Chapter-II

Compartmental binuclear ruthenium (III) complexes of thiosemicarbazones

Introduction

A large section of coordination chemistry is now being dominated by organic thio derivatives of hydrazine, *viz*, thiosemicarbazide, thiosemicarbazones, thiohydrazide thiohydrazones and thiocarbohydrozones. As early as 1934 Domagk *et al.* reported that thiosemicarbazones possessed anti-tubercular activity. Later on research on thiosemicarbazones and their metal complexes expanded to large extent. They have been found to be active against influenza, protozoa, smallpox and certain kinds of tumor and have been suggested as possible pesticides and fungicides. Their activity has frequently been thought to be due to their ability to chelate trace metals. Thus Liebermeister showed that copper ions enhance the anti-tubercular activity of *p*-acetamidobenzaldehyde thiosemicarbazones.

Thiosemicarbazone derivatives are emerging as a new class of non-platinum experimental anticancer chemotherapeutic compounds which not only show inhibitory activities against common cancers but which are also found to be potent inhibitors of a crucial enzyme, ribonucleotide diphosphate reductase (RDR), which is obligatory for DNA biosynthesis and cell division. The most active compounds of this class include copper complexes of 3-ethoxy-2-oxobutaraldehyde thiosemicarbazone (*Fig. 1*), commonly known as CuKTS and those of 4-N-heterocycle thiosemicarbazone.
Motivated by the potential antitumour activity of Quinones, which are presently in use in clinical practices, Padhye et al. synthesized napthoquinone-thiosemicarbazone hybrid molecules by combining structural features of both the groups with retention of their antitumor properties (Fig. 2). Such 'hybrid' antitumor agents involving cisplatin and doxorubicin moieties have been found to possess lower therapeutic dosages, minimal cytotoxicities and reasonable kidney clearance.

Tojal and Rojo have developed comparative structural studies and approximate molecular orbital calculations on Cu (II) complexes derived from pyridine-2-carbaldehyde thiosemicarbazone. The results allow explaining: (1) some significant structural differences between complexes containing the neutral ligand and those with the anionic one and (2) the formation of monomeric versus dimeric entities with the neutral ligand. In continuation of their work on binucleating ligands, Hoskin et al. designed a novel phenoxy bridged binucleating thiosemicarbazone ligand and
its Cu (II) and Ni (II) complexes (Fig.3). Also presented are some results of a single crystal X-ray study of one of the complexes, \([\text{Ni}_2\text{L(OC}_2\text{H}_5)]\) (DMF)_2.

![Fig. 3](image)

Fig. 3

Literature records several reviews on coordination chemistry of thiosemicarbazones.\(^{18-22}\)

Shetty et al.,\(^{23}\) reported binuclear molybdenum (V) and (VI) complexes of 2,6-diformyl-\(p\)-cresol bis \([4-(\text{X-phenyl thiosemicarbazone})]\) \((\text{X= various substitution on phenyl ring})\), the novel binucleating ligand is derived from the Schiff condensation of 2,6 diformyl-\(p\)-cresol and substituted thiosemicarbazides (Fig.4).

![Fig. 4](image)

Fig. 4

Exhaustive literature survey has revealed that recently large amount of work has been done on transition metal complexes with thiosemicarbazides and thiosemicarbazones as revealed by number of publications on this subject. In this chapter, recent work on thiosemicarbazones with special interest on Ruthenium complexes has been discussed.
H.K.Parwana et al.\textsuperscript{24} reported the divergent behaviour of thiosemicarbazones, derived by the condensation of pyridine-2-carboxaldehyde with thiosemicarbazide (Fig.5).

![Fig.5](image)

They observe that ligand exhibits three different kinds of behaviour towards different metal ion.

(i) It behaves as a neutral tridentate ligand coordinating through the ring nitrogen, azomethine nitrogen and sulphur atom in the complexes with Cu (II), Ni (II), and Zn (II).

(ii) It behaves as a tridentate monobasic acid in the complexes with Co (III) and Fe (III).

(iii) It behaves as a neutral bidentate ligand coordinating only through the nitrogen of the pyridine ring and nitrogen of the azomethine group in the cases of complexes with Ru (III), In (III) and Al (III).

Jain et al.\textsuperscript{25} synthesized Fe(III), Ru(III), Rh(III), Pd(III), Co(III) and Ni(II) complexes with N-(α-pyridyl) furfural-2-aldehyde thiosemicarbazones and N-(α-pyridyl) thiophene-2-aldehyde thiosemicarbazones. Complexes are of type [M (L)Cl\textsubscript{2}] Cl, where, M (III) = Fe, Ru, Rh. Ru (III) complexes are 1:1 electrolytes with octahedral geometry.

The platinum metal chelates of benzoin thiosemicarbazones obtained with Ru (III), Rh (III), Ir (III), Pd (II) and Pt (II) were prepared from their corresponding halide salts. Complexes of Ru (III), Rh (III) and Ir (III) are six coordinate octahedral while Pd (II) and Pt (II) halide complexes are four coordinate with halide bridging.

The same author\textsuperscript{27} reported the stereochemistry and complexation behaviour of diphenyldiketone monothiosemicarbazone with Cu (II), Co (II), Ni (II), Cd (II),
Zn (II), Ru (III), Rh (III), Ir (III), Pd (II) and Pt (II).

Maji et al. synthesized a series of complexes of thiosemicarbazones derived from 2, 6-diacetylpyridine (L₂H) starting with RuCl₃·xH₂O, Ru(PPh₃)₃Cl₂ and [Ru(NH₃)₃Cl]Cl₂. X-ray diffraction study of [Ru(L₂)(PPh₃)₂]ClO₄ reveals that the crystals are triclinic and coordination take place via oxygen of the carbonyl group, pyridine ring nitrogen, imine nitrogen and the thiolate sulphur atoms. Hence the ligands behave as tetradequate O-N-N-S donors.

The same author reported Ru (II) complexes of 2,6-diacetylpyridine bis (4-(p-tolyl) thiosemicarbazones) (L₁H₂) (Fig.6).

![Fig.6](image-url)

The complexes were of the type Ru(L₁H₂)X₂( X=Cl, Br, SCN), [Ru(L₁H₂) Y Cl] (Y= imidazole, pyridine-N-oxide) and [Ru(L₁H₂) (PPh₃)X]Y,( X=Cl, Br; Y=ClO₄/PF₆). The complexes were characterized on the basis of elemental analysis, IR, UV-Vis and nmr spectroscopy. Their electro chemical behaviour was examined by cyclic voltametry. They exhibit a reversible to quasi-reversible Ru⁰/Ru³ couple in MeCN solution at a glassy working electrode using an Ag/AgCl electrode as the reference. The ligand behaves as a pentadentate SNNNS chelating ligand giving unusual hepta coordinated ruthenium complexes. All the complexes are epr silent at room and also at liquid nitrogen temperature. This finding confirms the low-spin and diamagnetic character.

