

Synthesis and Characterization of Iron Complexes of Resacetophenone Salicyloyl Hydrazone

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Abstract: Iron complexes of resacetophenone salicyloyl hydrazone (RSH) were synthesized and characterized by elemental analyses, magnetic moment studies, molar conductance studies, thermal analyses (DTA and TGA) UV-VIS, IR and ¹HNMR, spectral studies. Molar conductance values in DMF indicate that the complexes are non-electrolytes. The spectral studies indicate that the complexes are octahedral and the ligand coordinates through azomethine nitrogen

(>C=N-) and amide nitrogen ($\begin{matrix} \text{O} \\ \parallel \\ -\text{C}-\text{NH}- \end{matrix}$).

Keywords: resacetophenone salicyloyl hydrazone, thermal analyses (DTA, TGA), UV-VIS, IR, ¹HNMR, spectral studies.

1. Introduction

The hydrazones constitute important class medicinal compounds due to their wide variety of pharmacological and analytical applications [1-3]. They also bestow applications in floral arena as plant growth regulators [4, 5]. The biological activity of hydrazones is often increased by bonding to transition metals [6-8]. This facilitates their use as antimicrobial, antifungal antitubercular [9] and psychotropic agents [10]. Further, the metal complexes of hydrazones have potential applications as active materials in non linear optics [11], catalysts [12], magnetic materials with diverse magnetic interaction [13], luminescent probes [14] and molecular sensors [15]. Due to their versatile applications, metal complexes of hydrazones have been under study since a long time. In continuation of our work on hydrazones [16, 17], the present study reflects characterization of iron complexes of RSH.

2. Experimental

Requisite amount of RSH was dissolved in 100 mL of the dimethyl formamide to prepare 0.1M hydrazone solution. Conductivity water was used to prepare solution of the metal.

Elemental analysis of ligand and complexes were obtained from CDRI, Lucknow, India. Magnetic susceptibility measurement data was obtained from RSIC, IIT, Madras, India. Thermal analysis data was obtained from RSIC, IIT, Bombay, India.

The IR spectra of the ligand and complexes were obtained using Perkin Elmer Spectrometer-283. The scanning time was 6 minutes and the range was 3800-300 cm⁻¹. UV-Vis spectrophotometer Model UV-160 manufactured by Shimadzu was employed for obtaining UV-Vis spectra.

Conductivity measurements were made employing Conductivity Meter Model no. 302, Systronics, India.

2.1. Procedure for the preparation of hydrazones

Equimolar solutions of salicylic acid hydrazide and 2,4-dihydroxy acetophenone in aqueous ethanol were refluxed for about two hours and the contents were cooled to room temperature. The yellow solid separated was washed with water, dried and recrystallised from hot aqueous ethanol.

2.2. Procedure for the preparation of complexes

A mixture of required concentration of aqueous salt solution, 2,4-dihydroxy acetophenone salicyloyl hydrazone dissolved in dimethyl formamide and 50 mL of methanol were refluxed in a round bottom flask for two hours. Black crystalline product obtained after cooling was washed with hot water and petroleum spirit. Fe(II) and Fe(III) complexes of resacetophenone salicyloyl hydrazone (RSH) so obtained were crystalline, non-hygroscopic and stable at room temperature.

3. Results and Discussion

3.1. Analytical data

The complexes were analyzed for carbon, hydrogen and nitrogen and the results are given in the Table 1. On the basis of data, stoichiometry of the complexes was found to be 1:1 (M:L). Further it was also found that these complexes contain water molecules.

3.2. Molar conductivity measurements

Conductivity measurements of complexes were carried out in 10^{-3} M DMF solution. The molar conductance values

are listed in the Table 1. The table reveals that the molar conductance values of iron-RSH complexes lie in the range normally recommended for non-electrolytes [18].

3.3. Thermal analysis

The thermograms of Fe(II)-RSH and Fe(III)-RSH complexes are shown in the Figures 1 and 2 respectively. The rate of heating was 10° per minute and the studies were carried out in nitrogen atmosphere. The decomposition temperature of the complexes obtained from the thermograms is given in the Table 2.

TABLE 1. Analytical data for iron complexes

Compound	Molecular weight	Decomposition Temperature ($^{\circ}$ C)	Found (Cal) %				Conductance ($\text{Ohm cm}^2 \text{mol}^{-1}$)	μ_{eff} (BM)
			C	H	N	Metal		
RSH	286.23	304	62.87 (62.93)	4.84 (4.93)	9.71 (9.78)	-----	-----	-----
Fe(II)-RSH complex	342.08	>300	55.14 (55.20)	4.80 (4.85)	9.92 (9.96)	16.08 (16.04)	2.34	5.10
Fe(III)-RSH complex	342.08	>300	52.02 (52.66)	4.44 (4.13)	9.66 (9.48)	16.23 (16.33)	72.76	5.76

