IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)
An International Open Access, Peer-reviewed, Refereed Journal

Synthesis and Characterisation of Iron(III) complex of N-Salicylidine-L-amino acid of type Fe(N-Sal-L-aa)Cl

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Abstract : The aim of the present work is to study about the Iron (III) complex of N-Salicylidine-L-amino acid of type Fe (Sal-L-aa) Cl. Where Sal= Salicyldehyde and aa=amino acid. Here amino acids used are alaline, valine and histidine. Here, the complex was synthesised and tried to characterise the prepared complex through spectroscopic techniques (Electronic and IR). It was also tried to observe the change of absorption with change of pH of the complex in aqueous solution. It has been observed that the iron tyrosinate protein shows various spectral properties. The optical spectra of the complexes are largely determined by transitions originating in the iron Salicyladiminate Chromophore. For this complex, Iron (III) charge transfer transitions are common spectral features.

Keywords: Schiff base, Salicyldehyde, Valanine, Histidine, Tyrosinate protein, Electronic spectra, Infrared spectra.

I. INTRODUCTION

Schiff bases are N-arylimides,

AR. N=CR2

Prepared by reaction of aromatic amides with aliphatic or aromatic aldehydes and ketones. They are crystalline, weakly basic compounds which give hydrochlorides in non-aqueous solvents. With dilute aqueous acids the parent amides and carbonyl compounds are regenerated. Reduction with sodium and alcohol gives a secondary base. They are hydrolysed by water and strong acids to form carbonyl compounds and amides. They are very useful when they form complex with metal atoms. Recent study has showed that they can form complexes with almost all transition metals. They can be used as chemical intermediates, perfume bases, used in dyes and in liquid crystals for electronics. Metals play an important range of functions in biology. The chemistry of metal complexes with multidentate ligands having delocalized π-orbitals like Schiff bases or porphyrins has recently gained much attention because of their use as models of biological systems, such as some respiratory pigments or the coenzyme of vitamin B12. One of the major roles played by metallic elements in biochemistry is in metalloenzymes, which may be considered as a subclass of the metalloproteins [1]. This includes not only enzymes but respiratory proteins like haemoglobin and myoglobin, electron transport proteins such as cytochromes and ferredoxins and metal storage proteins.

The Schiff bases constitute a series of molecules, some of which can be used to study the biological facts and the mode of action of some biomolecules.

Metal complexes of bases represent an important and interesting class of co-ordination compound. The participation of metal ions in many of the bond-forming and bond—breaking enzymatic processes of biochemistry makes it clear that individual chemical bonds in organic molecules are strengthened and at other times weakened, through coordination of the molecules with metal ions [2].

In this work, iron (III) tyrosinate [3] models are considered. The iron tyrosinate proteins are a heterogeneous group of non-heme iron proteins including the transferrins, the catechol dioxygenases [4].

Many Schiff's base complexes of iron (III) have been prepared. Among which a series of iron (III) complexes of the imines of L-amino acids derived from salicylaldehyde, Fe (Sal-L-aa) Cl (aa=ala, val, phe) also recognized as Tyrosinate Models [5-6] of iron, have been characterized by various spectroscopic techniques such as IR and electronic spectroscopy

Moreover the complexes are high spin and have five or six coordinate structures. They generally exist in solution as equilibrium mixtures of monomeric and dimeric forms, the ratio of which depends upon the solvent and the presence of externally added ligands.

The spectral features of the iron complexes have been discussed in relation to those of the iron tyrosinate proteins. These proteins display, as common spectral features a moderately intense absorption band in the range 400-600 nm that originates from a tyrosinate to iron (III) charge transfer transition. The position and intensity of this band are sensitive to the ligand environment of iron (III).

To isolate the complex in dried form, a sluggish isolation procedure is required because some inherent difficulty arises in crystallizing in the reaction medium.