O.E.Offiong and S-Martelli reported the synthesis and characterization of the complexes of the type [M(HL₂)]Cl₃, where M = Ru(III), Rh(III), Ir(III), HL=
neutral 2-acetylpyridine-(2-methyl thiosemicarbazones), 2-acetylpyridine-(4-methyl thiosemicarbazones) and 2-acetylpyridine-(4-phenylthiosemicarbazones). The complexes were characterized by elemental analysis, conductivity measurements, magnetic susceptibility measurements and spectroscopic (IR, Raman, UV-Vis and $^1$H and $^{13}$C nmr) studies. The ligands behave as neutral tridentate. The complexes have six coordinate distorted octahedral structures. The ligand and their complexes exhibit a potent cytotoxic activity against *Ehrlich* tumor cells in vitro but appear to be more in vivo. Ru (III) complexes show molar conductance of between 311 and $325 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ suggesting 1:3 electrolytic behaviour. All the three Ru (III) complexes were paramagnetic. The room temperature magnetic moments of the ruthenium (III) are 1.53, 1.49 and 1.50 BM for [Ru (2-mts)$_2$]Cl$_3$, [Ru (4-mts)$_2$]Cl$_3$ and [Ru (4-pts)$_2$]Cl$_3$ respectively, values that are lower than the spin-only value and thus, suggest the presence of low symmetry field. The spin orbit coupling constant ($\lambda$) calculated using the equation suggested by Figgis for low symmetry molecules lies in the range (-1120 to -1301), indicating distortion along one of the axis (z) of the octahedron structure of the complexes. The electronic spectra bands of ruthenium (III) complexes in the 13600-13800, 17500-17800, 22500-23000, 28000-32000 cm$^{-1}$ regions have been assigned to the $^2T_{2g} \rightarrow ^2A_{2g}$, $^2T_{2g} \rightarrow ^2E_g$, $^2T_{2g} \rightarrow ^2A_{1g}$ and the $\Pi \rightarrow ^2t_{2g}$ ($\Pi^*$) respectively, in an octahedral field (Fig.7).

![Diagram of Ru(III) complex](image)

R$_1$=H or CH$_3$, R$_2$=CH$_3$ or C$_6$H$_5$

**Fig. 7**
F. Basuli et al.\textsuperscript{31} synthesized ruthenium and osmium complexes of the ligand salicylaldehyde thiosemicarbazones. The compounds have the general formula \([M(PPh_3)_3X_2]\) (M=Ru, Os; X=Cl, Br). The ligand is coordinated as a bidentate N, S—donor ligand, inspite of having the phenolic oxygen as the potential donor site forming a four membered chelate ring. This unexpected coordination mode of the salicylaldehyde thiosemicarbazones ligand is due to steric bulk of the coligand PPh\(_3\). The complexes are diamagnetic, which corresponds to the bivalent state of the metals (low spin d\(^6\), S=0) in these complexes. The saltsc ligands are coordinated as shown in (Fig. 8), with a bite angle of \(\sim 66^0\), causing severe angular distortion of the RuN\(_2\)P\(_2\)S\(_2\) coordination sphere from ideal octahedral geometry. The structure of [Ru(PPh\(_3\))\(_2\)(saltsc)\(_2\)] has a C\(_2\) symmetry.

![Image of a chemical structure](Fig. 8)

The same authors\textsuperscript{32} reported the synthesis of ruthenium and osmium complexes of benzaldehyde thiosemicarbazones and \(p\)-substituted benzaldehyde thiosemicarbazones (HL-R, where H stands for dissociable proton and R for the substituent) (Fig. 9). Ligands of this type are known to bind to a metal ion as a monoanionic bidentate N, S donor forming stable five membered ring (Fig. 10).

![Image of chemical structures](Fig. 9)  

**Fig. 9**  

![Image of chemical structures](Fig. 10)  

**Fig. 10**
However, reaction of these ligands with \([\text{M} (\text{PPh}_3)\text{X}_2]\) (where \(\text{M}=\text{Ru}, \text{Os}\) and \(\text{X}=\text{Cl}, \text{Br}\) afforded complexes of type \([\text{M} (\text{PPh}_3)(\text{L-R})_2]\) where the thiosemicarbazones ligand is coordinated as a bidentate N,S donor ligand forming a four membered chelate ring (Fig. 11).

![Thiosemicarbazone](image)

**Fig. 11**

T.D.Thangdurai and K.Natarajan\(^{33}\) reported the synthesis of ruthenium(III) complexes of the type \([\text{RuY(LL'}^1(\text{E})_2)]\) \((\text{Y}=\text{Cl} \text{ or Br}; \text{LL'}^1=\text{salicylaldehyde thiosemicarbazone; E=PPh}_3 \text{ or AsPh}_3)\) by reacting \([\text{Ru X}_3 (\text{EPh}_3)_3]\) \((\text{X}=\text{Cl}, \text{E}=\text{P}, \text{X}=\text{Cl} \text{ or Br}, \text{E}=\text{As})\) or \([\text{RuBr}_3(\text{EPh}_3)_2 (\text{MeOH})]\) with Salicylaldehyde thiosemicarbazone. The complexes were characterized by elemental analysis, spectral (ir, electronic spectra, epr), magnetic moment and cyclic voltammetry data. All the ligands behave as a binegative tridentate (O, N, S-) manner. All the complexes are paramagnetic, showing a +3 oxidation state for ruthenium ion. In general the electronic spectra of all the complexes are characteristic of an octahedral environment around ruthenium (III) ions. The magnetic moments for some of the complexes have been measured at room temperature using a vibration sample magnetometer. The values obtained lie in the range 1.72- 1.92 BM range and correspond to one unpaired electron, suggesting a low spin \(t^{2}_{2g}\) configuration for the ruthenium (III) ion in pseudo-octahedral environment.

Cyclic voltammetric study reveals that, the complexes show a reversible oxidation (Ru\(^{IV}\) - Ru\(^{III}\)) wave with a peak to peak separation (\(\Delta\text{E}_p\)) ranging from 60-100 mV, indicating a single step one electron transfer process. The epr spectra of solid complexes recorded at room temperature showed no hyperfine splitting. The new complexes exhibit a \(g_{\perp}\) value at ca. 2.15-2.49 and \(g_{\parallel}\) at ca. 2.09-2.22. The two different ‘g’ values \((g_{z} \neq g_{\gamma})\) indicate a tetragonal distortion in octahedral environment.
complexes. The presence of two ‘g’ values also indicates an axial symmetry for these complexes and hence the trans positions are assigned for triphenylphospine/triphenylarsine groups (Fig.12).

