

Preparation and Spectral Studies of Cr(III), Fe(II) Chelates of Schiff bases Derived from Benzidine and 2-Nitrobenzaldehyde

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Abstract

In this paper, we report the synthesis and characterisation of Bis(2-nitrobenzylidene)benzidine Schiff base was prepared by the reaction of benzidine and 2-nitrobenzaldehyde 1:2 reaction. This ligand was used to form two chelates with Cr^{3+} and Fe^{2+} ions. The prepared compounds were analysed using elemental analysis, IR spectroscopy, 1H -NMR and mass spectroscopy. The obtained results confirmed the formation of proposed compounds, including the free ligand and the two chelates and were found in a good agreement with theoretical values.

Keywords: Schiff base; complexes; spectroscopy; 2-Nitrobenzaldehyde.

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I. Introduction

Many variously shaped polydentate chelating ligands have been prepared in the past and successfully used in the selective coordination of metal ions. The preparative work of Jorgenson, Werner and many others during the turn of the century opened up new vistas in the coordination chemistry of transition metals. It was Alfred Werner who systematised the subject coordination chemistry, by propounding theory in 1893, for which he awarded Nobel Prize in 1913. These ideas have considerably enriched the understanding of the nature of metal-ligand bonds, structure, and chemistry of metal complexes, their stabilities and liabilities and other properties. It is now the need of time that new ligands of detailed design should be synthesised, which could lead to metal complexes with select desired and possible predictable properties. The steady improvement in synthetic methodology allows us to foresee coordinating chemistry entering a phase of creative chemistry [1]. Schiff base complexes with transition metal have played a central role in the development of coordination chemistry. Because Schiff base ligands are capable of forming stable complexes with metal ions. Metal complexes play an important role in agriculture, pharmaceutical and industrial chemistry [2]. It is well known that azomethine of the general formula ($-C=N-$) has great attention as a precursor in huge organic synthesis and biological applications such as cycloaddition reaction, [3] optoelectronic properties [4], dyes and pharmaceuticals, antimicrobial activity [5], liquid membrane technology [6], anti-inflammatory [7], anticonvulsant [8], anti-tumour, antihypertensive activity [9] and anti-HIV activities [10].

Moreover the reactions of azomethine throughout ring-closing to generation a wide range of five, six and seven members ring of heterocyclic organic molecules such as 4-thiazolidinone derivatives [11], 1,2-Dihydro-1-arylnaphtho[1,2-e] [1,3] oxazine-3-one derivatives [6,12,13] and 1,3-oxazepinediones [14]. All of these derivatives of heterocyclic compounds have importance as pharmaceutical drugs, active substances in biological systems [15-17] and liquid-crystalline compounds. Therefore the synthesis of these kinds of organic compounds has become our impressive.

Benzidine (4,4'-diaminobiphenyl), another names for benzidine are [1,1'-Biphenyl]-4,4'-diamine, 4,4'-diamino-biphenyl, 4,4'-bianiline, 4,4'-diphenyldi-amine. It is a greyish-red, yellowish, or white-coloured, very toxic, crystalline aromatic amine that darkens when exposed to air and light. Benzidine has been widely used for the detection of blood and

a reagent in the manufacture of dyes. Ingestion of benzidine causes cyanosis, headache, mental confusion, nausea and vomiting. Its use is now limited because of the strong association between exposure to benzidine and an increased risk of bladder cancer in humans [18]. The chemical or enzymatic oxidation of benzidine proceeds via a radical cation detectable by electron spin resonance. Peroxidase-catalyzed oxidation of benzidine generates reactive electrophiles which readily form adducts with phenol and thiol compounds. The structures of these novel metabolites are described. Peroxidases, including prostaglandin synthetases, catalyse benzidine binding to protein and nucleic acid; the nature of the resulting adducts is unknown. The relevance of these processes to benzidine carcinogenesis in vivo is the subject of research and debate [19].