TABLE 2. TGA data for iron complexes

Complex	Initial decomposition temperature ($^{\circ}$ C)	Percent pyrolysed			
		Theoretical		Experimental	
		M	MO	M	MO
Fe(II)-RSH	303.7	83.67	78.99	81.71	76.40
Fe(III)-RSH	297.2	88.49	83.54	87.10	81.40

M: metal; MO: metal oxide

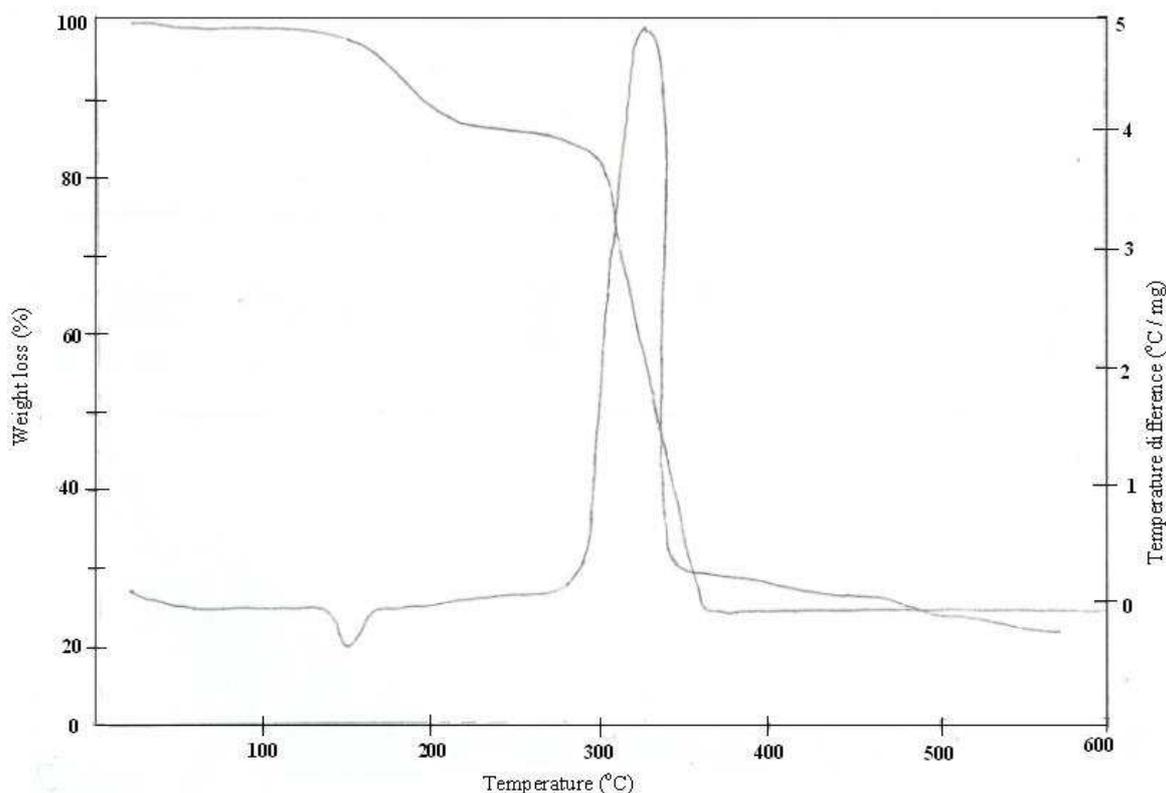
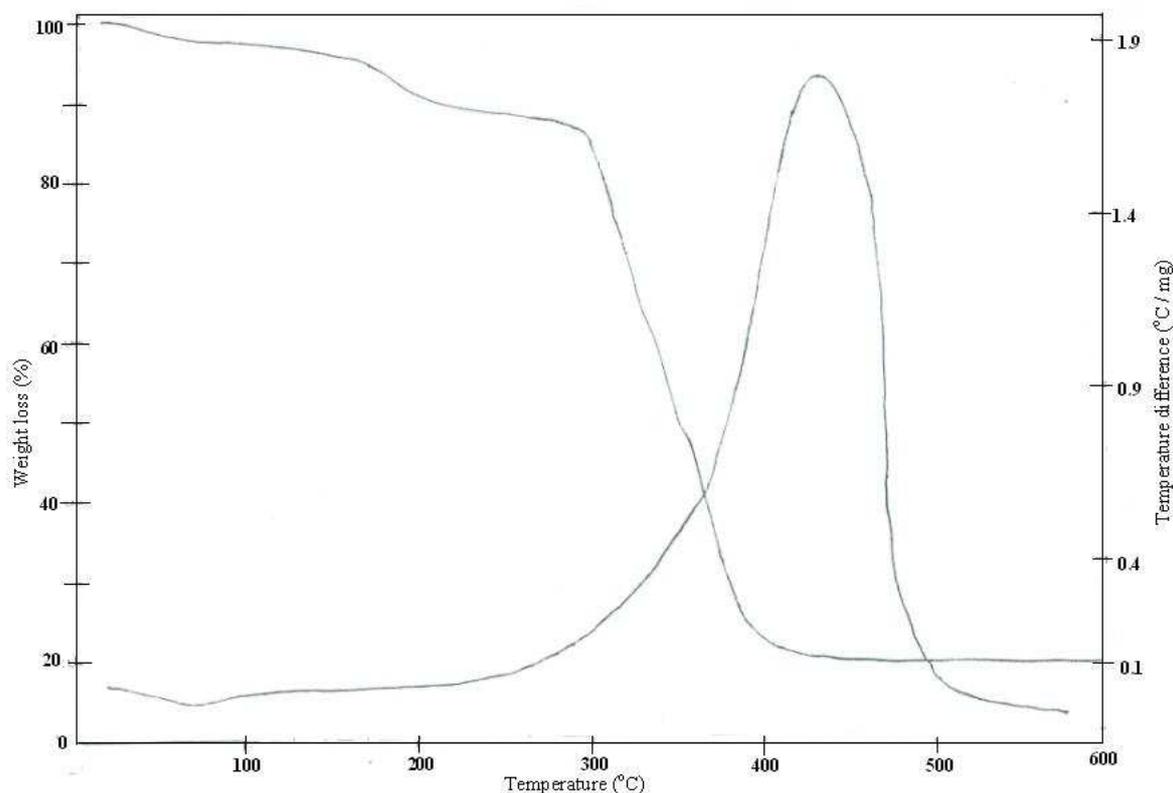