![Fig.12](image)

The same author reported\textsuperscript{34} the synthesis of Ruthenium(II) complexes of the type\([\text{Ru(CO)}(\text{B})(\text{LL'})\text{(PPh}_3\text{)}]\) (where\(\text{LL'}=\text{salicylaldehydesemicarbazone; } \text{B}=\text{PPh}_3, \text{pyridine, piperidine or morpholine}\) ) by reacting \([\text{RuHCl(CO)}\text{(PPh}_3\text{)}_3]\) or \([\text{RuHCl(CO)}\text{(PPh}_3\text{)}_2(\text{B})]\) with salicylaldehyde thiosemicarbazone, \(\text{o-hydroxyacetophenone thiosemicarbazone}\). The Schiff base ligand behaves as a binegative tridentate \((\text{O,N,S-})\) ligand to form five membered chelate ring (Fig.13).

![Fig.13](image)

Milan Maji \textit{et al.}\textsuperscript{35} reported the synthesis of series of Ruthenium (II) complexes of general formula \(\text{Ru(L)(bipy) Cl}_2\) with different thiosemicarbazides (\(\text{L}\)) which ligated to the metal ion in the thione form obtained by reacting \(\text{Ru (bipy)Cl}_4\) with the corresponding ligands in methanol. One bipyridine molecule and two chloride ligands complete the hexacoordination. The compounds have been characterized by elemental analysis, magnetic moment measurement and by different spectroscopic methods (Fig.14).
K.M.Ibrahim et al.\textsuperscript{36} reported the synthesis of ruthenium (II) complex of the ligand 1-acetoacet-o-toluidene-4-phenyl-3-thiosemicarbazone. The complex has the formula [Ru (Haatpt)$_2$ Cl (H$_2$O)]. The ligand act as a mononegative tridentate manner coordinating to the metal ion via the deprotonated thiol sulphur, azomethine nitrogen and carbonyl oxygen atoms. The complex is diamagnetic with a low spin octahedral geometry (Fig.15).

R.K.Agarwal and S.Prasad\textsuperscript{37} synthesized Ru(III),Rh(III),Ir(III),Pd(II) and Pt (II) complexes with 4[N-(Furan-2'-carboxalidene) amino] carboxalidene) amino] carboxalidene) amino] anti pyrine thiosemicarbazone(FFAAPTS) (Fig.16) and 4[N(3',4',5'trimethoxybenzalidene) amino] antipyrene thiosemicarbazones (TMBAAPTS) (Fig.17). All the compounds have the general composition MCl$_2$ (L) (M= Pd$^{2+}$ or Pt$^{2+}$; L=FFAAPTS or TMBAAPTS) or MCl$_3$ (L) (M= Ru$^{3+}$, Rh $^{3+}$ or Ir $^{3+}$; L=FFAAPTS or TMBAAPTS).The complexes were characterized by elemental analysis, molar conductance, molecular weight, magnetic measurements and infrared and electronic spectra. The magnetic and electronic spectra suggest that Pd$^{2+}$ and Pt$^{2+}$
complexes are square planar, while Ru$^{3+}$, Rh$^{3+}$ and Ir$^{3+}$ complexes have octahedral geometry.

![FFAAPTS](image1.png)  
**Fig. 16**

![TMBAAPTS](image2.png)  
**Fig. 17**

Ru (III) complexes are non-electrolyte. IR spectra of ligands and complexes imply that the both ligands behave as neutral tridentate and the metals are coordinated through N and N of the 2 azomethine groups and S of the thio-keto group. Ru$^{3+}$ complexes show magnetic moments of 1.83-1.87 BM at room temperature. The lowering of $\mu_{\text{eff}}$ values may arise due to the effect of the ligand field, metal-metal interaction of considerable delocalization.

**Aim of Research**

By condensing aliphatic, aromatic or heterocyclic aldehydes or ketones with thiosemicarbazides have derived a large number of thiosemicarbazones ligands. Many of the compounds possess a wide spectrum of medicinal properties. Molecular models essential for medicinal or biological activities must be ascertained by designing new molecular models of thiosemicarbazones. The strategies for modifying the thiosemicarbazones ligand are namely,

1) Changing the point of attachment of the thiosemicarbazones moiety in the parent aldehyde or ketone

2) Substitution on the terminal $^{4}\text{N}$ position

3) Variation of parent aldehyde or ketone.

Although the investigations of metal complexes of a variety of
thiosemicarbazides and thiosemicarbazones have been subject of intensive research, those of $^4\text{N}$ substituted thiosemicarbazones and ligands that can bind two metal ions in close proximity have received little attention.

An important development in the field of coordination chemistry has been the design and synthesis of ligands capable of binding two metal ions. Much of the interest in multimetal complexes originates from their potential as models for metalloproteins. In particular, the binuclear metal complexes are of interest because, it is known or believed that many of the biological functions performed by certain metalloproteins are consequences of the metal centres occurring in pairs.$^{38-40}$

These facts created interest in the author to design and synthesize new compartmental ligands capable of binding two metal ions. The ligand 2, 6-diformyl-$p$-cresol bis (4-phenyl thiosemicarbazone) and substituted thiosemicarbazones were prepared. The ligands have few interesting features.

1. The ligands contain SNONS donor sequences possessing five potential coordinating sites.

2. The ligand can bind two metal ions leading to oxobridged binuclear complex keeping option for exogenous bridge.

3. The ligand can behave as monobasic, dibasic, or tribasic depending on reaction conditions and nature of metal ions.

Keeping in view, the present trends in the field of coordination chemistry, we have attempted the synthesis and characterization of Ruthenium (III) complexes using above ligands.

This work has been directed towards an understanding of the chemistry, electronic structures and spin-exchange coupling between metal centers.
Experimental

Preparation of 2, 6-diformyl-p-cresol

Preparation of 2,6-diformyl-p-cresol was carried out according to the method reported by Denton\textsuperscript{41} with slight modification. Phosphorus pentoxide (75g) was mixed with preheated phosphoric acid (80ml). The reaction was carried out in a three-necked flask fitted with a stirrer, a guard tube and thermometer. The reaction mixture was stirred at 150\(^0\)C until all phosphorus pentoxide dissolved into phosphoric acid. The resultant product, polyphosphoric acid was cooled to 50-60\(^0\)C. Then, hexamine (30g) and p-cresol (12ml) were added slowly with stirring. The temperature was raised carefully up to 125\(^0\)C. The yellow pasty mass was cooled and treated with water. The yellow precipitate was separated by filtration. The crude product was purified by steam distillation, which gave pale yellow needles. M.p. 130-131\(^0\)C. Yield 6g.

