

**PHYSICOCHEMICAL CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF FE(III) WITH PYRUVIC ACID SEMICARBAZONE****P.R.Shirode<sup>1</sup>, R.K.Agrawal<sup>1</sup>, A.M.Jain<sup>1</sup> and P.M.Yeole<sup>2</sup>**

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Article Received on  
04 Jan 2014,

Revised on 29 Jan 2015,  
Accepted on 23 Feb 2015

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**ABSTRACT**

The mixed ligand complexes of the type  $[FeL_1L_2]Cl_3$ . Where  $L_1$ =Pyruvic acid semicarbazone  $L_2$ = semicarbazone of acetone, acetophenone, Benzaldehyde, cyclohexanone, salicylaldehyde semicarbazone, O-hydroxy acetophanone. These complexes have been synthesized, by the reactions of metal chlorides with two different semicarbazones in 1:1:1 molar ratio. The resulting products have been characterized on the basis of elemental analysis, magnetic measurement, IR and Electronic spectra, conductivity measurement, thermal analysis, antimicrobial activities. The metal complexes show ratio 1:1:1 with metal, ligand  $L_1$  and ligand  $L_2$ . The ligands are bonded through oxygen and nitrogen to metal ion.

**KEYWORDS:** Mixed ligand complexes, semicarbazone, pyruvic acid, acetone, acetophenone, Benzaldehyde, cyclohexanone, O-hydroxy acetophanone, thermal analysis, antimicrobial analysis.

**INTRODUCTION**

Metal complexes containing Fe(III) metal ions are extensively studied containing different ligands because of having valuable applications in biological, biochemical, analytical, antimicrobial system, anticancer, antibacterial and antifungal activities.<sup>[1-15]</sup> Semicarbazone shows a wide range of bioactivities, and their chemistry and pharmacological applications have been extensively studied. The biological properties of semicarbazone are often related to metal ion coordination. In contrast to thiosemicarbazone, literature records fewer examples of semicarbazone presenting significant anticancer and cytotoxic activity but some nitro so, naphthopyran, and fluorine derivatives showed anti-leukemia effect in mice.<sup>[16]</sup>

### Objectives and scope of the present work

There has been considerable interest in the studies of semicarbazone due to their coordination modes when bound to metals. The wide applications and structural diversity of metal complexes of semicarbazone encouraged us to synthesize the tridentate ONO-donor semicarbazone and their metal complexes. Metal complexes of pyruvic acid semicarbazone, semicarbazone of acetone, acetophenone, Benzaldehyde, cyclohexanone, O-hydroxy acetophanone and their derivatives as ligands with transition metal Cr(III) as (ML<sub>2</sub>) complexes have been already reported in early days.

Due to good chelating ability, the present work is mainly concerned on the studies of two novel semicarbazone, pyruvic acid semicarbazone[L<sub>1</sub>] and acetone semicarbazone, acetophanone semicarbazone, benzaldehyde semicarbazone, salicylaldehyde semicarbazone, O-hydroxy acetophanone [L<sub>2</sub>]. The compositions of these semicarbazones were determined by the CHN analyses. For the characterization of these compounds we have used IR and UV spectral studies. We have synthesized iron (III) complexes of these semicarbazones, in the ratio 1:1:1.

### EXPERIMENTAL TECHNIQUE

The compounds pyruvic acid, acetone, acetophenone, Benzaldehyde, cyclohexanone, O-hydroxy acetophanone and semicarbazide hydrochloride and chlorides of Fe(III) used were of E MEARK, BDH analytical grade. The amount of metal is determined volumetrically by EDTA using **double burette technique for optimum utilization of reagents**. Indicator used for Fe(III). Carbon, hydrogen and nitrogen analysis were carried from SAIF, Mumbai. Specific conductances were measured at room temperature in DMF by a Systronics direct reading 304 conductivity meter using a glass conductivity cell having a cell constant.