Figure 1. TGA and DTA curves of $[\text{Fe}(\text{RSH})_2 \cdot 2\text{H}_2\text{O}]$

Figure 2. TGA and DTA curves of $[\text{Fe}(\text{RSH})_2 \cdot 2\text{H}_2\text{O}] \text{Cl}$.

The complexes exhibit two steps. The first step in the temperature range $140\text{--}150^\circ\text{C}$ was due to the expulsion of coordinated water molecule. The corresponding percentage weight loss was 10.5%. This suggests that two water molecules are present in the coordination sphere. The second step was due to the sharp decomposition associated with loss of ligand, starts above 300°C in case of $\text{Fe}(\text{II})\text{-RSH}$ complex and above 295°C in case of $\text{Fe}(\text{III})\text{-RSH}$ complex. In both the cases, final products of decomposition above 385°C correspond to metallic oxide. The results are presented in the Table 2. The decomposition temperatures indicated reveal that the thermal stabilities of the complexes are in the order $\text{Fe}(\text{II})\text{-RSH} > \text{Fe}(\text{III})\text{-RSH}$.

3.4. Electronic spectral studies

The electronic spectral data of the complexes is shown in the Table 3.

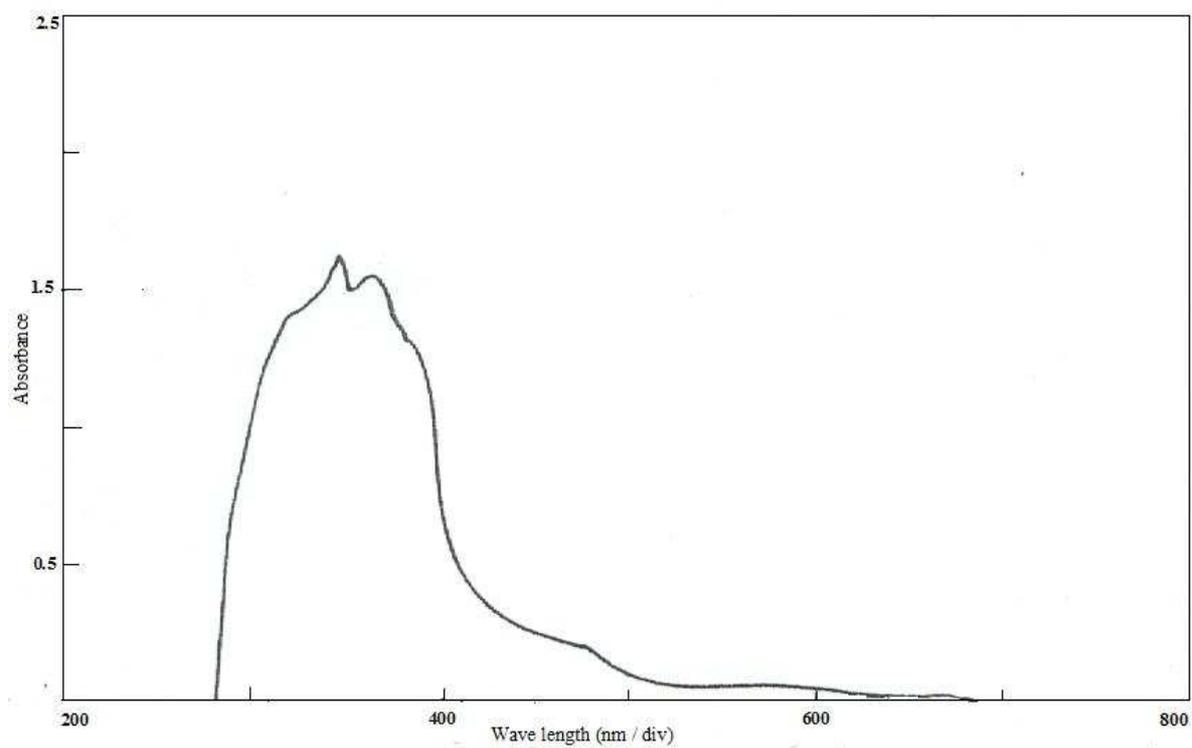
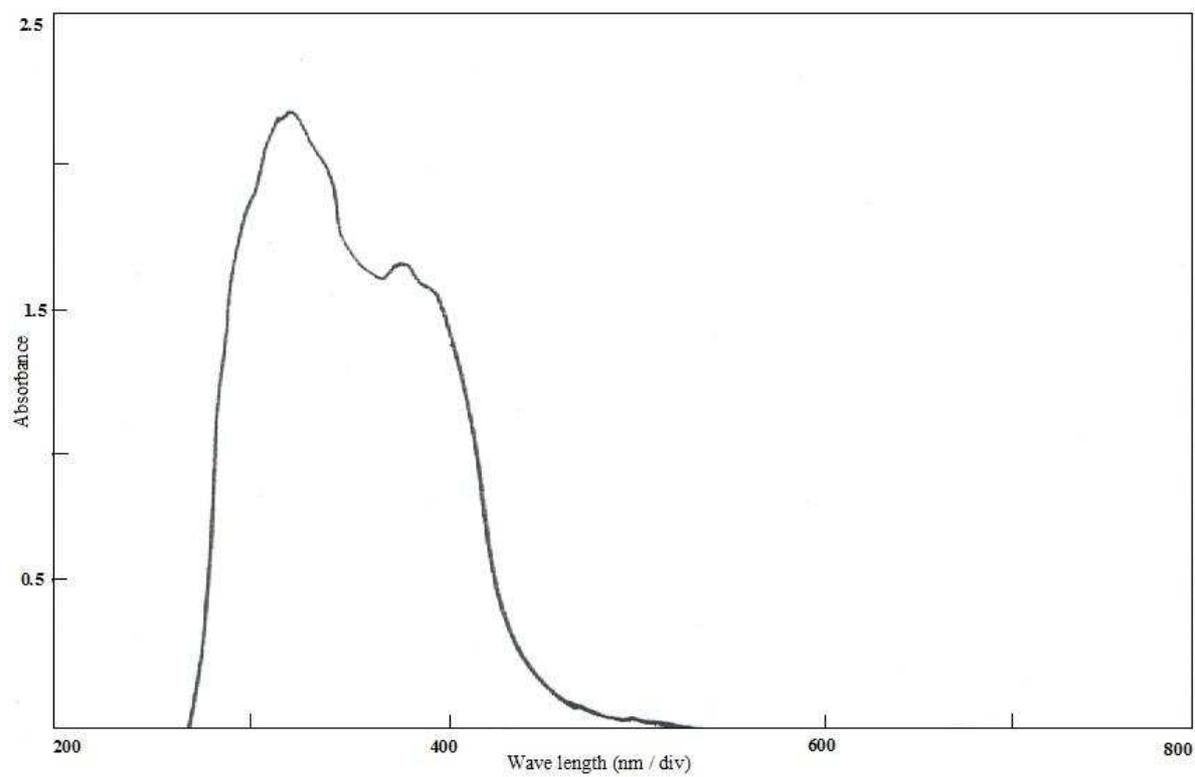
Inspection of the electronic spectrum of $\text{Fe}(\text{II})\text{-RSH}$ complex (Figure 3) indicates that the complex exhibits intense charge transfer bands in the region $25000\text{--}30000\text{ cm}^{-1}$ due to $\pi\text{--}\pi^*$ transition. Since the d-d transitions were obscured by intense charge transfer bands, the corresponding bands in the lower energy region were not observed.

The complex was found to be paramagnetic with a μ_{eff} value of 5.10 BM at room temperature and was in good agreement with the reported value for high spin tetrahedral and octahedral iron complexes [19].

The electronic spectrum of $\text{Fe}(\text{III})\text{-RSH}$ complex (Figure 4) was almost similar to that of $\text{Fe}(\text{II})\text{-RSH}$ complex. The weak d-d transition bands were masked by the intense charge transfer bands and were observed in the high energy region of the spectrum. The observed μ_{eff} value of 5.76 BM was in good agreement with that reported for high spin complexes of iron [19].