Benzidine is prepared in a two-step process from nitrobenzene. First, the nitrobenzene is converted to 1,2-diphenylhydrazine, usually using iron powder as the reducing agent. Treatment of this hydrazine with mineral acids induces a rearrangement reaction to 4, 4'-benzidine. Smaller amounts of other isomers are also formed. The benzidine rearrangement, which proceeds intramolecularly, is a classic mechanistic puzzle in organic chemistry. Benzidine, the trivial name for 4,4'-diaminobiphenyl, is the solid organic compound with the formula (C₆H₄NH₂)₂. This aromatic amine is a component of a test for cyanide and also in the production of dyes. Benzidine has been linked to bladder and pancreatic cancer. Since August 2010 benzidine dyes are included in the EPA's List of Chemicals of Concern. Benzidine is no longer produced in the United States, although benzidine-based dyes may be imported into this country. No information is available on the acute (short-term) effects of benzidine in humans by inhalation exposure, but benzidine is considered to be very acutely toxic to humans by ingestion. Chronic (long-term) exposure to benzidine in humans may result in injury to the bladder. Epidemiological studies have shown occupational exposure to benzidine to result in an increased risk of bladder cancer. Animal studies have reported various tumour types at multiple sites from benzidine exposure via oral, inhalation, and injection exposure. EPA has classified benzidine as a Group A, known human carcinogen [20].

Benzidine derivatives have received increasing attention in recent years because of their applications in a wide variety of domains, for instance as building blocks in the construction of functionalised organic/organometallic materials and as sensor materials [21–23]. The chemical and physical properties of benzidine based compounds have enabled their use in cell biology as staining reagents [24]. Benzidine has been used since the 1850s as the reagent base for the production of a large number of dyes, particularly azo dyes for wool, cotton, and leather. However, because benzidine was found in the 1970s to be carcinogenic to humans, there has been a considerable decline in the use of the benzidine dyes. Benzidine is used for the quantitative determination of sulfuric acid and the detection and determination of numerous anions and metal ions. The reaction of benzidine with pyridine in the presence of elemental chlorine is suitable for detecting traces of free chlorine or pyridine in drinking-water. The green to blue colouration that occurs when benzidine reacts with hydrogen peroxide in the presence of peroxidases can be used to detect blood. Benzidine still plays a role in many chemical syntheses [25]. In the past, benzidine also has been used as a rubber compounding agent, in the manufacture of plastic films, for detection of hydrogen peroxide in milk, and the quantitative determination of nicotine. Most of these uses have been discontinued, although some dyes that may contain benzidine as an impurity are still used as stains for microscopy and similar laboratory applications [26].

2-nitrobenzaldehyde is a benzaldehyde with a nitro group substituted in the ortho position. It is a yellow crystalline powder. 2-nitrobenzaldehyde is used in the preparation of dyes and colourants such as Indigo carmine. 2-nitrobenzaldehyde has been shown to be a useful photo removable protecting group as well as in the preparation of more effective ones such as 2-nitrophenylethylene glycol.[27] The nitro derivatives of benzaldehyde are used as intermediates in the synthesis of fine chemicals. They are essential for the preparation of dyes, pesticides, non-linear optic materials and pharmaceutical drugs. [28]

The main routes to nitrobenzaldehyde begin with the nitration of styrene and cinnamic acid followed by the conversions of the resulting 2-nitrostyrene and 2-nitrocinnamic acids. Cinnamaldehyde can also be nitrated, e.g., in a solution of acetic anhydride in acetic acid, in high-yield to 2-nitrocinnamaldehyde. This compound is then oxidised to 2-nitrocinnamic acid, which is decarboxylated to the 2-nitrostyrene. The vinyl group can be oxidised in some different ways to yield 2-nitrobenzaldehyde.[29] In one synthetic process, toluene is mono-nitrated at cold temperatures to 2-nitrotoluene, with about 58% being converted to the ortho- isomer, the remaining forming meta- and para- isomers.[30] The 2-nitrotoluene can then be oxidised to yield 2-nitrobenzaldehyde.[31,32] The nitration of benzaldehyde produces mostly 3-nitrobenzaldehyde, with yields being about 19% for the ortho-, 72% for the meta- and 9% for the para isomer.[33,34] For this reason, the nitration of benzaldehyde to yield 2-nitrobenzaldehyde is not cost-effective.

In present work, The chelates of Cr(III) and Fe(II) ions with the Schiff bases derived from the condensation of 2-nitrobenzaldehyde and benzidine were synthesised and characterised by different techniques.