Synthesis of ligands

The synthesis of ligand involves two steps

1) Preparation of thiosemicarbazides and 2) Preparation of thiosemicarbazones

Amines and other chemicals used for the preparation were of reagent grade. Amines were distilled or recrystallized prior to use.

Preparation of thiosemicarbazides\textsuperscript{42}

Freshly distilled aniline (0.1mol) was dissolved in ammonia solution (20ml, d=0.88) and carbon disulphide (8.0ml) was added to it, gradually with stirring in ice bath. Ethanol (30ml) was added and stirring was continued till carbon disulphide completely dissolved. The reaction mixture was allowed to stand for 2-3 hours. An aqueous sodium chloroacetate (0.1mol) solution was added followed by hydrazine hydrate (10ml, 50%). The reaction mixture was stirred for 2-3 hours and allowed to stand overnight. The crystals separated were filtered and recrystallized from ethanol. Same method was followed for other substituted thiosemicarbazides using different substituted anilines. Yield 70-75%

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Preparation of alkyl/aryl thiosemicarbazone

0.021 Mole of alkyl/aryl thiosemicarbazide in ethanol (100ml) was treated with 0.01 mole of 2, 6-diformyl-p-cresol. The reaction mixture was refluxed for 3-4 hours. The yellow solid separated was filtered, washed with ethanol 2-3 times and dried. Yield 80-90%.

![Structure of ligand (L1-L4)](image)

<table>
<thead>
<tr>
<th>Code</th>
<th>Ligand</th>
<th>M.p</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>2,6-diformyl-p-cresol-bis (4-methyl thiosemicarbazone)</td>
<td>&gt;280°C</td>
</tr>
<tr>
<td>L2</td>
<td>2,6-diformyl-p-cresol-bis (4-ethyl thiosemicarbazone)</td>
<td>&gt;270°C</td>
</tr>
<tr>
<td>L3</td>
<td>2,6-diformyl-p-cresol-bis (4-dimethyl thiosemicarbazone)</td>
<td>&gt;266°C</td>
</tr>
<tr>
<td>L4</td>
<td>2,6-diformyl-p-cresol-bis (4-diethyl thiosemicarbazone)</td>
<td>&gt;282°C</td>
</tr>
<tr>
<td>L5</td>
<td>2, 6-diformyl-p-cresol-bis (4-phenyl thiosemicarbazone)</td>
<td>&gt;270°C</td>
</tr>
<tr>
<td>L6</td>
<td>2,6-diformyl-p-cresol-bis(4-o-chlorophenylthiosemicarbazone)</td>
<td>&gt;270°C</td>
</tr>
</tbody>
</table>

![Structure of ligand (L5-L14)](image)

Structure of ligand (L1-L4) Structure of ligand (L5-L14)

<table>
<thead>
<tr>
<th>R</th>
<th>R1</th>
<th>L1</th>
<th>R = -H</th>
<th>L5</th>
</tr>
</thead>
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<td>R1 = C₂H₅</td>
<td>(L2)</td>
<td>R = -o-Cl , -m-Cl , - p- Cl</td>
<td>(L6, L⁷, L⁸)</td>
</tr>
<tr>
<td>R = R1 = CH₃</td>
<td>(L³)</td>
<td>R = -o- CH₃ , -m- CH₃ , - p- CH₃</td>
<td>(L⁹, L¹⁰, L¹¹)</td>
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<tr>
<td>R = R1 = C₂H₅</td>
<td>(L⁴)</td>
<td>R = -o- OCH₃ , -m- OCH₃ , - p- OCH₃</td>
<td>(L¹², L¹³, L¹⁴)</td>
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</tbody>
</table>
L^7 2, 6-diformyl-p-cresol-bis (4-m-chlorophenyl thiosemicarbazone) >270°C
L^8 2, 6-diformyl-p-cresol-bis (4-p-chlorophenylthiosemicarbazone) >270°C
L^9 2, 6-diformyl-p-cresol-bis (4-o-methylphenylthiosemicarbazone) >270°C
L^10 2, 6-diformyl-p-cresol-bis (4-methylphenyl thiosemicarbazone) >270°C
L^11 2, 6-diformyl-p-cresol-bis (4-p-methylphenylthiosemicarbazone) >270°C
L^12 2, 6-diformyl-p-cresol-bis (4-o-methoxyphenylthiosemicarbazone) >270°C
L^13 2, 6-diformyl-p-cresol-bis (4-methoxyphenyl thiosemicarbazone) >270°C
L^14 2, 6-diformyl-p-cresol-bis (4-p-methoxyphenylthiosemicarbazone) >270°C

Preparation of the complexes

Thiosemicarbazone ligand (0.001 mol) in ethanol (~30cm³) was treated with a solution of Ruthenium (III) chloride (0.002 mol) in ethanol (~20cm³). The mixture was stirred and refluxed for 4-5 hours. After concentration to ~3cm³ by heating the solution, the product was separated by addition of small quantity of ether. It was then filtered and washed with ethanol and ether and dried over anhydrous calcium chloride. Yield 60-80%, m.p. >250 °C.

Physical measurements

Estimation of Carbon, Hydrogen and Nitrogen

All the compounds were analyzed for carbon, hydrogen and nitrogen by VarioEL III CHNS analyzer at STIC Cochin University of science and Technology, Cochin
Conductivity measurements

Conductance measurements were done on ELICO-CM82 Conductivity Bridge, provided with a dip type conductivity cell fitted with platinum electrodes. The cell constant was determined by measuring the conductance of aqueous KCl solution of known specific conductance. The value of cell constant was found to be 0.51.

The conductance values of the complexes were determined by using $10^{-3}$M solution in dimethyl formamide. The molar conductance is calculated as follows.

$$\Lambda_M = 1000 \times K \times \text{obs. Conductance (in mhos)} / C$$

Where, $\Lambda_M$ = molar conductance

$K$= Cell constant

$C$= Molar concentration ($10^{-3}$M).

Magnetic susceptibility measurements

Magnetic susceptibility measurements of the complexes were carried out at room temperature, using Faraday method. The previously weighed and calibrated tube was uniformly filled with finely powdered sample of the complex up to the mark. The tube was suspended vertically from the pan of a semi micro single pan balance, at the center of the pole-gap between the poles of a strong magnet. The weight of the tube along with the complex was recorded without applying magnetic field. When a strong magnetic field (~6000 gauss) was applied, the paramagnetic sample experienced magnetic gradient. This causes a change in the weight of the sample and thus the weight was recorded under the influence of magnetic field. The process of recording the weights with and without magnetic field, was repeated thrice and the mean of the three observation taken as apparent change in the weight. The compound Hg [Co (SCN)$_4$] was employed as a calibrant.
**Electronic spectral measurements**

Electronic spectra of the ligands and the complexes in DMF solution were recorded using Hitachi 150-20 spectrophotometer in the range 1100-200 nm.