TABLE 3. Electronic spectral data of iron complexes

Complex	$\nu\text{ (cm}^{-1}\text{)}$	ϵ
$\text{Fe}(\text{II})\text{-RSH}$	32680	14995
	31546	
	27397	
$\text{Fe}(\text{III})\text{-RSH}$	31546	17110
	30769	
	28985	
	27472	
	25907	

Figure 3. Electronic spectrum of [Fe(RSH).2H₂O]Figure 4. Electronic spectrum of [Fe(RSH).2H₂O] Cl.

3.5. ^1H NMR spectral studies

The ^1H NMR spectra of ligand and its complexes recorded in DMSO-d_6 using TMS as an internal standard are shown in the Figures 5A-5C and the data is given in the Table 4.

TABLE 4. ^1H NMR spectral data (δ ppm) for iron complexes

Compound	$-\text{CH}_3$	Aromatic proton signals	N-H signal	Phenolic proton signals
RSH	3.417	6.285 6.300 6.990 7.100 7.430 7.920	11.120	9.939 10.588 10.676
Fe(II)-RSH complex	3.417	6.289 6.350 7.017 7.200 7.460 7.950	11.416	9.943
Fe(III)-RSH complex	3.442	6.237 6.347 6.980 7.400 7.627 7.949	11.406	9.939

The ^1H NMR spectra of the ligand contains a signal at $\delta 3.4$ ppm due to $-\text{CH}_3$ protons. The signal due to

amide $-\text{NH}$ group ($-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-$) appears at $\delta 11.12$ ppm. Signals corresponding to the aromatic protons were observed at $\delta 6.285$, 6.300 , 6.990 , 7.100 , 7.430 and 7.920 ppm. The signals corresponding to the three phenolic $-\text{OH}$ groups present in the ligand were observed at $\delta 9.939$, 10.588 and 10.676 ppm. The nonexistence of two phenolic $-\text{OH}$ proton signals at $\delta 10.588$ and 10.676 ppm in the ^1H NMR spectra of Fe(II)-RSH and Fe(III)-RSH complexes infers the involvement of these two deprotonated phenolic $-\text{OH}$ groups in the complex formation [20]. The presence of signal at $\delta 9.939$ ppm in the spectra of these complexes indicates the presence of free phenolic group. The down

field shift of $-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-$ proton around $\delta 11.4$ ppm in the spectra of the complexes as compared to that of ligand ($\delta 11.1$ ppm) may be attributed to (a) the coordination of

amide ($-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-$) nitrogen with the metal and (b) a probable existence of hydrogen bonding between oxygen atom of the amide carbonyl and hydrogen atom of the amid $-\text{NH}$ group

$\begin{array}{c} \text{O} \cdots \text{H} \\ \parallel \quad | \\ -\text{C} - \text{N} = \text{C} < \end{array}$. The isotopic shifts observed for the aromatic protons in the spectra of complexes indicate the presence of high spin ferrous and ferric ion with short electron spin-lattice relaxation times [21]. The signals corresponding to $-\text{CH}_3$ protons at $\delta 3.4$ ppm observed in the spectrum of the ligand are not displaced in the spectra of the complexes.