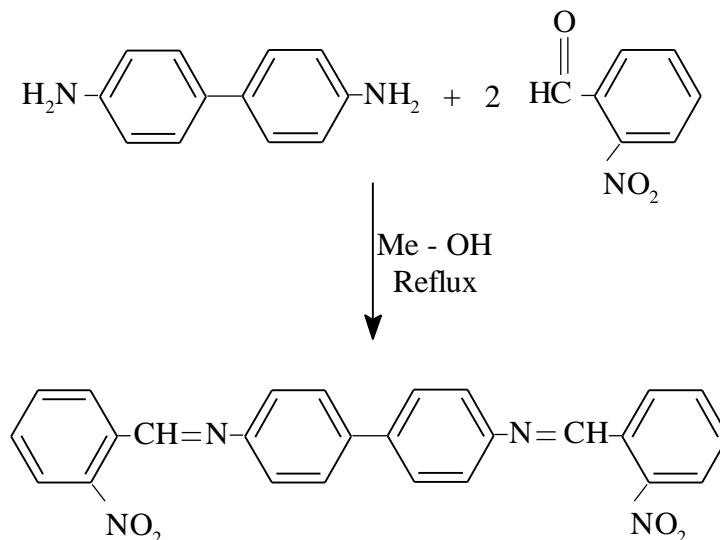
II. Materials and Methods

2.1 Materials

All chemicals and reagents used in this work were laboratory pure (BDH or Aldrich) and used without further purification, these include, benzidine, 2-nitrobenzaldehyde, Cr(NO₃)₃, FeCl₂, NaOH, CH₃OH, THF and distilled water. Melting points were determined on a Gallenkamp melting point apparatus. The ¹H NMR spectra were recorded on a Bruker Avance II 500 MHz Spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS). Infrared spectra were recorded as KBr pellets on a Shimadzu FTIR-408 spectrophotometer. All previous analysis was done at the micro-analytical centre, Cairo University, Giza, Egypt.

2.2 Preparation of Schiff Base

Schiff base under investigation was prepared by dissolved 0.01 mol; 1.842 g of Benzidine in 25ml methanol, 0.02 mol; 3.023g of 2-nitrobenzylidene was added to this solution with reflux for 2-3 h. The formed yellow precipitate was filtered, washed with hot methanol until the filtrate became clear and finally dried in excellent yield(87%) and M.P. 225-227 °C. The chemical reaction is represented in Scheme 1.



Scheme 1: Synthesis of Schiff base

2.3 Preparation of metal chelates

Bis(o-nitrobenzaldehyde) benzidine (2.25g; 0.005 mol) was dissolved in 25mL of THF solvent, and a solution of 0.01 mol of metal salt in methanol was slowly added to this solution. Few drops of sodium hydroxide solution were added slowly to adjust the pH value at 7.5, and the reaction mixture was refluxed at 60°C for 5–6 h. The coloured crystalline product obtained after filtration was washed with hot THF several times and finally with diethyl ether. Yield: 75%, 1.60 g.

III. Results and Discussion

3.1 Elemental Analysis

The prepared Schiff base compound and the mixed ligand metal chelates were subjected to several physiochemical techniques to establish the geometrical structures of the free Schiff base and the chelates. Physical properties of the Schiff base and its complexes were given in Table 1.

Table 1. Physical characteristics and the elemental analysis of the free Schiff base

Name of compound	N, N'-bis(2-nitrobenzaldehyde) benzidine		
Molecular formula	C ₂₆ H ₁₈ N ₄ O ₄		
Molecular weight	450.4		
Colour	Yellow		
M.P.	225-227 C ⁰		
Solubility	DMF, THF, hot CH ₃ OH		
Percentage composition (Calc.)	C%	H%	N%
	12.00 (12.43)	4.00 (4.03)	67.87 (69.31)