**Synthesis of Ligands:** Ligands L<sub>1</sub> and L<sub>2</sub> were prepared. The methods of their preparation are given below.

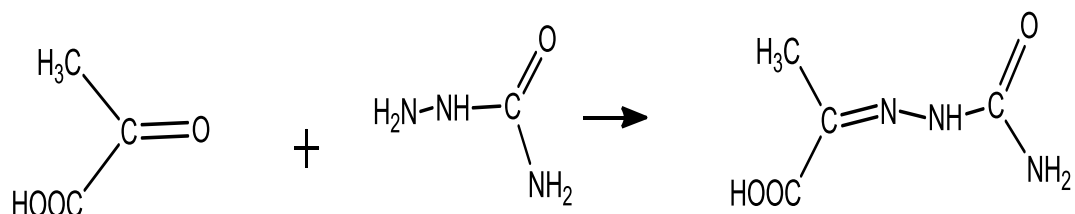
#### Ligand: L<sub>1</sub>

#### PYRUVIC ACID SEMICARBAZONE

Dissolve 2 gm. of Semi carbazide hydrochloride and 3 gm. of sodium acetate in a 100 ml beaker than add 20-30ml diluted water & stir continuously to obtained a clear solution of mixture of semicarbazide hydrochloride & sodium acetate, filter the solution & place ice bath. Take 2ml of pyruvic acid in a test tube and cool it in ice bath. This ice cooled solution of

pyruvic acid is very slowly drop wise added in a ice cooled solution of mixture of sodium acetate and semicarbazide hydrochloride with constant stirring. Stir the reaction mixture for another half an hour to separate out white precipitate of pyruvic acid semicarbazone. Recrystallize the crude product from hot water, dry and then melting point and yield is recorded.

### Reaction



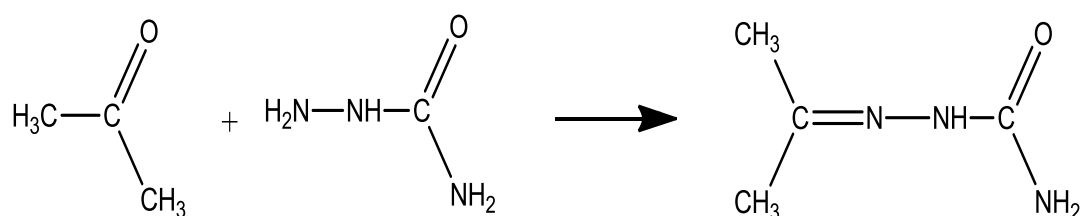
### Ligand: L<sub>2</sub>

#### 1. ACETONE SEMICARBAZONE

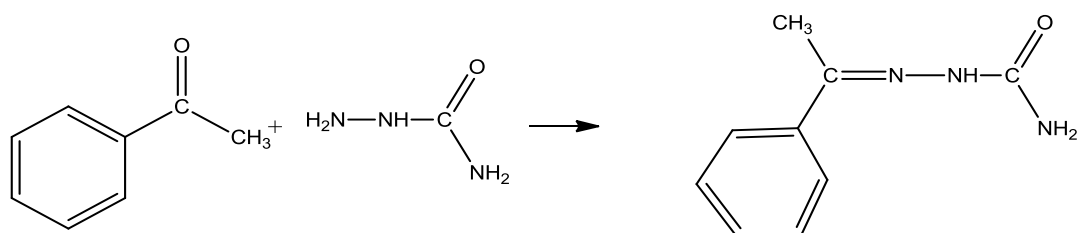
Dissolved 2gm. of semicarbazide of hydrochloride & 3gm. of crystallized sodium acetate in about 25-30ml distilled water in a hard glass test tube, cool in ice bath, to this solution add 2ml of aldehyde or ketone drop by drop with constant stirring for half an hour. White crystals of the semicarbazone derivative are separated out from the solution. Filter the crystals & recrystallized from ethyl alcohol, dry and then melting point and yield is recorded.

