

Synthesis and Spectral Studies of Mixed Ligand Complexes of Trivalent Metal Ions

F. Y. Larial

Chemistry department, Faculty of Science, Benghazi University, Benghazi, Libya

M. M.El-ajaily (Corresponding Author)

Chemistry department, Faculty of Science, Benghazi University, Benghazi, Libya

Email: melajaily@gmail.com

N. M. El-Barasi

Chemistry department, Faculty of Science, Benghazi University-Tawkra branch, Benghazi, Libya

A. A. Maihub

Chemistry department, Faculty of Science, Tripoli University, Tripoli, Libya

R. K. Mohapatra

Department of Chemistry, C. V. Raman College of Engineering, Bhubaneswar, Odisha, India

T. H. Al-Noor

Chemistry Department, Ibn-Al-Haithem College of Education for Pure Science, Baghdad University, Baghdad, Iraq

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Abstract

Novel three mixed ligand complexes derived from the interaction of Cr(III), Fe(III) and La(III) ions with a Schiff base resulted from the condensation process of 2-aminophenol and 2-hydroxyacetophenone(HL1) as primary ligand (HL1) and anthranilic acid (L2) as a secondary ligand. The formed mixed ligand complexes were synthesized and characterized using elemental analysis, FTIR, ¹HNMR, UV-visible and mass spectroscopy as well as molar conductance and magnetic measurements. The obtained results revealed that the mixed ligand complexes were formed in 1:1:1[L1ML2] ratio and non-electrolytic in nature.

Keywords: Schiff base; 2-aminophenol; 2-hydroxyacetophenone; Anthranilic acid; Mixed ligand complexes.

1. Introduction

The Schiff bases were first synthesized by Hugo Schiffs (German chemist) in 1864, by the reaction of organic compounds containing carbonyl group(C=O); aldehydes or ketones with primary amines or amino acids in the presence or absence of bases, acids in organic solvents [1]. They revealed many applications such as in chemistry and medicine. Bouhdada, *et al.* [2] Mixed ligand complexes play an important role in biological and chemical processes such as antioxidants, Yousef, *et al.* [3] water smoothing Girgaonkar and Shirodkar [4], ion exchange resin, Agarwal, *et al.* [5] photosynthesis in plants Geary [6] and the removal of unwanted and hazardous metals from the electrical components of living organisms. Sankhala and Chaturvedi [7], Al-braki, *et al.* [8]. Prepared and investigated some mixed ligand chelates. Also the antibacterial activity of mixed ligand chelates were tested against five pathogenic bacteria species, like *Staphylococcus aureus* and *Enterococcus faecalis*, *Pseudomonas aeruginosa*, *Klebsiella sp.* and *Escherichia coli* using the agar well diffusion assay Maihub, *et al.* [9]. Prepared and characterized some mixed ligand complexes of benzoin and phthalic acid.

This work aims to establish the geometrical structure of Cr(III), Fe(III) and La(III) mixed ligand complexes resulted from the reaction of Schiff base[2-hydroxyacetophenone with 2-aminophenol] as primary ligand and anthranilic acid as secondary ligand.