3.2 Infrared spectra of Schiff base and chelates

The infrared spectral data of the Schiff base and its chelates are listed in **table 2**, and their spectra are shown in **figures 1-3**. The IR spectra of the Schiff bases indicate the absence of the carbonyl group (1700cm⁻¹) band and the appearance of an influential band in the region (1620- 1635cm⁻¹) assignable to the ν (C=N) of the azomethine [35,36]. This stretching frequency at 1620 cm⁻¹ C=N bond in the ligand is shifted to 1635 cm⁻¹ and 1627 cm⁻¹ in Cr³⁺ and Fe²⁺ chelates, indicating coordination of azomethine group through nitrogen atom with a metal ion [37]. IR spectral data shows that the Schiff base is bidentate, and the binding sites are azomethine nitrogen and ν (-NO₂ Nitro group) (1342,1512 cm⁻¹) [38]. In the chelates, the shifting of this band to a higher

frequency compared with the free Schiff base suggesting coordination of metal ions through nitrogen atom of azomethine group and free nitro group. The presence of bands in the region $516-524\text{ cm}^{-1}$ due to the (M-N) [39,40]. The appearance of broad around $3390-3444\text{ cm}^{-1}$ in the spectra of chelate has been assigned to associated water molecules. A medium intensity band in the IR spectrum of the complex at 740 cm^{-1} is assignable to rocking mode due to coordinated water molecules [41].

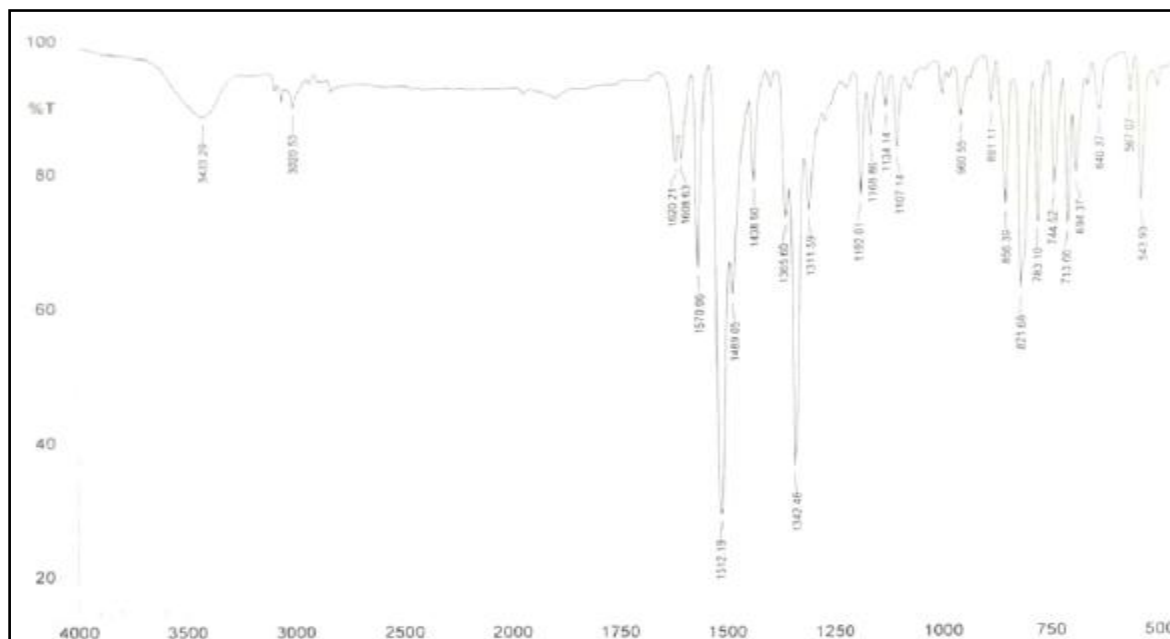


Fig.1: Infrared spectrum of Schiff base.