**Infra red spectral measurements**

I.r. spectra were recorded in the 4000-400 cm\(^{-1}\) region (KBr disc) on a Nicolet 170 SX FT-IR. Far I.r. were recorded in the region 500-100 cm\(^{-1}\) on Bruker IFS66V (Polythene discs).

**Nuclear Magnetic Resonance**

Proton and carbon magnetic resonance spectra were recorded on a Bruker 300 M Hz spectrometer in DMSO-d\(_6\) and CDCl\(_3\) using TMS as an internal standard.

**Electron spin resonance spectral measurements**

E.s.r. spectra of polycrystalline sample were recorded at room temperature on a Varian E-4 X-band spectrometer using TCNE/DPPH as <g> marker, at SAIF, Indian Institute of Technology, Mumbai. The \(g_{||}\) and \(g_{\perp}\) are compared with the resonance position of diphenyl picryl hydrazyl (DPPH) or tetracyanoethylene radical (TCNE). The \(g_{||}\) and \(g_{\perp}\) values are calculated using the following equations,

\[
g_{||} = \frac{g_{\text{DPPH}} \times H_{\text{DPPH}}}{H}
\]

\((g_{\text{DPPH}} = 2.0023)\)

\[g_{av} = \frac{1}{3}(g_{||} + 2g_{\perp})\]

Scan range 5000G; Field set 3000G

**Cyclic voltammetric measurements**

The cyclic voltammetric measurements were carried out by using CH1110A electrochemical analyzer (USA) with a three-electrode assembly comprising glassy carbon working electrode, a platinum auxiliary electrode and saturated calomel reference electrode (SCE) was used. The electrochemical experiments were carried out and the positions of the waves were compared to the potential of the
ferrocene/ferrocenium couple. The DMSO solution (containing 0.1 M tetrabutylammonium-perchlorate [(n-But)_4N(ClO_4)_2], as supporting electrolyte, 10^{-3} molar concentration of the ligand and each of the complexes) was placed in a single compartment electrochemical cell degassed by bubbling with N_2(g) saturated with DMSO. A nitrogen atmosphere was continuously maintained in the solution while the experiments were in progress.

**Results and Discussion**

All the complexes are non-hygroscopic. Complexes contain 2:1 metal-to-ligand ratio. They are formed by the loss of three protons. They are insoluble in water, EtOH, MeOH 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 all the complexes are above 250 °C.

**Molar conductivity measurements**

Molar conductivity of all the complexes was measured in DMF solution at 10^{-3} M concentration. The observed molar conductance values (2.6-18.5 mho cm^2 mol^{-1}) suggest that all the complexes are non-electrolytes (Table-1).

**Magneto chemistry**

Transition metal complexes containing more than one metal atom with unpaired electrons can generally be categorized according to their magnetic behavior into three main groups depending on the strength of the metal-metal interaction. In the *non-interacting* type the magnetic properties of the dimer are essentially unchanged from the paramagnetic monomer. In the strongly interaction type formation of relatively strong metal-metal bonds occurs, and the molecule will display simple diamagnetic behavior (from even numbers of electrons).

All the complexes show magnetic moments of 1.73-1.87 BM per nuclei at room temperature. These values indicate Ruthenium is in +3 oxidation state with d^5 system. On the basis of magnetic data inner orbital octahedral geometry around the metal ion due to a donor atom in all the Ru^{3+} complexes.\(^{30,43}\)
Electronic spectral studies

Electronic spectra of all the complexes are scanned in DMF solution. The spectral data are given in Table-2. The representative electronic spectra are reproduced in Fig -18 a - d. All ligands show band at 260-270, 312-335 and 370-380 nm. The broad intense band around 260 nm is assigned to intra ligand П-П* transition. This band is almost unchanged in the spectra of complexes. The band around 320 nm with shoulder on lower energy side is assigned to n→П* transition associated with azomethine linkage. This band in all complexes have shown red shift due to the donation of lone pair of electron to the metal and hence the coordination of azomethine. The shoulder centered around 380 nm in the ligand was assigned to n→П* of thioamide chromophore, which suffer blue shift in complexes due to thioenolization. The moderately intense broad band for the complex around 410 nm is assigned to ligand to metal charge transfer transition (LMCT).

The LMCT maxima for the phenolate complex show line broadening, with a tail running into the visible part of the spectrum. This may result from a phenolate to M (III) LMCT band being superimposed on the low energy side of S→M (III) LMCT. The more intense charge transfer bands which extends deep into the visible region, prevents any analysis of d-d transition in the complex. Analysis of Table 2 reveals that the position of both the ligand bands and the LMCT bands is only slightly affected by the change in the substituents on the phenyl ring of thiosemicarbazides moiety in all complexes. Nevertheless, this small change cannot be directly with the electron donor or acceptor ability of the substituents44−46.

I.r spectral studies

Infrared spectra of ligands and complexes were recorded in KBr pellet from 4000-400 cm⁻¹. Important bands with assignments are shown in Table-3 and spectra are reproduced in Fig.19a - l. Comparison of the spectrum of ligand with its complex forms the basis of assignments of the bands.
The possibility of thione-thiol tautomerism (H-N-C=S $\rightleftharpoons$ C=N-SH) in these ligands has been ruled out for no bands around 2500-2600 cm$^{-1}$ characteristics of thiol group, are displayed in the infrared absorption.$^{37,47,48}$

The alkyl/ aryl (phenyl) $\nu$(^4NH) and hydrazone $\nu$(^2NH) are observed around 3300 and 3100 cm$^{-1}$ respectively. Coupled vibration among thioamide bands I $\beta$(NH) + $\nu$(CN), II $\nu$(CN) + $\beta$(NH), III and IV are distributed around 1540, 1450, 1330 and 930 cm$^{-1}$ regions.