2. Material and Methods

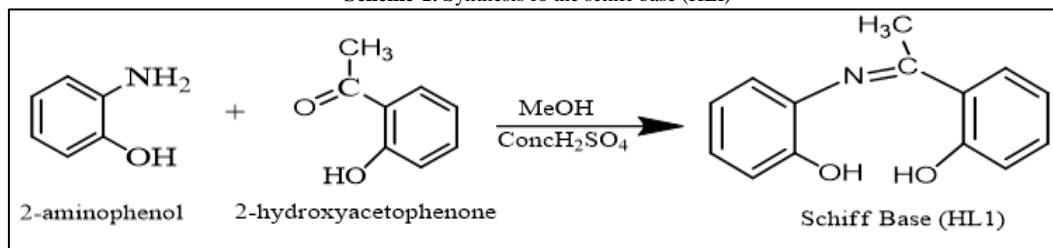
All chemicals used in this investigation were of pure grade (BDH or Aldrich). Include; 2-aminophenol, 2-hydroxyacetophenone, Conc.H₂SO₄, DMF, anthranilic acid, DMSO, NaOH, methanol, ethanol, Fe(NO₃)₃. 6H₂O, CrCl₃. 6H₂O, La (NO₃)₃. 6H₂O and distilled water. The CHN analyses for the synthesized compounds were made on 2400-CHN elemental analyzer. The molar conductivity was determined in DMFsolvent on CMD-650 digital conductivity meter, Benghazi University. The infrared spectra were carried out on IFS-25 DPUS/I spectrometer. The ¹HNMR spectra were recorded on Varian Gemini 200–200 MHz spectrometer using TMS as internal standard in d₆-DMSO.The electronic and mass spectra were recorded on Perkin-Elmer lambda-365 spectrophotometer and Shimadzu QP-2010 Plus spectrometer, respectively.

3. Experimental

3.1. Synthesis of Schiff Base (HL1)

A hot methanol solution of 2-aminophenol (1.09 g, 0.01 mol) and 2-hydroxyacetophenone (1.39 g, 0.01 mol) was mixed in presence of concentrated sulphuric acid and refluxed for three hours on a hot plate with magnetic stirrer. The resulting mixture collected by filtration and dried on air. The obtained product was recrystallized with absolute methanol to obtain yellow crystals. The chemical structure of the synthesized Schiff base under investigation is shown in scheme-1.

Scheme-1. Synthesis for the schiff base (HL1)



3.2. Synthesis of the Mixed Ligand Complexes

The mixed ligand complexes of these ligands were synthesized by refluxing an methanolic solution of Schiff base (2.28 g, 0.01 mole) and same amounts of the metal salts [FeCl₃.6H₂O; 2.70g, La(NO₃)₃.6H₂O; 4.3g and CrCl₃.6H₂O; 2.67g] for two hours. Few drops of 10% sodium hydroxide solution were added slowly to adjust the pH value at 8 until the complexes separated, and then the secondary ligand, 2-aminobenzoic acid (anthranilic acid) (L2) (0.01 mole, 1.37g) in 25cm³ of absolute methanol was added dropwise. The products were again refluxed for extra 3 hours. The obtained products were filtered and washed several times with hot ethanol until the filtrates become clear. The resulted complexes were dried in desecator under calcium chloride.

4. Results and Discussion

4.1. Microanalysis and Molar Conductance Measurements

The CHN elemental analysis data of the Schiff base and the mixed ligand complexes are given in table-1. These analyses are partially useful in determining of the empirical formula of the chelates. The experimental results are in a good agreement with the calculated ones and reveal that the complexes are formed in 1:1:1 [M:L1:L2] ratios. The molar conductance values of the mixed ligand complexes (zero values) reveal the existence of non-electrolytic nature for all the mixed ligand complexes, indicating that they are pure [6].

Table-1. Microchemical analysis data and some physical properties of Schiff base and mixed ligand chelates

Ligand-complexes	M.Wt	Color	C% (Calc.) Found	H% (Calc.) Found	N% (Calc.) Found	μ (BM)
Schiff base(HL1)	228	yellow	(73.68) 73.20	(5.70) 5.94	(6.14) 6.54	-----
[Cr(L1)(L2)(H ₂ O)]H ₂ O	538	Moss	(46.84) 46.64	(3.71) 3.60	(5.20) 5.41	3.95
[Fe(L1)(L2)(H ₂ O)]H ₂ O	454	Black	(55.51) 56.02	(4.63) 3.80	(6.17) 6.43	5.47
[La(L1)(L2)(H ₂ O)]H ₂ O	537	Wood	(46.93) 47.30	(3.91) 4.07	(5.21) 4.48	0.00