Infrared spectral analysis indicates band at 3300-3400 cm-1, which confirms the presence of some water in the complexes. Also, elemental analysis shows that some water is retained by the complexes in the solid state. An assignment of low energy phenolate to iron (III) LMCT bands has been made possible by the analysis of the electronic spectra of the complexes. For this complexes iron (III) charge transfer transitions are common spectral feature. The proposed structures1 for the complexes are-

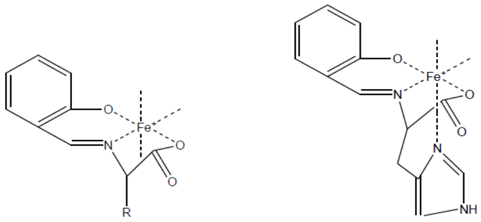


Fig (a) Fig (b)

Fig (a) and Fig (b) are proposed structure for Fe (III) (Sal-ala), Fe(III) (Sal-val) and Fe(III) (Sal-his) respectively.

II. THEORY

SYNTHESIS OF THE COMPLEXES

The complexes Fe (Sal-L-ala) and Fe (Sal-L-val) Cl were prepared according to the following procedure. Salicylaldehyde (5m mol) and alanine or valine were refluxed in ethanol-water (50ml, 9:1v/v) for 30 minutes. To the cooled yellow solution, solid $FeCl_3.6H_2O$ (5m mol) was added with stirring, followed by addition of methanolic~1.0 N Sodium hydroxide (10 m mol). The dark brownish solution was stirred for 6-7 hours at room temperature and then evaporated to dryness under vacuum. The solid residue was treated several times with small volumes of 1:1 ethanol-tolune mixture and evaporated to dryness in order to eliminate water as much as possible. The solid residue was finally treated with toluene-ethanol (100ml, 4:1v/$_v$) and filtered to remove sodium chloride. The filtrate was concentrated and the product was formed as violet solids on dropwise addition of hexane.

The complex Fe (Sal-L-his) Cl is obtained similarly except that the ligand solutions were prepared only by warming. For this complex final addition of hexane was not necessary.

The complex Fe III (Sal-L-aa) Synthesized was confirmed by estimating the metal quantitatively.

Theory of estimation of the metal (Fe):

The amount of metal present in the various complexes of type Fe (Sal-L-aa) Cl (aa=ala, val, his) were determined chemically. Here, the prepared complexes are given below with their formula.

Compound	Formula
Fe (Sal-L-ala) $Cl.H_2O$	$FeC_{10}H_9NO_3Cl.H_2O$
Fe (Sal-L-val) $Cl.H_2O$	$FeC_{12}H_{13}NO_3Cl.H_2O$
Fe (Sal-L-his) $Cl.H_2O$	$FeC_{13}H_{11}N_3O_3Cl.H_2O$

Where, Sal – aa = N – Salicylideneamino acidato dianion;
ala = condensed alaninate anion; val = condensed valinate anion;
his = condensed histidinate anion.
The theory of the estimation of the metal Fe (III) in the complex is given below:

In acidic solution, ferric ion is quantitatively reduced to ferrous ion with the help of $sncl_2$ solution.

$$2Fe^{3+} + SnCl_2 + 2Cl^- \longrightarrow 2Fe^{2+} + SnCl_4$$

The excess of $SnCl_2$ solution is destroyed by addition of $HgCl_2$ solution.

$$SnCl_2 + 2HgCl_2 \longrightarrow Hg_2Cl_2\downarrow + Sn^{4+} + 4Cl^-$$

The resultant solution contains all the iron as ferrous which is made to react with $K_2Cr_2O_7$ according to the following reaction.

$$Cr_2O_7^{2-} + 14H^+ + Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Preparation of solutions:

(i) A known amount of the complex was dissolved in 50ml. of H_2O.
Initially a few drops of conc. H_2SO_4 is used for the complete breakdown of the complex.
(ii) 0.1 N solution of $k_2Cr_2O_7$ was prepared by dissolving 1.2258g of $k_2Cr_2O_7$ in 250ml of distilled water.