The phenolic $\nu$(OH) is found around 2900 cm$^{-1}$ as a weak broad band which disappears in all complexes indicating deprotonation and coordination to metal. This is further supported by shift of phenolic $\nu$(C-O) at 1260-1280 cm$^{-1}$ in ligand to higher frequency by about 50-60 cm$^{-1}$ on complexation$^{49,50}$

The absorptions at 1590-1610 cm$^{-1}$ in free ligands can be attributed to $\nu$(C=N) and these frequencies were shifted to a higher energy by 3-10 cm$^{-1}$ in the spectra of all the complexes, showing the coordination of azomethine nitrogen to the metal. Coordination of azomethine nitrogen has been proposed for the majority of thiosemicarbazone complexes with evidence based on shifting of $\nu$(C=N). Interestingly, the shifting has been reported both to higher$^{51-54}$ and lower$^{55-58}$ energies. The shift of these bands depends on bond order of $\nu$(C=N) on coordination, which in turn depends on group attached to $\nu$(C=N) band. Further there is no splitting or shoulder on $\nu$(C=N) band suggesting both azomethine nitrogens are coordinated to ruthenium.

Thioamide bands III and IV which have major contribution of $\nu$(C=S) have undergone considerable reduction in intensity in all the complexes due to thioenolization and subsequent coordination to metal which is supported by the shift of $\nu$(C=S) band in the free ligands appearing at 830 cm$^{-1}$ to lower frequencies (700-750 cm$^{-1}$) on complex formation.$^{34}$

A strong band at 3100cm$^{-1}$ attributed to $\nu$(^2N-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 around 3400 cm\(^{-1}\) followed by a sharp peak around 950 cm\(^{-1}\) is due to presence of coordinated water.\(^{59}\)

Thus the ligands 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\(^{-1}\) regions are assigned to \(\nu\) (M-N), \(\nu\) (M-O) and \(\nu\) (M-S) respectively.\(^{60-64}\)

\(^1\)H NMR spectral studies

\(^1\)H NMR spectra of two ligands were scanned in DMSO d\(_6\)- solvent on a Bruker 300 M Hz spectrometer (USA) in DMSO-d\(_6\) and CDCl\(_3\) using TMS as an internal standard. The assignment of chemical shifts is presented in Table-4 and spectra are reproduced in Fig-20.

The NMR spectra of ligands L\(^5\) and L\(^{14}\) show a singlet at 2.30 ppm (in L\(^5\)) and 2.29 ppm (in L\(^{14}\)), are accounted to –CH\(_3\) of \(p\)-cresol moiety of ligands. A multiplet at 6.91-7.76 ppm is assigned to aromatic protons. In case of L\(^5\), the protons adjacent to –CH\(_3\) group of \(p\)-cresol moiety have appeared as a singlet at 7.76 ppm. In L\(^{14}\), a singlet at 3.77 ppm is assigned to protons of –OCH\(_3\) which accounts for 6-protons. A singlet corresponds to two protons adjacent to –CH\(_3\) group in \(p\)-cresol moiety and two doublets correspond to ortho and meta protons in \(p\)-anisolyl moiety. The azomethine proton is observed at 8.46 and 8.44 ppm in L\(^5\) and L\(^{14}\) respectively. The phenyl –NH proton signal is observed at 10.18, 10.07 ppm and hydrazine –NH proton signal is observed at 11.86, 11.77 ppm in L\(^5\) and L\(^{14}\) respectively.\(^{65}\) Phenolic proton signal is not observed in the 0-15 ppm region. On D\(_2\)O exchange, both –NH signals disappear.\(^{23}\) No signal around 4.00 ppm due to the S-H proton was observed.

ESR Spectral study

ESR is a useful method to investigate geometry around the metal ions and to determine the ground state of electrons in metal ions. The fundamental principles of ESR are essentially same as those of NMR. In ESR a transition between two different
electron spin energy states occur upon absorption of quantum radiation in the microwave region. The energy of the transition is given by,

$$\Delta E = h\gamma = g\beta H$$

Where, \(\gamma\) = Frequency of radiation

\(h\) = Plank’s constant

\(g\) = Spectroscopic splitting factor

\(\beta\) = Bohr magneton

\(H\) = Magnetic field

The ESR instruments are operated in the region of 9000 MHz with the corresponding field intensity ~ 3000 Gauss. Owing to the orbital moment contribution the values of “\(g\)” will differ from 2.0027. The value of \(g\) in any arbitrary direction can be expressed as the resultant of the tensor components \(g_x\), \(g_y\) and \(g_z\) corresponding to the direction of the x,y and z- axis. The average value \((g_{av})\) is given by the relation,

$$g_{av}^2 = \frac{1}{3} (g_x^2 + g_y^2 + g_z^2)$$

Measurements on homologous powder samples give \(g_{\parallel}\) and \(g_{\perp}\) values only as observed in the case of complexes under study. The \(g_{\parallel}\) and \(g_{\perp}\) values are compared with resonance position of diphenyl picryl hydrazyl (DPPH) or tetracyano ethylene radical (TCNE). The \(g_{\parallel}\) and \(g_{\perp}\) values are calculated according to the procedure indicated by Peisach and Blumberg$^{66}$.

\[g_{\parallel} \text{ or } g_{\perp} = g_{TCNE} \times \frac{H_{(TCNE)}}{H}\]

\((g_{TCNE} = 2.0027)\)

\[g_{av} = \frac{1}{3} (g_{\parallel} + 2g_{\perp})\]

The ESR spectra are recorded for the complexes in powdered form and the spectra are reproduced in Fig. 21 a & b. ESR studies of the complexes were conducted for three primary purposes.

(i) to determine the geometry around the metal ion.
(ii) to know the ground state of unpaired electron

(iii) to investigate whether the ESR spectra show evidence of metal-metal interactions.

[Ru(C23H19ON6S2)Cl3.2H2O] (C5) in the solid state at room temperature shows an isotropic resonance (giso = 2.19) with unresolved hyperfine structure due to Ruthenium. Since Ruthenium has two magnetic nuclei 99Ru and 101Ru and nuclear moments of 0.63 and 0.9nm respectively. Both isotopes have a nuclear spin of 5/2. Isotopic lines are usually observed either due to intramolecular spin exchange which can broaden the lines or to the occupancy of the unpaired electron in a degenerate orbital. The nature and pattern of the ESR spectra suggest an almost octahedral environment around Ruthenium (III) ion in the complexes.67-68

**Electrochemistry**

The cyclic voltammetric measurements were carried out by using CH1110A electrochemical analyzer (USA) with a three-electrode assembly comprising glassy carbon working electrode, a platinum auxiliary electrode and saturated calomel reference electrode (SCE) was used. The electrochemical experiments were carried out and the positions of the waves were compared to the potential of the ferrocene/ferrocenium couple. The DMSO solution (containing 0.1 M tetrabutylammonium-perchlorate [(n-But)4N(ClO4)2], as supporting electrolyte, 10^{-3} molar concentration of the ligand and each of the complexes) was placed in a single compartment electrochemical cell degassed by bubbling with N2(g) saturated with DMSO. A nitrogen atmosphere was continuously maintained in the solution while the experiments were in progress.