4.2. Infrared Spectra

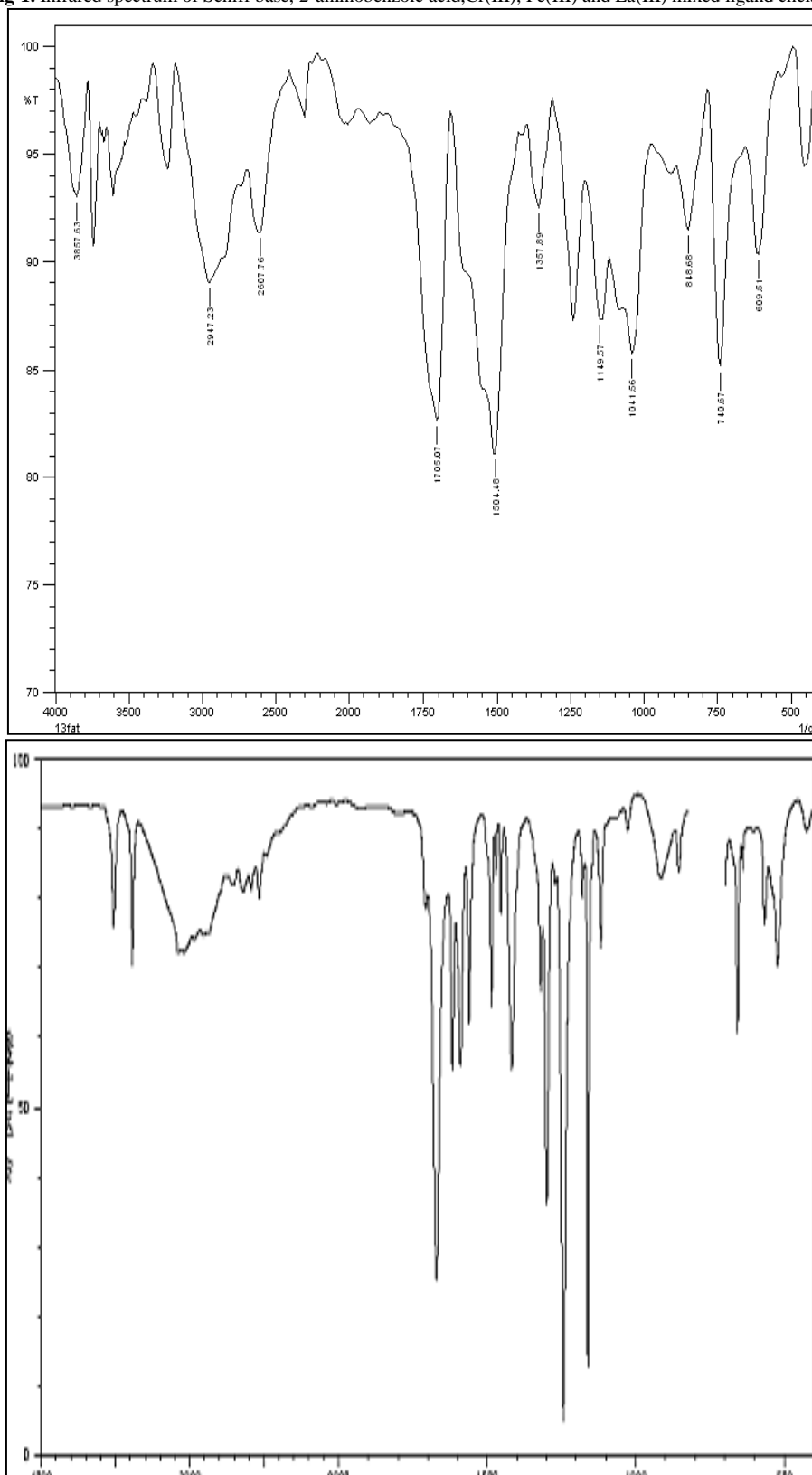
The infrared spectral data of the Schiff base and mixed ligand complexes were listed in table-2 and their spectra were given in figure (1). The infrared spectra of the synthesized mixed ligand complexes exhibit bands in the range of 3470-3485cm⁻¹ corresponding to the existence of water molecules as hydrated and coordinated Beecroft, *et al.* [10]. Meanwhile, the same spectra show bands in the range of 1520-15951cm⁻¹ attributed to ν(C=N) vibration, the lowering of these bands to lower frequency comparing to the Schiff base(HL1) confirmed the participation of this group in chelation through nitrogen atom Silverstein and Webster [11]. The other coordination sites of which can take apart in coordination are -NH₂ and -COO⁻ groups, the strong evidence of sharing of these groups can be seen from the position of the bands at 3500 and 3200 cm⁻¹, respectively. In the spectrum of anthranilic acid (L2), the shifting of the -NH₂ group to lower frequency in the spectra of the Fe(III) and La(III) mixed ligand complexes, confirms the bonding of this group to metal ions, but in the Cr(III)L1L2mixed ligand complex, this group is overlapped with the bands of water molecules Nakamoto [12]. These changes suggest the involvement of this group in chelation through nitrogen atom Etoriki, *et al.* [13]. The disappearance of -COO⁻ group band of the 2-aminobenzoic acid in the spectra of the mixed ligand complexes indicates the involvement of this group in bonding with the metal ions Karidi, *et al.* [14]. New bands in the range of 655-670 and 460-480cm⁻¹ which are not present in the free ligands are assigned to ν(M-O) and ν(M-N) vibrations and their appearance supports the entering of oxygen