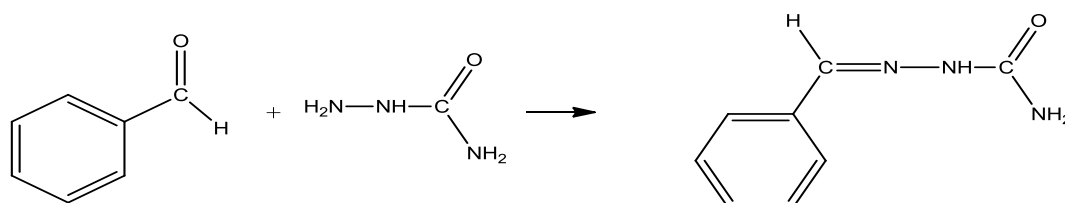
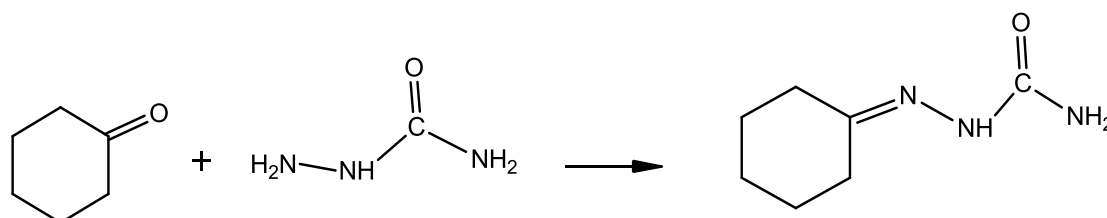
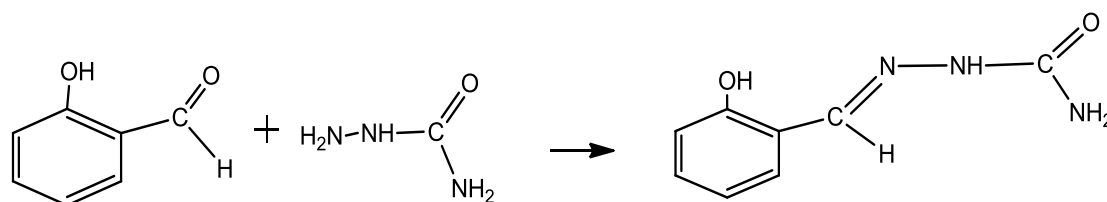
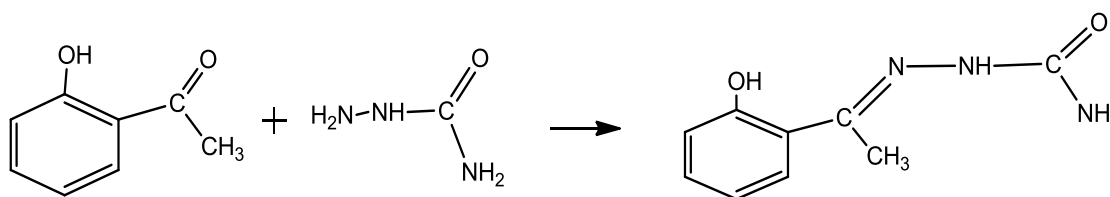
#### 1. ACETONE SEMICARBAZONE

### Reaction



#### 2. ACETOPHENONE SEMICARBAZONE



**3. BENZALDEHYDE SEMICARBAZONE****4. CYCLOHEXANONE SEMICARBAZONE****5. SALICYLALDEHYDE SEMICARBAZONE****6. ORTHO HYDROXY ACETOPHENONE SEMICARBAZONE****Synthesis Of complexes****1) Preparation of M (L<sub>1</sub>)<sub>2</sub> and M(L<sub>2</sub>)<sub>2</sub> complexes**

Aqueous 25ml (0.01M) solution of ferric chloride were mixed slowly with hot aqueous 25 ml (0.02M) solution of the Pyruvic semicarbazone (L<sub>1</sub>) with constant stirring. The reaction mixture is heated in water bath for three hours. Then the reaction was stirred for further one hour after which colored solid product was obtained, which was then washed with ethanol and dried in air. Similarly, the complexes of Fe(III) are prepared by mixing solution of corresponding metal chlorides and semicarbazone ligand (L<sub>2</sub>) in 1:2 molar ratio respectively.