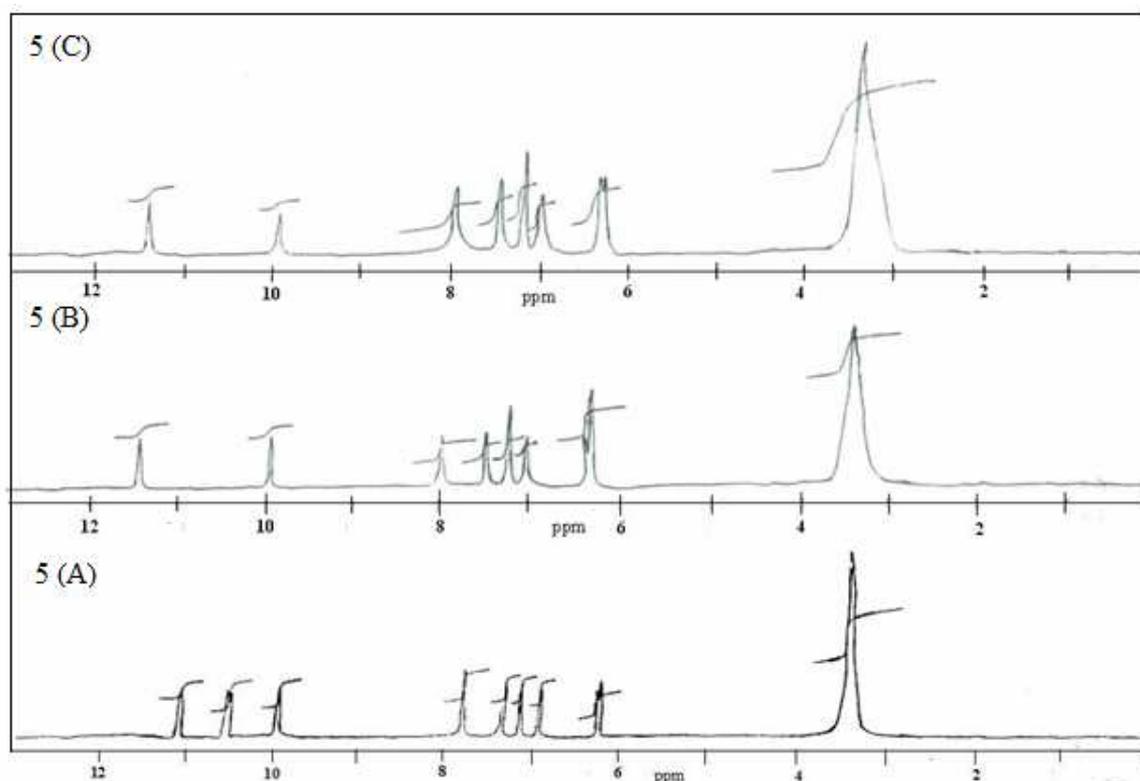


Figure 5 (A), (B) and (C): ^1H NMR spectrum of RSH, $[\text{Fe}(\text{RSH})_2 \cdot 2\text{H}_2\text{O}]$ and $[\text{Fe}(\text{RSH})_2 \cdot 2\text{H}_2\text{O}] \text{Cl}$.

3.6. Infrared spectral studies

The IR spectra of ligand and complexes are shown in the Figures 6-8 and the data is shown in the Table 5.

TABLE 5. IR spectral data (cm^{-1}) for iron complexes

RSH	Fe(II)-RSH complex	Fe(III)-RSH complex	Assignment
3577, 3320	3365	3365	$\nu_{\text{O-H}}$
3260	3215	3235	$\nu_{\text{N-H}}$
1610	1608	1605	$\nu_{\text{C=O}}$
1707	1656	1653	$\nu_{\text{C=N}}$
1101	1140	1149	$\nu_{\text{N-N}}$
----	503	513	$\nu_{\text{M-O}}$
----	421	422	$\nu_{\text{M-N}}$

The IR spectrum of the ligand in the solid state contains weak to medium intensity bands between $3577\text{-}3320\text{ cm}^{-1}$. These bands were attributed to the stretching vibrations of hydrogen bond. The band at around 1707 cm^{-1} was due to the coupled vibrations $\nu(\text{C=N})$ and $\nu(\text{C=C})$ modes. The bands at 3260 and 1610 cm^{-1} were attributed to the $\nu(\text{N-H})$

and hydrogen bonded amide carbonyl group ($\text{---}\overset{\text{O}}{\parallel}{\text{C}}\text{---}\overset{\text{H}}{\text{N}}\text{---}$) respectively. The band corresponding to the phenolic $\nu(\text{C-O})$ group was observed at 1240 cm^{-1} . The band at 1100 cm^{-1} was attributed to $\nu(\text{N-N})$ vibrational modes.

IR spectra of complexes indicated that the ligand acts as bidentate ligand and coordinates through azomethine

nitrogen ($>\text{C=N-}$) and amide nitrogen ($\text{---}\overset{\text{O}}{\parallel}{\text{C}}\text{---}\overset{\text{H}}{\text{N}}\text{---}$). The mode of complexation is supported by following evidences.

- A shift of $\nu(\text{C=N})$ to lower side [22] by about 50 cm^{-1} .
- A shift of $\nu(\text{N-H})$ to lower side [22] by about 35 cm^{-1} .
- A shift of $\nu(\text{N-N})$ to the higher side [23] by about 45 cm^{-1} .
- The appearance of new bands in the range $490\text{-}510\text{ cm}^{-1}$ and $420\text{-}422\text{ cm}^{-1}$ were assigned to $\nu(\text{Fe-O})$ [24] and $\nu(\text{Fe-N})$ [25] respectively.

A broad absorption band in region $3000\text{-}3500\text{ cm}^{-1}$ noticed in the spectra of complexes was ascribed to the presence of free phenolic -OH group. However, ^1H NMR spectra of the complexes indicate that two other phenolic -OH groups were involved in the complex formation. This fact cannot be exactly known from IR spectrum of the complexes.