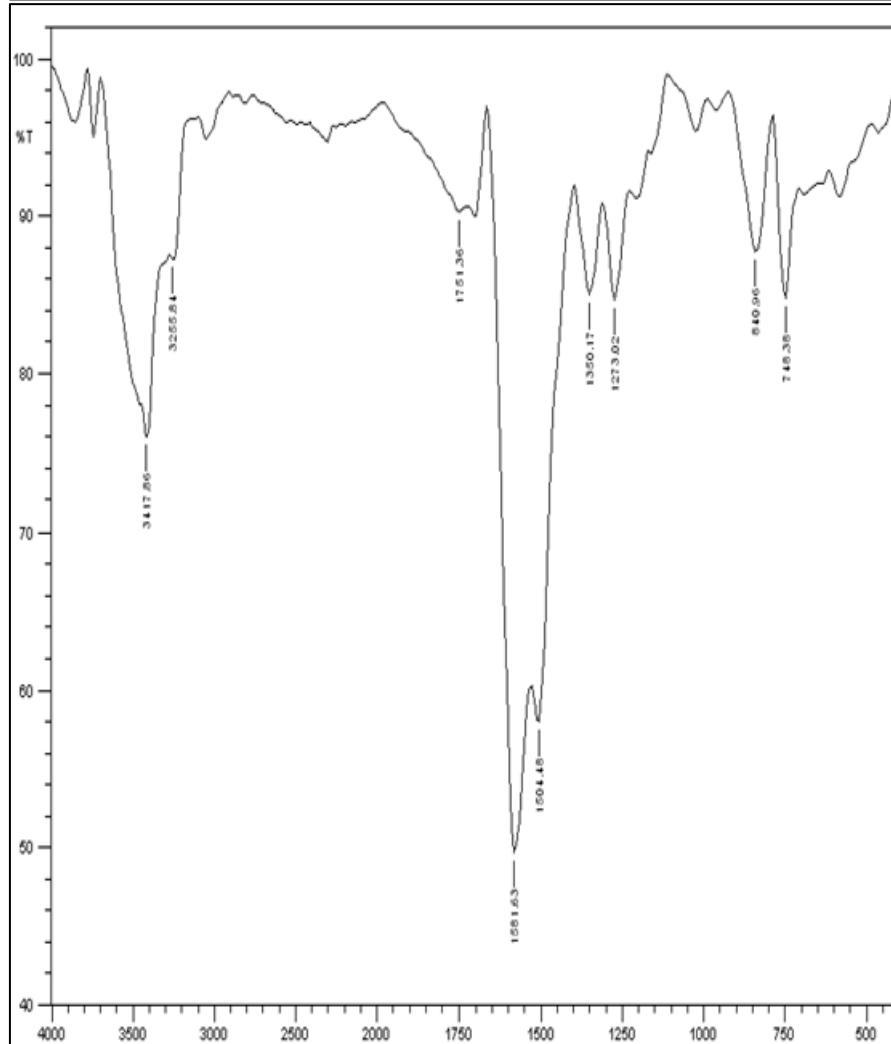
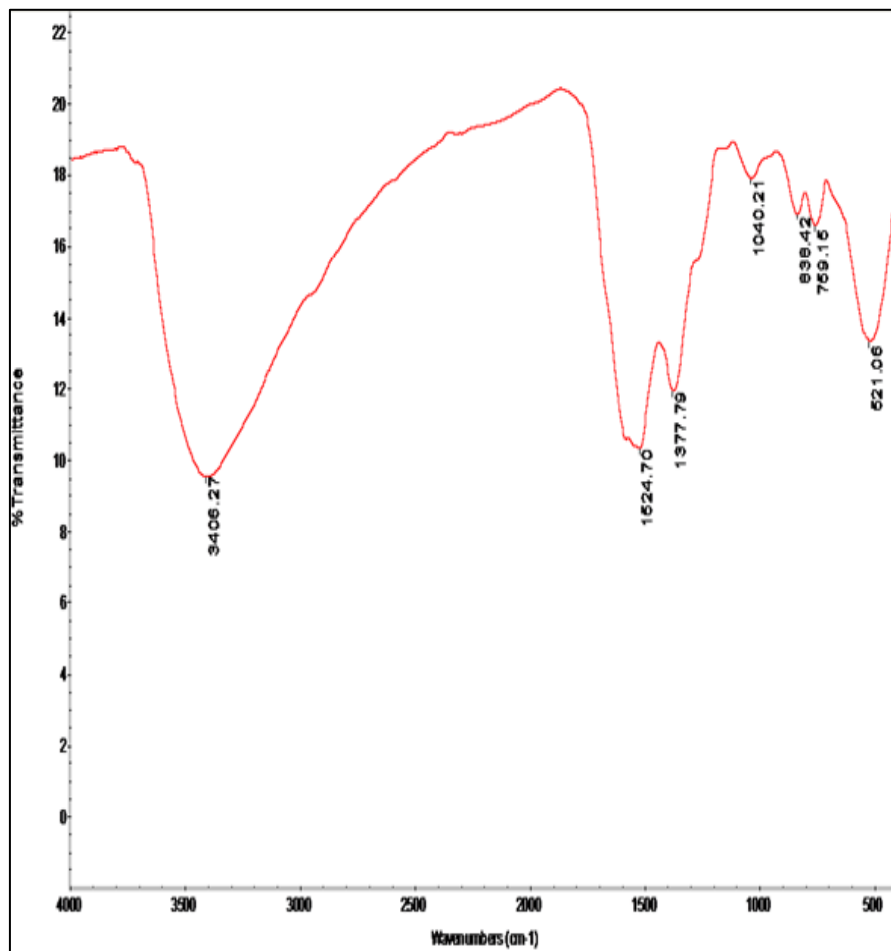
and nitrogen atoms of the azomethene, OH and COOH groups of the free ligands in chelation process Saranya, *et al.* [15].