## 2) Preparation of mixed ligand complexes the type $ML_1L_2$

To a 20ml (0.02M) aqueous solution of ferric chloride, a mixture of 20ml (0.02M) aqueous solution of Pyruvic semicarbazone and 20ml (0.02M) ethanolic solution of benzaldehyde semicarbazone were added slowly with constant stirring. This reaction mixture is refluxed in waterbath for 3 to 4 hours. and then 10% sodium hydroxide is added to adjust the  $p^H$  to about 7 to 7.5. The  $p^H$  of the solution is tested by  $p^H$  paper. In case of complexes of cobalt and copper the  $p^H$  of the reaction mixture must not exceed 7.5 unless the color of the complexes darken more and more to give a black color. The solution is stirred further for one hour, cooled to separate the solid coloured complex. It is filtered, washed with ethanol and dried in air.

By using similar procedure other complexes were prepared by mixing aqueous solution of ferric chloridewith pyruvic semicarbazone **and other semicarbazone** in the ratio **1:1:1**.

## RESULTS AND DISCUSSION

The reactions of metal chlorides with pyruvic acid semicarbazone and semicarbazones of acetone, acetophenone, Benzaldehyde, cyclohexanone, O-hydroxy acetophanone in the 1:1:1 molar ratio results in the formation mixed ligand complexes. The resulting complexes were having different colors as given in the table II. They are insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF. The properties of indicated in table III. The conductance of the complexes are very low (6.01 to  $14.43 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) indicating their non-electrolyte nature.

The TLC of the mixed ligand complexes exhibit single spots with  $R_f$  values being intermediate of the two corresponding symmetrical bis-complexes indicating that these are mixed ligand complexes rather than a mixture of two corresponding bis-complexes. From the magnetic moments these complexes shows octahedral geometry.

In the IR spectra of the mixed ligand complexes the bands at  $1540-1604 \text{cm}^{-1}$  may be assigned to the symmetric and asymmetric  $\nu(\text{C}=\text{N})$  vibrations. A strong band in the region  $1699-1647 \text{cm}^{-1}$  are due to  $\nu(\text{C}=\text{O})$  groups. On complex formation, the position of these bands is shifted toward lower side as compared to the metal free ligand. This indicates that the coordination takes place through the nitrogen and oxygen atom of the  $(\text{C}=\text{N})$  and  $(\text{C}=\text{O})$  groups. A broad band appears in the region at  $3200-3750 \text{cm}^{-1}$  for complexes 1 to 4b attributed to the coordinated water molecule, while this band is absent in complexes 5 and 6

indicating absence of water molecule. Thermogravimetric analysis shows presence of one water molecules in the complexes 1 to 4 supports the octahedral nature of complexes.

The electronic spectra of Fe(III) complexes exhibits three bands shown in table V are corresponding to  ${}^6A_{1g} \rightarrow {}^4T_{1g} ({}^4G)$ ,  ${}^6A_{1g} \rightarrow {}^4E_{2g} ({}^4G)$ , and  ${}^6A_{1g} \rightarrow {}^4E_{2g} ({}^4D)$ , transitions respectively. The complexes shows magnetic moment in the range 5.22 to 5.89 suggesting octahedral environment around Fe(III) ion.

### Antimicrobial assay

From the antimicrobial studies it inferred that, the Schiff bases was found to be potentially active against *E. Coli*, *P. aeruginosa* and *Aspergillus Niger*. Some of the complexes shown high antimicrobial activity against *E. Coli*, *Pseudomonas* and *Aspergillus Niger*. This enhancement in the activity of the metal complexes can be explained on the basis of chelation theory.

