nu\) (CN), II \(\nu\) (C N) + \(\beta\) (NH), III \(\nu\) (CN) + \(\nu\) (C=S) and IV \(\nu\) (CN) +\(\nu\) (C=S) are distributed around 1516, 1458, 1234 and 944 cm\(^{-1}\) regions.

The phenolic \(\nu\) (OH) is found around 2900 cm\(^{-1}\) as a weak broad band, which disappears in the complex indicating deprotonation and coordination to metal. This is further supported by shift of phenolic \(\nu\) (C-O) at 1234cm\(^{-1}\) in ligand to higher frequency by 50-60 cm\(^{-1}\) on complexation\(^{55-56}\). The band at 1605 cm\(^{-1}\) in free ligand can be attributed to \(\nu\) (C=N)\(^{57}\) and this band has shifted to a higher by 10 cm\(^{-1}\) in the spectra of the complex, showing the coordination of azomethine nitrogen to the metal\(^{58}\). Thiomide bands III and IV which have major contribution of \(\nu\) (C=S) have undergone considerable reduction in intensity in the complex due to thioenolization and subsequent coordination to metal which is supported by the shift of \(\nu\) (C=S) band in the free ligand appearing at 862 cm\(^{-1}\) to lower frequencies (800 cm\(^{-1}\)) on complex
formation\textsuperscript{59}. A strong band at 3139 cm\textsuperscript{-1} attributed to ν (\(\ddot{\text{N}}\)-H) in the spectra of ligands disappeared in the complexes. This indicates the deprotonation of ligand occurs prior to coordination through the secondary NH group. The broad band at 3439 cm\textsuperscript{-1} followed by a sharp peak around 950 cm\textsuperscript{-1} is due to presence of coordinated water\textsuperscript{60}. Thus the ligand act as tribasic pentadentate molecule, coordinating through two azomethine nitrogen atoms via deprotonation, two sulphur atoms after thioenolization and one phenolic oxygen atom via deprotonation.

The low frequency bands in the 500-470, 412-350 and 370-292 cm\textsuperscript{-1} regions are assigned to ν (M-N), ν (M-O) and ν (M-S) respectively\textsuperscript{61}. The presence of Chloro Bridge is evident from the IR band in the 270-240 cm\textsuperscript{-1} region\textsuperscript{61-65}.

\textit{ESR Spectral study}

The ESR spectra are recorded for the complexes in powdered form and the spectra are reproduced in Fig. 8a & b.

The ESR spectra of the complexes are characteristic of an octahedral, which shows a single isotropic resonance with ‘g’ values in the range of 2.18-2.22. The g values indicate an almost octahedral environment around the ruthenium ion.

\textbf{Conclusion}

All the complexes were insoluble in polar solvents but soluble in DMF and DMSO and are non-electrolytes. The elemental analysis shows that metal to ligand ratio is 1:1((except C5, which is 2:1). Magnetic study had revealed that all the complexes were paramagnetic. IR studies show that C1 coordinates through carbonyl oxygen and azomethine nitrogen atom to metal atom and hence behaves as a neutral bidentate ligand. In the complexes C2-C4, the ligands (L\textsuperscript{2-4})coordinates through two phenolic OH( oxygen) via deprotonation and two azomethine nitrogen atoms to metal atom and hence behaves as a dibasic tetrade late ligands. 2,6-diformyl-p-cresol bis thiocarbohydrazone act as tribasic pentadentate molecule, coordinating through two azomethine nitrogen atoms via deprotonation, two sulphur atoms after thioenolization
and one phenolic oxygen atom via deprotonation. Tentative structures of these complexes are as shown below.
Table 1. Analytical, conductance and magnetic moment data of the ligands and complexes

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<th>No</th>
<th>Compounds</th>
<th>Found (Calcd) %</th>
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<td>H</td>
<td>N</td>
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Table-2. Electronic spectral data of the ligands and their complexes

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<th>Charge-transfer transition</th>
<th>d-d transition</th>
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<td>π→π*</td>
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<tr>
<td>L&lt;sub&gt;1&lt;/sub&gt;</td>
<td>276</td>
<td>320</td>
<td>369</td>
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<tr>
<td>C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>270</td>
<td>330</td>
<td>-</td>
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<tr>
<td>L&lt;sup&gt;2&lt;/sup&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>262</td>
<td>348</td>
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<tr>
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<td>347</td>
<td>412</td>
</tr>
<tr>
<td>L&lt;sup&gt;3&lt;/sup&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>264</td>
<td>345</td>
<td>410</td>
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<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>376</td>
<td>410</td>
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<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>266</td>
<td>382</td>
<td>440</td>
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<tr>
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<td>316</td>
<td>383</td>
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<td>C&lt;sub&gt;5&lt;/sub&gt;</td>
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<td>323</td>
<td>379</td>
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Table 3: Infrared spectral data of the ligands and their complexes (in cm\(^{-1}\))

<table>
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<tr>
<th>No</th>
<th>v(NH)</th>
<th>v(C=N)</th>
<th>v(CO) Lactone/Phenol</th>
<th>v(C-S)</th>
<th>v(M-N)</th>
<th>v(M-O)</th>
<th>v(OH)/H(_2)O</th>
<th>v(OH)/Phenol</th>
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<td>L(_1)</td>
<td>3151</td>
<td>1612</td>
<td>1715</td>
<td>756</td>
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<td>1560</td>
<td>1718</td>
<td>1657</td>
<td>760</td>
<td>457</td>
<td>368</td>
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<td>1615</td>
<td>1295</td>
<td>755</td>
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<td>2800</td>
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<tr>
<td>C(_2)</td>
<td>3218</td>
<td>1611</td>
<td></td>
<td></td>
<td>758</td>
<td>465</td>
<td>380</td>
<td>3376</td>
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<td>780</td>
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<td></td>
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<td>460</td>
<td>375</td>
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<td>1611</td>
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</table>
Fig. 6a. Electronic spectrum of C1

Fig. 6b. Electronic spectrum of L^4H

Fig. 6c. Electronic spectrum of L^5H_3

Fig. 6d. Electronic spectrum of C5
Fig. 7a; IR spectrum of L

Fig. 7b; IR spectrum of C₁
Fig. 7c; IR spectrum of $L^2H_2$

Fig. 7d; IR spectrum of $C_2$
Fig. 7e; IR spectrum of $L^3H_2$

Fig. 7f; IR spectrum of $C_3$
Fig. 7g: IR spectrum of \( L^4H_2 \)

Fig. 7h: IR spectrum of \( C_4 \)
Fig. 7i: IR spectrum of L₅H₃

Fig. 7j: IR spectrum of C₅
Fig. 8a: ESR spectrum of $C_1$

Fig. 8b: ESR spectrum of $C_5$