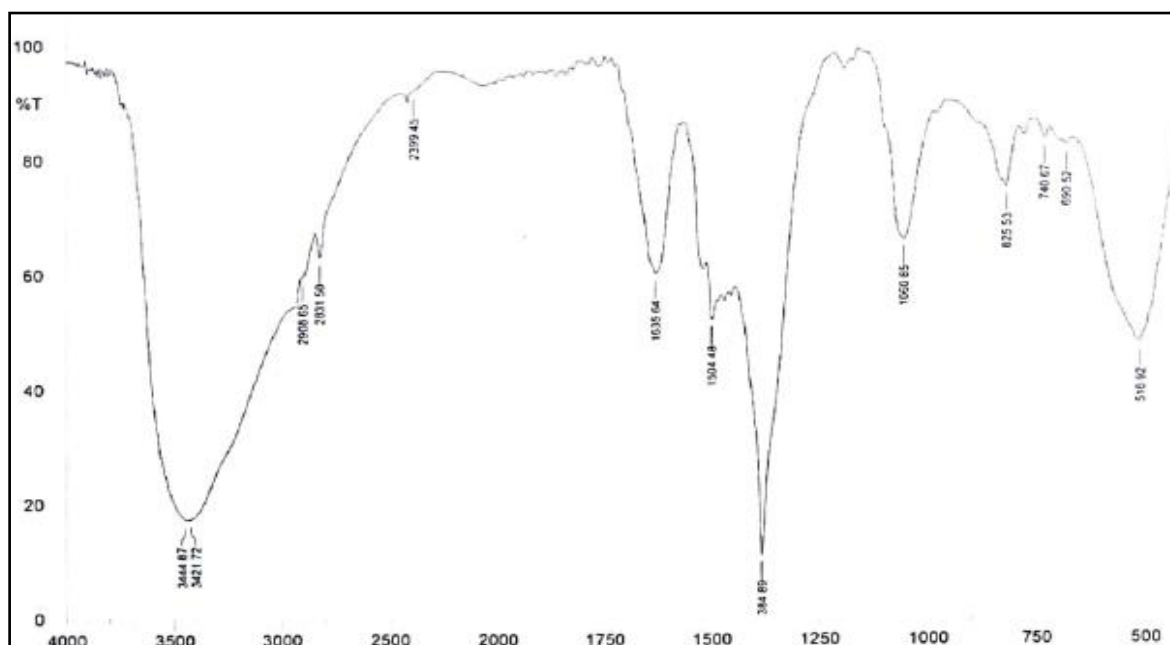


Fig.2: Infrared spectrum of Cr (III) chelate.

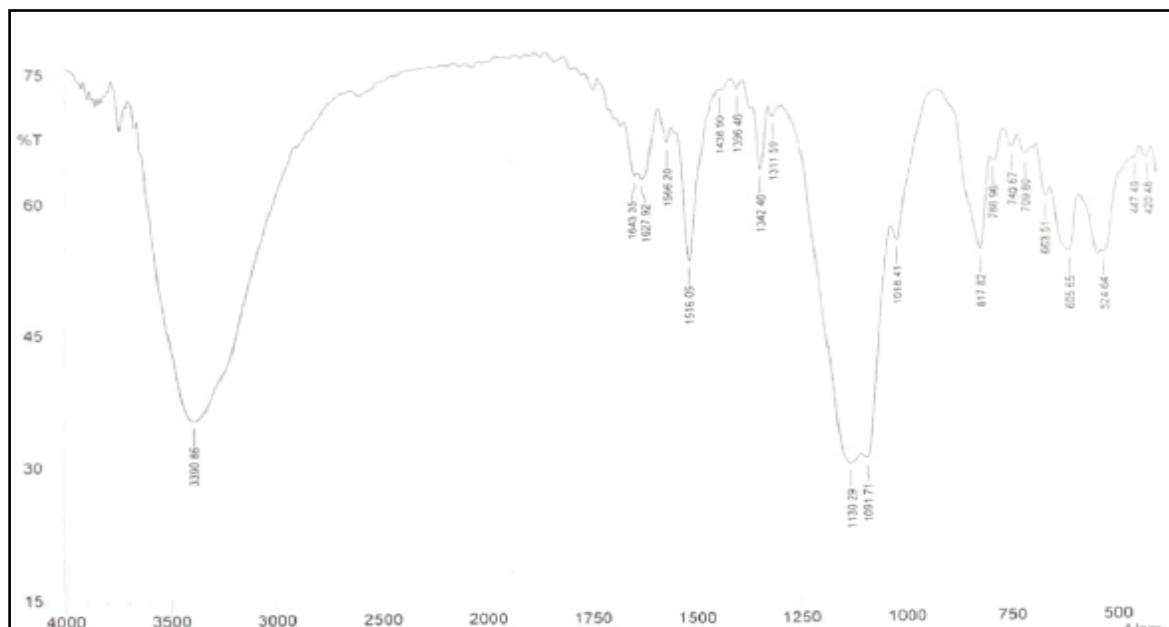


Fig3: Infrared spectrum of Fe(II) chelate.