III. Procedure:

10 ml of the test solution is taken in a 500 ml beaker. To the solution, about 10 ml of conc. HCI is added and heated upto 80^{o}C. $SnCI_2$ Solution is added drop wise from a burette till the solution become colourless. The solution is then diluted to 200 ml with distilled water. 5ml of $HgCl_2$ is added followed by addition of about 10 ml of conc. Sulphuric acid -phosphoric acid mixture. Now the titration is performed with constant stiring using diphenylamine as indicator. Appearance of purple colour throughout the solution indicates the end point.

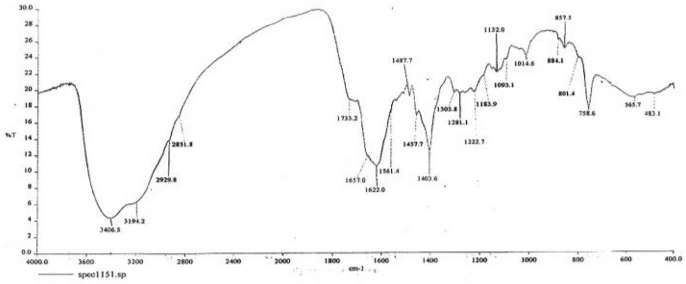
The amount of iron is calculated from the following relationship-

$$1ml\ 0.1N\ K_2Cr_2O_7 = 0.005585g.\ of\ Fe$$

IV. PRESULTS AND DISCUSSION

Spectral analysis of the complex :

IR SPECTRA:- I.R. spectra of the complex, Fe^{III} (Sal-L-ala) $CI.H_2O$ was recorded in KBr. The imine structure of the ligand is indicated by intense and well-resolved v (C = N) bands at 1622 $cm^{—}$ in I.R. spectra. The band observed at 3406.5 $cm^{—1}$ is due to v (OH) indicating that some water is retained by the complex in solid state. The band at 1733.2 is due to v (C = O) stretching. The band at 1303.8 is due to v (C – O) stretching. The IR Spectra is shown in Fig. 1.



I. I.R. spectra of Fe(III) (Sal–L–ala)cl.

Electronic spectra of the complexes:

The electronic spectra of the Fe (Sal-L-aa) CI complexes display several bands in the near-uv and visible regins. The absorption maximum in methanol or aquous solution occurs near 230, 260, 295 and 320 nm. and in the range 490 – 540 nm. The visible band is responsible for the purple colour of these complexes.

The spectra show solvent dependence. This is partly due to solvent coordination to iron (III) but is also due to a different degree of association of the complexes in various solvents.

The electronic bands near 230 and 260 nm are due to the benzenoid $\pi \longrightarrow \pi^*$ transition of the salicylaldimine residue.

The other bands near 295, 320 and 420 nm and in the range 490 – 540 nm must be LMCT in origin, since their intensity is too hihg for ligand field transitions of high – spin Fe (III) complexes [4-5]. The visible band and the near 320 m have been assigned to charge – transfer transitions from phenolate to iron (III). Spectrum of the various complexes was recorded using distilled water as reference and methanol and aquous methanol as solvents.

Electronic spectra of Fe (III) (Sal-L-ala) Cl. (Fig.2)

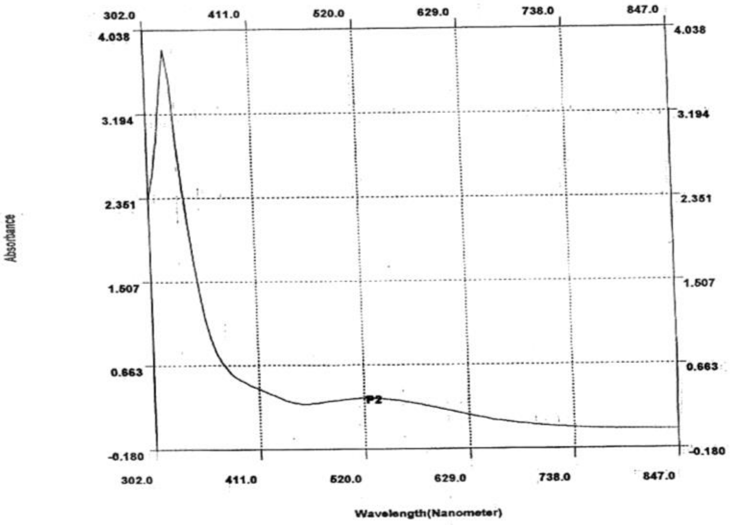
SL. No.	Wave length (In nanometer) nm	Absorbance
1.	320.9	3.912
2.	534.2	0.526