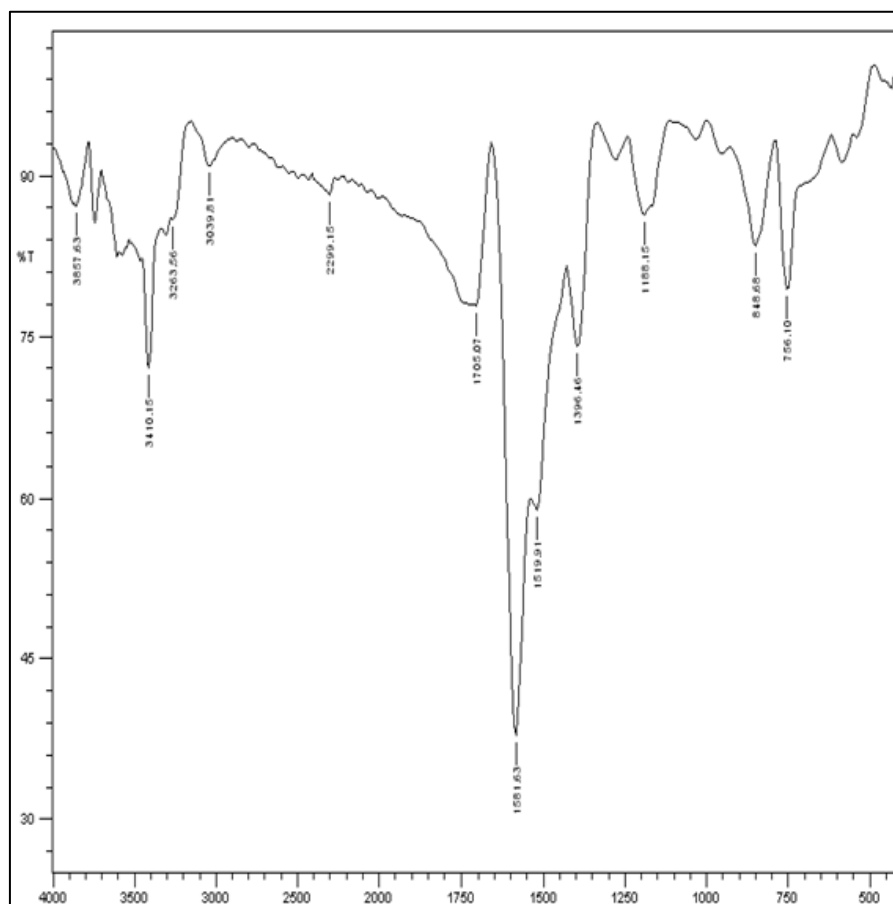
Table-2. Infrared frequencies (cm^{-1}) and electronic spectra of the Schiff base (HL1), anthranilic acid L2 and mixed ligand complexes (nm , cm^{-1})