Table 2. Infrared spectral data(cm^{-1}) of the Schiff base and its chelates

Schiff base / Chelates	IR bands cm^{-1}			
	γ (OH) Water	γ (HC=N)	γ (-NO ₂)	γ (M-N)
L(C ₂₆ H ₁₈ N ₄ O ₄)	3433	1620	1342,1512	-
[Cr ₂ L(H ₂ O) ₆ (NO ₃) ₂]	3444	1635	1384,1504	516
[Fe ₂ L(H ₂ O) ₄ (Cl) ₄]	3390	1627	1396,1516	524

3.3¹H-NMR and Massspectral studies

The ¹H-NMR main signals-chemical shifts of the investigated heterocyclic Schiff bases recorded in DMSO are given in figure 4. The DMSO solvent signal appears at 2.5 ppm. The aromatic region was a set of multiples in the range 7.3–7.9 ppm for the Schiff base ligand, while the azomethine protons were observed in the range 8.9 ppm. [42]

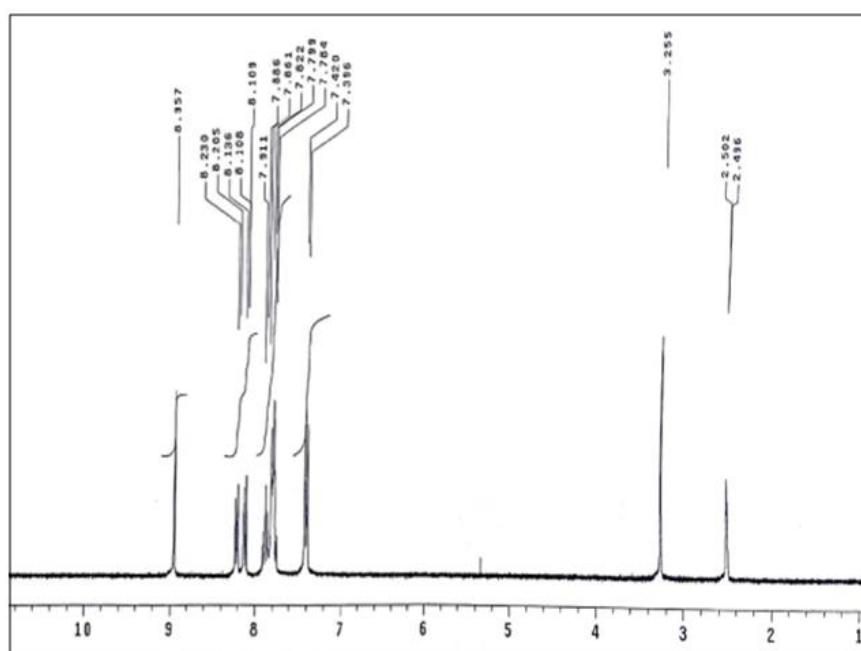


Fig. 4: ¹H-NMR spectrum of Schiff base

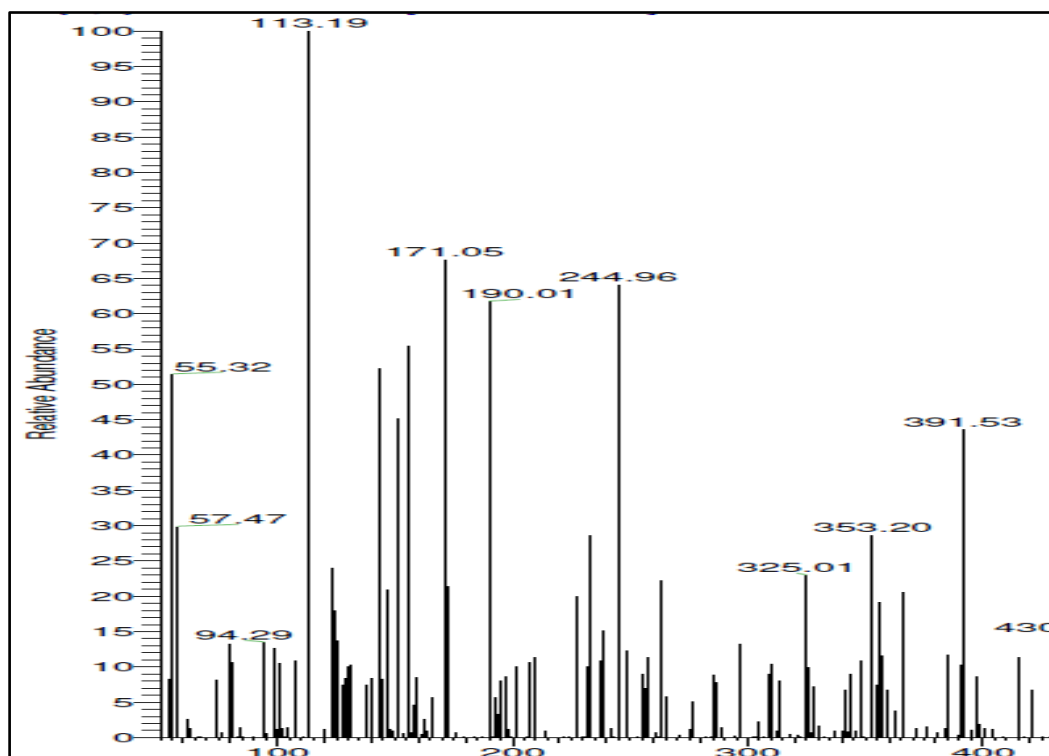


Fig. 5: Mass spectra of Schiff bases