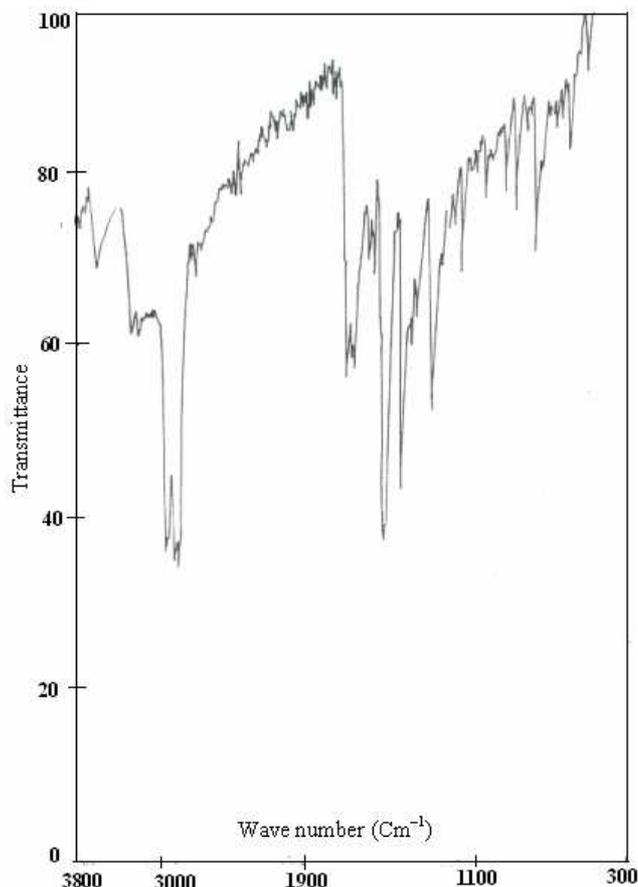
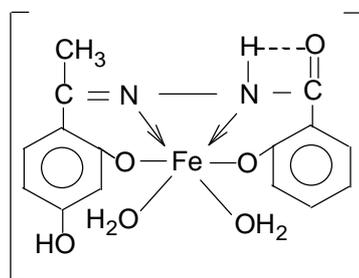
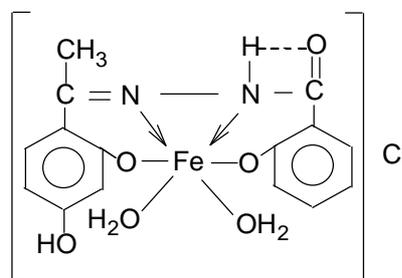


Figure 6. IR spectrum of RSH

Based on the above discussion, following structure was proposed for the complexes.