Electronic spectra of Fe (III) (sal-L-vla) Cl. (Fig.3)

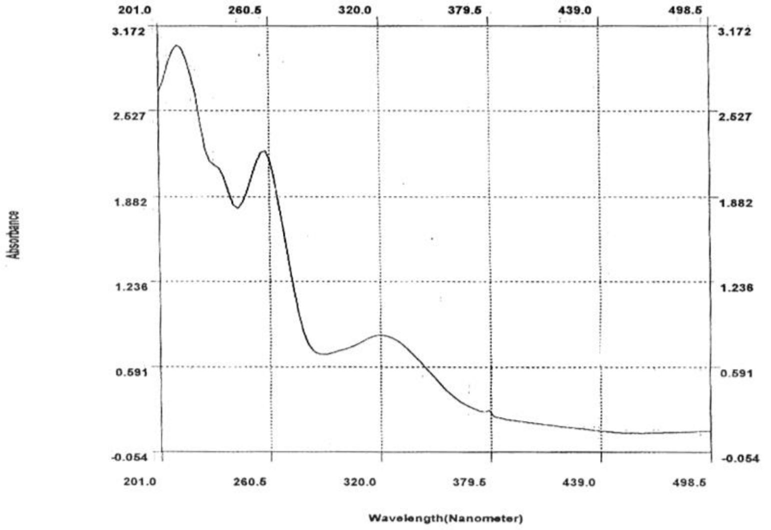
SL. No.	Wave length (in nm)	Absorbance
1.	230.6	2.326
2.	260.3	1.691
3.	295.8	0.885
4.	319	0.83
5.	522.2	0.11

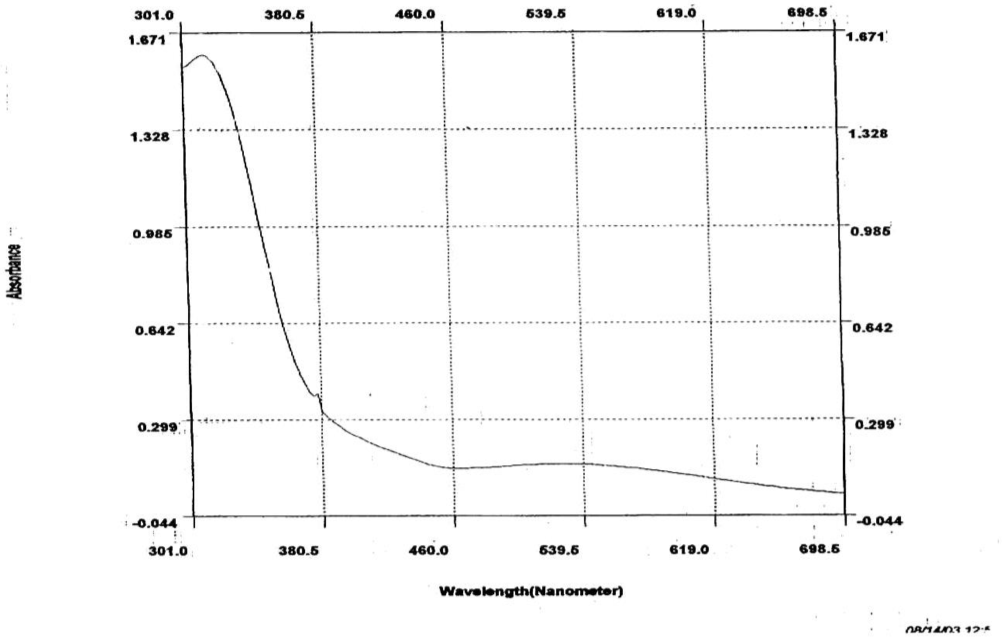
Electronic spectra of Fe (III) (sal-L-his) Cl. (Fig.4)