The mass spectral pattern of a (Fig.5) shows a molecular ion peak (m/z 430, 15%) which loses water from the molecular weight of the Schiff base. From the analysis carried out on free ligand and compared with complexes, the proposed structures of complexes which confirmed by these analyses will be as follows as shown in Figure 6 & 7.

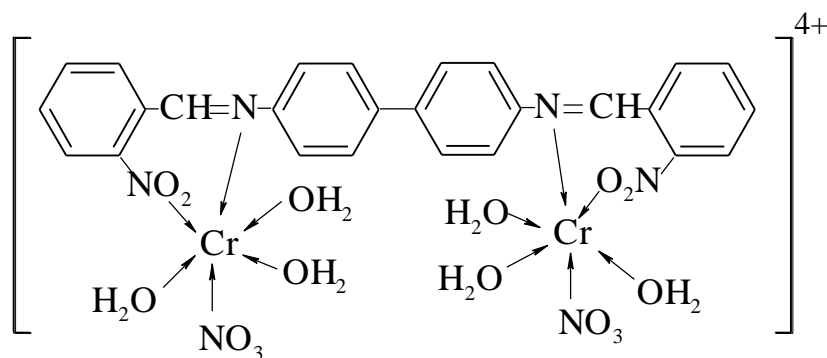


Fig. 6: Proposed Structure of $[Cr_2 L (H_2O)_6 (NO_3)_2]^{4+}$

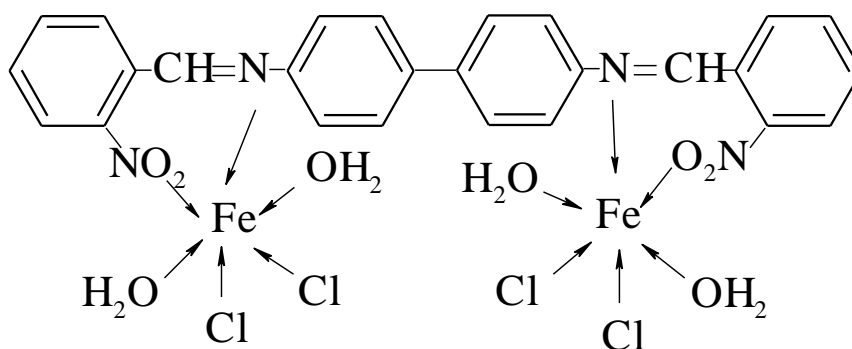


Fig. 7 Proposed Structure of $[Fe_2 L (H_2O)_4 (Cl)_4]$

IV. Conclusion

The Schiff base ligand in the present work was synthesised with good yield by convenient procedures. The results of the spectroscopy investigation support the suggested structure of the Schiff base ligand and Cr(III) and Fe(II) complexes. Formation of the azomethine group and the presence of a primary amine group were confirmed by IR, ¹H NMR and mass spectroscopy.

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