The physical properties of ligands and complexes are given in table I and II. IR spectra and are listed in table III and magnetic properties and molar conductivities are shown in table IV.

**Table I: Physical properties of ligands.**

Name of the ligand	Color and nature	Method purification.	M.P. °c (observed)reported	Mol. wt	Molecular formula
Pyruvic acid semicarbazone	White shining crystals	Recrystallization from water	215 (214)	145	C <sub>4</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub>
Acetone semicarbazone	White shining crystals	Recrystallization from CCl <sub>4</sub>	190 (188)	115	C <sub>4</sub> H <sub>9</sub> N <sub>3</sub> O
Acetophenone semicarbazone	White shining crystals	Recrystallization from ethanol	199 (200)	177	C <sub>9</sub> H <sub>12</sub> N <sub>3</sub> O
Benzaldehyde semicarbazone	White shining crystals	Recrystallization from ethanol	222 (221)	163	C <sub>8</sub> H <sub>9</sub> N <sub>3</sub> O
Cyclohexanone semicarbazone	White shining crystals	Recrystallization from ethanol	167 (167)	155	C <sub>7</sub> H <sub>13</sub> N <sub>3</sub> O
Salicylaldehyde semicarbazone	Yellowish shining crystals	Recrystallization from ethanol	225(225)	179	C <sub>8</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>
O-Hydroxy acetophenone semicarbazone	White shining crystals	Recrystallization from aq. ethanol	213 (211)	193	C <sub>9</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub>

**Table II: Characterization data of the complexes found (Calculated.) %**

Sr. No.	Ligand/ Complex	Color	Mole. Wt.	%Yield of the comp.	%of metal (Calculated)	%of C	% of H	% of N
1	Fe[(PASC) <sub>1</sub> (ACSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	Orange	440.35	68	12.68 (11.94)	21.80 (21.71)	4.08 (4.03)	19.08 (19.05)
2	Fe[(PASC) <sub>1</sub> (ACPHSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	Brown	502.35	72	11.71 (11.72)	31.05 (30.97)	3.88 (3.86)	16.72 (16.69)
3	Fe[(PASC) <sub>1</sub> (BZSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	Brown	488.35	65	11.43 (11.72)	23.34 (23.28)	3.68 (3.64)	17.20 (17.21)
4	Fe[(PASC) <sub>1</sub> (CYSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	Dark brown	480.35	72	11.62 (11.55)	27.47 (27.36)	4.16 (4.13)	17.48 (17.46)
5	Fe[(PASC) <sub>1</sub> (SYLSC) <sub>1</sub> ]Cl <sub>3</sub>	Red	486.35	71	11.48 (11.42)	32.98 (32.91)	3.95 (3.91)	17.27 (17.21)
6	Fe[(PASC) <sub>1</sub> (OACPHSC) <sub>1</sub> ]Cl <sub>3</sub>	Orange	500.35	68	11.72 (11.67)	31.17 (31.12)	3.69 (3.67)	16.59 (16.57)

**Table III. IR spectra (cm<sup>-1</sup>) bands of the parent and mixed ligand transition metal complexes**

Sr. No.	Name of the Complex	v- (OH) from H <sub>2</sub> O	v- COOH	v(C=O)	v(C=N)	Monosubstituted benzene ring
1	Fe[(PASC) <sub>1</sub> (ACSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	3175	2360	1698	1582	-
2	Fe[(PASC) <sub>1</sub> (ACPHSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	3328	2360	1680	1540	693
3	Fe[(PASC) <sub>1</sub> (BZSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	2922		1690	1583	698
4	Fe[(PASC) <sub>1</sub> (CYSC)(H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	3361	2360	1647	1547	-
5	Fe[(PASC) <sub>1</sub> (SYLSC) <sub>1</sub> ]Cl <sub>3</sub>	-	2360	1655	1583	689
6	Fe[(PASC) <sub>1</sub> (OACPHSC) <sub>1</sub> ]Cl <sub>3</sub>	-	2360	1699	1600	691