Criteria for the reversibility of electrode processes were those of Nicholson and I.Shain.69. Measurements were done in 0.1 M tetraethylammonium chloride in DMSO and the data are uncorrected for junctional potentials. Under these same experimental conditions, the ferrocenium/ferroccne couple has an E_{1/2} value of +0.41 V vs SCE.
DAPHTSC complex in 0.1 M tetraethylammonium chloride in DMSO shows two reversible responses near +0.10, and -0.614 V vs SCE (Fig.22). The observed redox couples were presumably corresponding to the two stepwise one electron reduction processes designated in eq 1.

\[
\begin{align*}
\text{E}_{1/2} & \quad \text{E}_{1/2} \\
[\text{Ru}_2^{\text{III}}(\text{DAPHTSC})\text{Cl}_3,2\text{H}_2\text{O}] & \leftrightarrow [\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}(\text{DAPHTSC})\text{Cl}_3,2\text{H}_2\text{O}] \\
& \leftrightarrow [\text{Ru}^{\text{II}}(\text{DAPHTSC})\text{Cl}_3,2\text{H}_2\text{O}]^{2-} \\
\end{align*}
\]

The most remarkable feature is the large separation between the two redox potentials \( E_{1/2}^{1} \) and \( E_{1/2}^{2} \) \( \Delta E_{1/2} = (E_{1/2}^{1} - E_{1/2}^{2}) = 0.714 \). The cyclic voltammogram also shows an oxidation process tentatively corresponds to the one electron oxidation of

\[
[\text{Ru}_2^{\text{III}}(\text{DAPHTSC})\text{Cl}_3,2\text{H}_2\text{O}] \leftrightarrow [\text{Ru}^{\text{III}}\text{Ru}^{\text{IV}}(\text{DAPHTSC})\text{Cl}_3,2\text{H}_2\text{O}]^{+}
\]

**Conclusion**

All the Schiff base 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 2:1. Magnetic study had reveal that all the complexes were paramagnetic. IR studies show that ligands coordinate to the metal through phenolic oxygen via deprotonation; two azomethine nitrogen atoms and two sulphur atoms via thioenolisation and behave as a tribasic pentadentate ligand. Tentative structures of these complexes are as shown below.
Structure of complex (C\textsuperscript{1}-C\textsuperscript{4})  
\[
\begin{align*}
R = H, R_1 = \text{CH}_3 & \quad \text{(L}\textsuperscript{1}\text{)} \\
R = H, R_1 = \text{C}_2\text{H}_5 & \quad \text{(L}\textsuperscript{2}\text{)} \\
R = R_1 = \text{CH}_3 & \quad \text{(L}\textsuperscript{3}\text{)} \\
R = R_1 = \text{C}_2\text{H}_5 & \quad \text{(L}\textsuperscript{4}\text{)}
\end{align*}
\]

Structure of complex (C\textsuperscript{5}-C\textsuperscript{14})  
\[
\begin{align*}
R = -\text{H} & \quad \text{(L}\textsuperscript{5}\text{)} \\
R = -\text{OCH}_3, -\text{OCH}_3, -\text{OCH}_3 & \quad \text{(L}\textsuperscript{12}, \text{L}\textsuperscript{13}, \text{L}\textsuperscript{14}\text{)}
\end{align*}
\]
Table-1. Analytical, conductivity and magnetic moment data of the ligands and their complexes