Fe(II)-RSH complex



Fe(III)-RSH complex

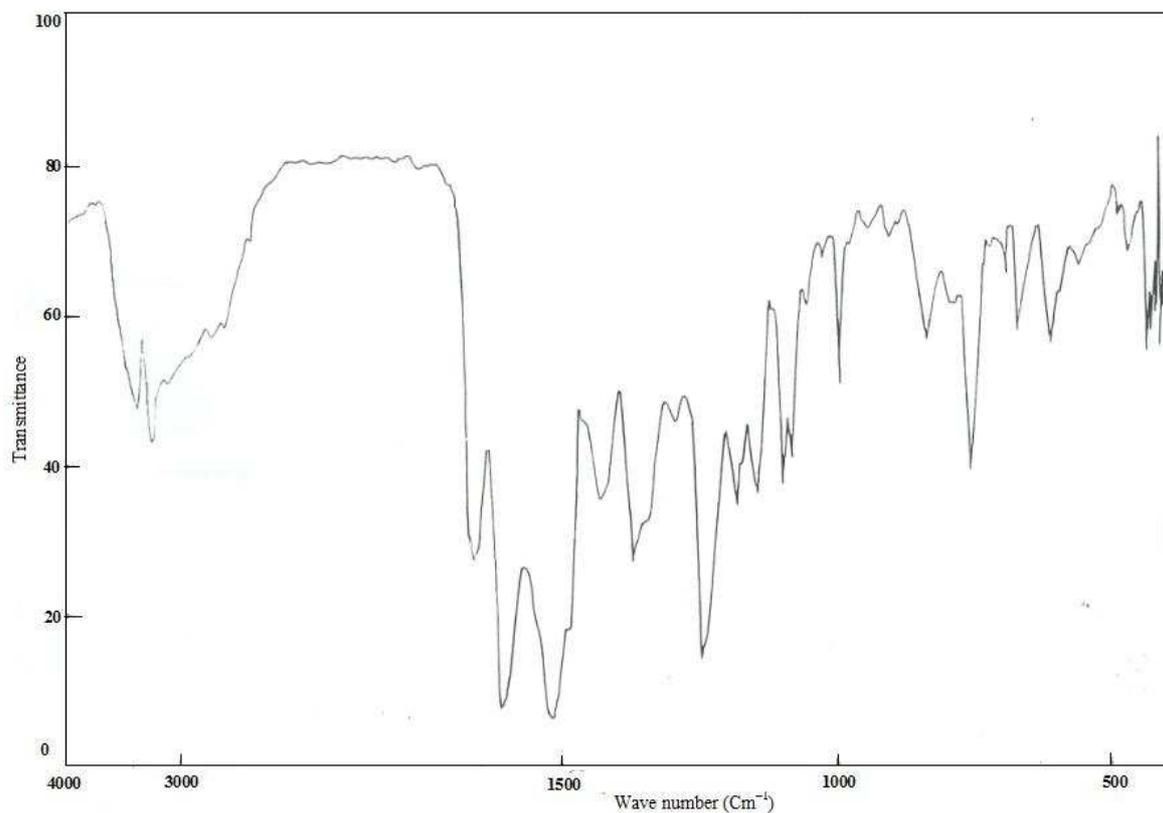


Figure 7. IR spectrum of [Fe(RSH).2H₂O]

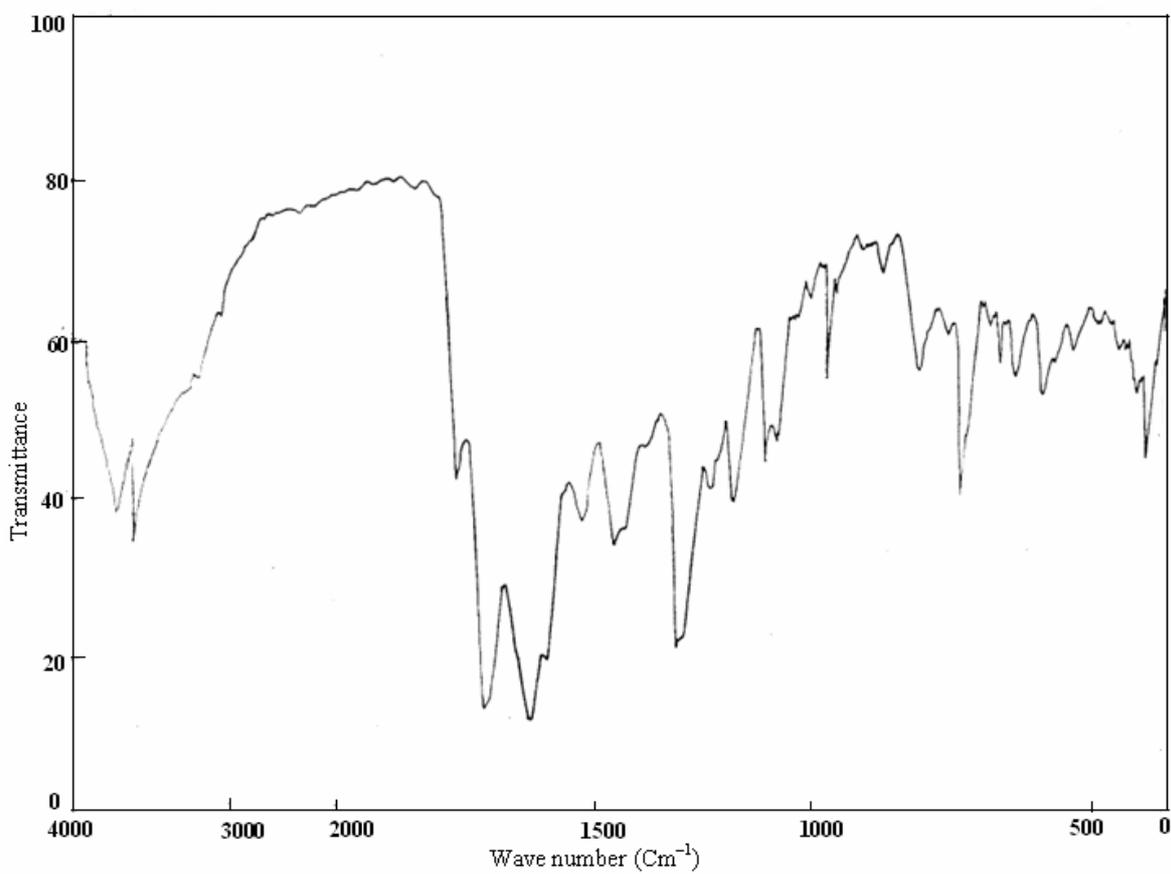


Figure 8. IR spectrum of [Fe(RSH).2H₂O] Cl.

4. Conclusion

RSH and its Fe(II) and Fe(III) complexes were prepared and characterized using elemental analysis, ¹H NMR, IR and electronic spectra. Studies confirmed that the ligand was coordinated to the metal ion through azomethine nitrogen and amide nitrogen. Molar conductivity values of the complexes indicated that these complexes were non electrolytes. Thermal analysis studies indicated that the Fe(II)-RSH complex was thermally more stable than the corresponding complex of Fe(III). Based on the data obtained, the stoichiometry and the tentative structure for Fe(II)-RSH and Fe(III)-RSH complexes were proposed.

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