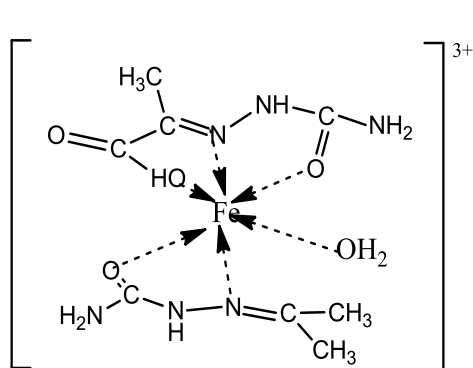
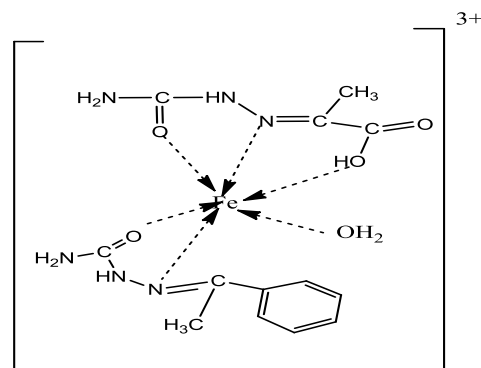
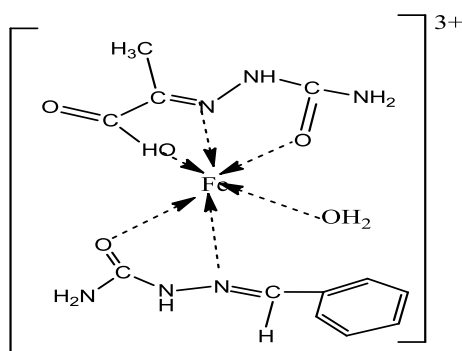
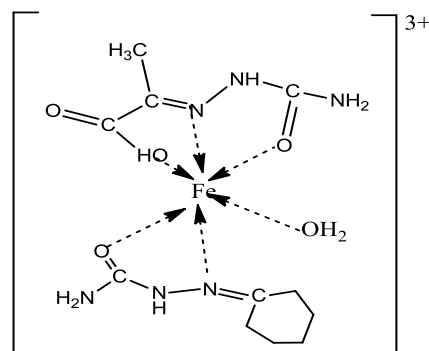
**Table IV. Magnetic moment and molar conductance values of the complexes**

Sr. No.	Name of the Complex	Magnetic moment	Molar cond. Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> at room temp. (29°C)	Molar cond. Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> at roomtemp+10°C (39°C)
1	Fe[(PASC) <sub>1</sub> (ACSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	5.6752	14.43	18.4
2	Fe[(PASC) <sub>1</sub> (ACPHSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	5.22	12.60	16.2
3	Fe [(PASC) <sub>1</sub> (BZSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	5.445	6.011	10.75
4	Fe [(PASC) <sub>1</sub> (CYSC)(H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	5.7123	11.23	15.45
5	Fe [(PASC) <sub>1</sub> (SYLSC) <sub>1</sub> ]Cl <sub>3</sub>	5.89	12.45	17.45
6	Fe [(PASC) <sub>1</sub> (OACPHSC) <sub>1</sub> ]Cl <sub>3</sub>	5.7365	10.55	16.25