<table>
<thead>
<tr>
<th>No</th>
<th>Compounds</th>
<th>Found (Calcd) %</th>
<th>Molar conductance $\lambda m(\Omega^{-1}cm^2mol^{-1})$</th>
<th>Magnetic moment BM</th>
</tr>
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<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>L$^1$</td>
<td>(C$<em>{13}$H$</em>{18}$ON$_6$S$_2$)</td>
<td>46.10 (46.15)</td>
<td>5.28 (5.32)</td>
<td>24.75 (24.85)</td>
</tr>
<tr>
<td>C$_1$</td>
<td>[Ru$<em>2$(C$</em>{13}$H$_{18}$ON$_6$S$_2$)Cl$_3$.2H$_2$O]</td>
<td>23.15 (22.95)</td>
<td>2.83 (2.79)</td>
<td>12.24 (12.36)</td>
</tr>
<tr>
<td>L$^2$</td>
<td>(C$<em>{15}$H$</em>{22}$ON$_6$S$_2$)</td>
<td>49.15 (49.18)</td>
<td>5.95 (6.01)</td>
<td>22.90 (22.95)</td>
</tr>
<tr>
<td>C$_2$</td>
<td>[Ru$<em>2$(C$</em>{15}$H$_{22}$ON$_6$S$_2$)Cl$_3$.2H$_2$O]</td>
<td>25.39 (25.44)</td>
<td>3.45 (3.25)</td>
<td>11.43 (11.87)</td>
</tr>
<tr>
<td>L$^3$</td>
<td>(C$<em>{15}$H$</em>{22}$ON$_6$S$_2$)</td>
<td>49.12 (49.18)</td>
<td>5.98 (6.01)</td>
<td>22.91 (22.95)</td>
</tr>
<tr>
<td>C$_3$</td>
<td>[Ru$<em>2$(C$</em>{15}$H$_{22}$ON$_6$S$_2$)Cl$_3$.2H$_2$O]</td>
<td>25.32 (25.44)</td>
<td>3.58 (3.25)</td>
<td>11.75 (11.87)</td>
</tr>
<tr>
<td>L$^4$</td>
<td>(C$<em>{19}$H$</em>{38}$ON$_6$S$_2$)</td>
<td>54.10 (54.02)</td>
<td>7.05 (7.10)</td>
<td>19.80 (19.90)</td>
</tr>
<tr>
<td>C$_4$</td>
<td>[Ru$<em>2$(C$</em>{19}$H$_{37}$ON$_6$S$_2$)Cl$_3$.2H$_2$O]</td>
<td>29.83 (29.86)</td>
<td>3.92 (4.06)</td>
<td>10.77 (10.99)</td>
</tr>
<tr>
<td>L$^5$</td>
<td>(C$<em>{23}$H$</em>{32}$ON$_6$S$_2$)</td>
<td>59.70 (59.74)</td>
<td>4.75 (4.76)</td>
<td>18.14 (18.18)</td>
</tr>
<tr>
<td>C$_5$</td>
<td>[Ru$<em>2$(C$</em>{23}$H$_{19}$ON$_6$S$_2$)Cl$_2$.2H$_2$O]</td>
<td>34.04 (34.34)</td>
<td>2.96 (2.86)</td>
<td>10.40 (10.45)</td>
</tr>
<tr>
<td>L$^6$</td>
<td>(C$<em>{23}$H$</em>{20}$ON$_6$S$_2$Cl$_2$)</td>
<td>51.92 (51.98)</td>
<td>3.70 (3.76)</td>
<td>15.76 (15.81)</td>
</tr>
<tr>
<td>C$_6$</td>
<td>[Ru$<em>2$(C$</em>{23}$H$_{17}$ON$_6$S$_2$-o-Cl$_2$) ]Cl$_2$.2H$_2$O</td>
<td>31.30 (31.63)</td>
<td>2.39 (2.40)</td>
<td>9.61 (9.62)</td>
</tr>
<tr>
<td>L$^7$</td>
<td>(C$<em>{23}$H$</em>{20}$ON$_6$S$_2$Cl$_2$)</td>
<td>51.92 (51.98)</td>
<td>3.70 (3.76)</td>
<td>15.76 (15.81)</td>
</tr>
<tr>
<td>C$_7$</td>
<td>[Ru$<em>2$(C$</em>{23}$H$_{17}$ON$_6$S$_2$-m-Cl$_2$) ]Cl$_2$.2H$_2$O</td>
<td>31.30 (31.63)</td>
<td>2.39 (2.40)</td>
<td>9.61 (9.62)</td>
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<tr>
<td>L$^8$</td>
<td>(C$<em>{23}$H$</em>{20}$ON$_6$S$_2$Cl$_2$)</td>
<td>51.92 (51.98)</td>
<td>3.70 (3.76)</td>
<td>15.76 (15.81)</td>
</tr>
<tr>
<td>C$_8$</td>
<td>[Ru$<em>2$(C$</em>{23}$H$_{17}$ON$_6$S$_2$-p-Cl$_2$) ]Cl$_3$.2H$_2$O</td>
<td>31.30 (31.63)</td>
<td>2.39 (2.40)</td>
<td>9.61 (9.62)</td>
</tr>
<tr>
<td>L$^9$</td>
<td>(C$<em>{23}$H$</em>{26}$ON$_6$S$_2$)</td>
<td>61.20 (61.22)</td>
<td>5.42 (5.30)</td>
<td>17.06 (17.14)</td>
</tr>
<tr>
<td>C$_9$</td>
<td>[Ru$<em>2$(C$</em>{23}$H$_{23}$ON$_6$S$_2$Cl$_2$)Cl$_3$.2H$_2$O]</td>
<td>31.30 (31.63)</td>
<td>2.39 (2.40)</td>
<td>9.61 (9.62)</td>
</tr>
<tr>
<td>L$^{10}$</td>
<td>(C$<em>{23}$H$</em>{26}$ON$_6$S$_2$)</td>
<td>61.20</td>
<td>5.42</td>
<td>17.06</td>
</tr>
<tr>
<td></td>
<td>Molecular Formula</td>
<td>Mass %</td>
<td>mol %</td>
<td>mp/C</td>
</tr>
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<td>-------------------</td>
<td>--------</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td><strong>C10</strong></td>
<td>[Ru₂(C₂₅H₂₃ON₆S₂Cl₂)Cl₃]·2H₂O</td>
<td>31.30 (31.63)</td>
<td>2.39 (2.40)</td>
<td>9.61 (9.62)</td>
</tr>
<tr>
<td><strong>L¹¹</strong></td>
<td>(C₂₅H₂₆ON₆S₂)</td>
<td>61.20 (61.22)</td>
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<td>17.06 (17.14)</td>
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<tr>
<td><strong>C11</strong></td>
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</tr>
<tr>
<td><strong>L¹²</strong></td>
<td>(C₂₅H₂₆O₃N₆S₂)</td>
<td>57.40 (57.47)</td>
<td>5.02 (4.98)</td>
<td>16.04 (16.09)</td>
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<tr>
<td><strong>C12</strong></td>
<td>[Ru₂(C₂₅H₂₃ON₆S₂Cl₂)Cl₃]·2H₂O</td>
<td>34.73 (34.74)</td>
<td>3.19 (3.13)</td>
<td>9.66 (9.73)</td>
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<td><strong>L¹³</strong></td>
<td>(C₂₅H₂₆O₃N₆S₂)</td>
<td>57.40 (57.47)</td>
<td>5.02 (4.98)</td>
<td>16.04 (16.09)</td>
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<td><strong>C13</strong></td>
<td>[Ru₂(C₂₅H₂₃ON₆S₂Cl₂)Cl₃]·2H₂O</td>
<td>34.73 (34.74)</td>
<td>3.19 (3.13)</td>
<td>9.66 (9.73)</td>
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<td><strong>L¹⁴</strong></td>
<td>(C₂₅H₂₆O₃N₆S₂)</td>
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<td>34.73 (34.74)</td>
<td>3.19 (3.13)</td>
<td>9.66 (9.73)</td>
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Table-2. Electronic spectral data of the ligands and their complexes

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<tr>
<th>No</th>
<th>Peak values in $\lambda_{\text{max}}$ nm. ($\nu_{\text{Max}}$ in cm$^{-1}$)</th>
<th>Charge-transfer transition</th>
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<td></td>
<td>$\pi \rightarrow \pi^*$</td>
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<td>L$^3$</td>
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Table 3. Infrared spectral data of the ligands and their complexes (in cm⁻¹)

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Table 4. ¹H NMR Spectral data of the ligands

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<tr>
<th>Ligand</th>
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<th>Azomethine proton</th>
<th>-⁴NH (phenyl)</th>
<th>-²NH (hydrazine)</th>
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Fig. 18 a. UV spectrum of \( L^1H_3 \)

Fig. 18 b. UV spectrum of C3

Fig. 18 c. UV spectrum of \( L^5H_3 \)

Fig. 18 d. UV spectrum of C5
Fig. 19 a: IR spectrum of L\textsuperscript{1}H\textsubscript{3}

Fig. 19 b: IR spectrum of C1
Fig. 19 c: IR spectrum of $L^2H_3$

Fig. 19 d: IR spectrum of C2
Fig. 19 e: IR spectrum of $L^3H_3$

Fig. 19 f: IR spectrum of C3
Fig. 19 g: IR spectrum of $L^4H_3$

Fig. 19 h: IR spectrum of C4
Fig. 19 i: IR spectrum of $L^2H_3$

Fig. 19 j: IR spectrum of C5
Fig. 19 k: IR spectrum of $\text{L}^8\text{H}_3$

Fig. 19 l: IR spectrum of C8
Fig. 20 : Nmr spectrum of Ligand  $L^5H_3$
Fig. 21 a: ESR spectrum of C1

Fig. 21 b: ESR spectrum of C5
Fig. 22. Cyclic voltammogram of C 5
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