SL. No.	Wave length (in nanometer)	Absorbance
1.	314.1	1.594
2.	539.3	0.134



2. Electronic spectra of Fe(III) (Sal–L–ala) cl.





4. Electronic spectra of Fe(III) (Sal–L–his) cl.

Estimation of central metal :

Estimation of the metal (Fe) in the complexes are found to be –

Table

Compound	**Theoretical Amount**	**Amount found**	**Error**
Fe (Sal-L-ala) Cl.H_2O	18.59%	18.5%	0.484%
Fe (Sal-L-vla) Cl.H_2O	17%	16.93%	0.411%
Fe (Sal-L-his) Cl.H_2O	15.24%	15.18%	0.394%

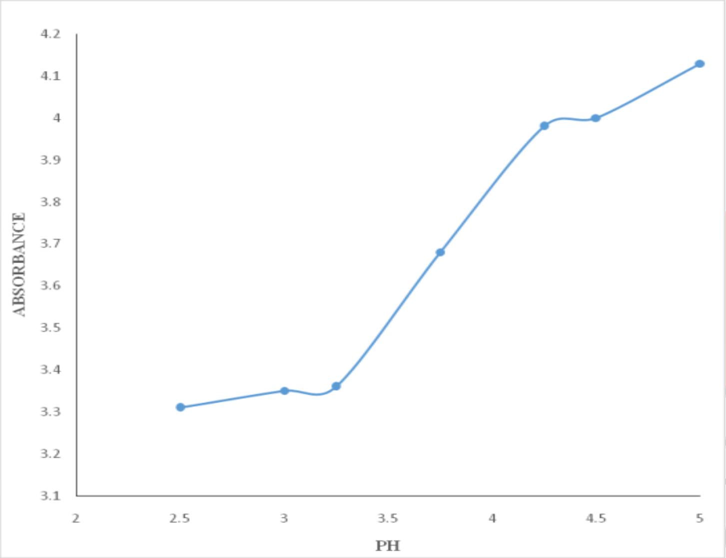
The amount of iron estimated from the compound is in good agreement with those of the theoretical values.

Spectrophotometric determination of acid-base Equlibiria of Fe^{III} (Sal-L-ala) $(H_2O)^+$ in water

The electronic spectra of aquous solution of the complex Fe (III) (Sal-L-ala) Cl is p^H dependent. λ_{max} varies in the variation of p^H. λ_{max} increases when the p^H of the solution increases and vice-versa. The complex is soluble in water and dissociated as-

$$\text{Fe (III) (Sal-L-ala) Cl} + H_2O \leftrightharpoons \text{Fe (III) (Sal-L-ala)} (H_2O)^+ + Cl^-$$

The absorption band at 320 nm as a function of p^H. The variation of absorbance with increasing p^H can be recorded spectrophotometrically and the S – shaped curve is obtained. (Fig.5).



5. Variation of absorbance with P^H

V. Conclusion

An important feature of model studies of these and other iron (III) salicylaldiminate complex is the sensitivity of the phenolate to iron (III) charge transfer band to the ligand environment of the metal center. The complex Fe (III) (Sal-L-aa) Cl was synthesized and studied which is described in the previous chapters. In un-visible spectra a LMCT band is observed in the visible region 490 – 540 nm, which is the main characteristic of this complex. The electronic spectra is p^H dependent. When p^H increases λ_{max} also increases. Here it is confirmed from the spectroscopic data.

In the iron (III) chelates of type described earlier in Fig a, the ligands provide three equatorial donor atoms, while in histidine complex (Fig b), an additional donor group can bind to the iron (III) center in an axial position [4]. It is assumed that the chloride ions are coordinated in solid state, the iron (III) centers can achieve five or six-coordinate structures by binding to polar groups of neighbouring molecules.

The infrared and electronic spectral analysis of these prepared complexes are found to be good aggrement with the literature.

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