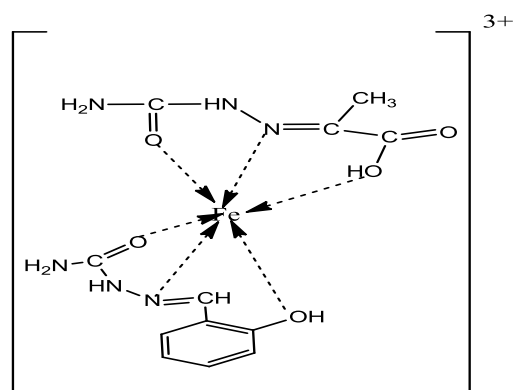
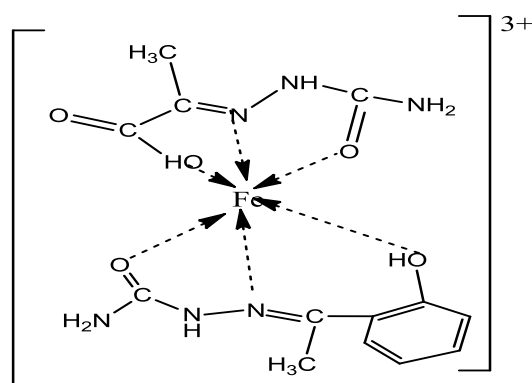
Table V: Electronic Spectra

Sr. No.	Name of the Complex	Absorbance wavelength in nm	Electronic transition	Geometry of the complex	Magnetic moment
1	Fe[(PASC) <sub>1</sub> (ACSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	11778	${}^6A_{1g} \rightarrow {}^4T_{1g}$	octahedral	5.6752
		20112	${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4G)$		
		28328	${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4D)$		
2	Fe[(PASC) <sub>1</sub> (ACPHSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	11618	${}^6A_{1g} \rightarrow {}^4T_{1g}$	octahedral	5.22
		24339	${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4G)$		
		30674	${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4D)$		
3	Fe [(PASC) <sub>1</sub> (BZSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	11600	${}^6A_{1g} \rightarrow {}^4T_{1g}$	octahedral	5.445
		27932	${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4G)$		
		32216	${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4D)$		
4	Fe [(PASC) <sub>1</sub> (CYSC)(H <sub>2</sub> O) <sub>1</sub> ]Cl <sub>3</sub>	11627	${}^6A_{1g} \rightarrow {}^4T_{1g}$	octahedral	5.7123
		16722	${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4G)$		
		25839	${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4D)$		
5	Fe [(PASC) <sub>1</sub> (SYLSC) <sub>1</sub> ]Cl <sub>3</sub>	11428	${}^6A_{1g} \rightarrow {}^4T_{1g}$	octahedral	5.89
		26385	${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4G)$		
		32051	${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4D)$		
6	Fe [(PASC) <sub>1</sub> (OACPHSC) <sub>1</sub> ]Cl <sub>3</sub>	11160	${}^6A_{1g} \rightarrow {}^4T_{1g}$	octahedral	5.7123
		17123	${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4G)$		
		27548	${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4D)$		

## Structure of the Complexes

1. Fe[(PASC)<sub>1</sub>(ACSC)<sub>1</sub>(H<sub>2</sub>O)<sub>1</sub>]Cl<sub>3</sub>2. Fe[(PASC)<sub>1</sub>(ACPHSC)<sub>1</sub>(H<sub>2</sub>O)<sub>1</sub>]Cl<sub>3</sub>3. Fe [(PASC)<sub>1</sub>(BZSC)<sub>1</sub>(H<sub>2</sub>O)<sub>1</sub>]Cl<sub>3</sub>4. Fe [(PASC)<sub>1</sub>(CYSC)(H<sub>2</sub>O)<sub>1</sub>]Cl<sub>3</sub>



5. Fe [(PASC)<sub>1</sub>(SYLSC)<sub>1</sub>]Cl<sub>3</sub>6. Fe [(PASC)<sub>1</sub>(OACPHSC)<sub>1</sub>]Cl<sub>3</sub>

### AKNOWLEDGEMENT

I am grateful to Principal, Pratap college, Amalner AND the Head Chemistry Department Pratap college, Amalner for laboratory facilities. I am also thankful to the Head Physics Department Pratap college, Amalner for Electronic spectra and IR spectra and Head, SAIF, IIT Mumbai for elemental analysis.

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