Ligand-complexes	νCOO^-	νOH	NH_2^{ν}	$\nu\text{C}=\text{N}$	$\nu\text{M-O}$	$\nu\text{M-N}$	$\text{nm}(\text{cm}^{-1})$
Schiff base (HL1)	-	3875	-	1687	-	-	289(34602)-310(32258)
2-aminobenzoic acid(L2)	3200	-	3500	-	-	-	
[Cr(L1)(L2)(H ₂ O)]H ₂ O	-	3475	-	1520	670	470	310(32258)-408(24509)
[Fe(L1)(L2)(H ₂ O)]H ₂ O	-	3485	-	1595	665	460	380(26315)
[La(L1)(L2)(H ₂ O)]H ₂ O	-	3470	-	1590	655	480	377(26525)-394(25380)

Fig-1. Infrared spectrum of Schiff base, 2-aminobenzoic acid, Cr(III), Fe(III) and La(III) mixed ligand chelates







4.3. ^1H NMR Spectra of Schiff Base (HL1) and La (III) Mixed Ligand Complex

The ^1H NMR spectra of the Schiff base (HL1) and La (III) mixed ligand complex show signals in the range 6.50-6.77ppm are assigned to the presence of protons of the phenyl rings. The signals at 7.80-7.90ppm is attributed to OH groups of the Schiff base (HL1), [figure \(2\)](#). The methyl group and DMSO solvent are appeared at 2.35 and 2.75ppm, respectively. The signals at 3.60 and 8.20 ppm are assigned to $-\text{COOH}$ and NH_2 groups of the 2-aminobenzoic acid ligand. The signals in the range 6.45-6.80 are assigned to the presence of protons of the phenyl rings. The shifting of the NH_2 and the disappearing of $-\text{OH}$ and $-\text{COOH}$ groups during the complexation process indicate the participation of these groups in bonding with metal ions, [figure \(3\)](#).

Fig-2. Proton nuclear magnetic resonance of Schiff base (HL1)

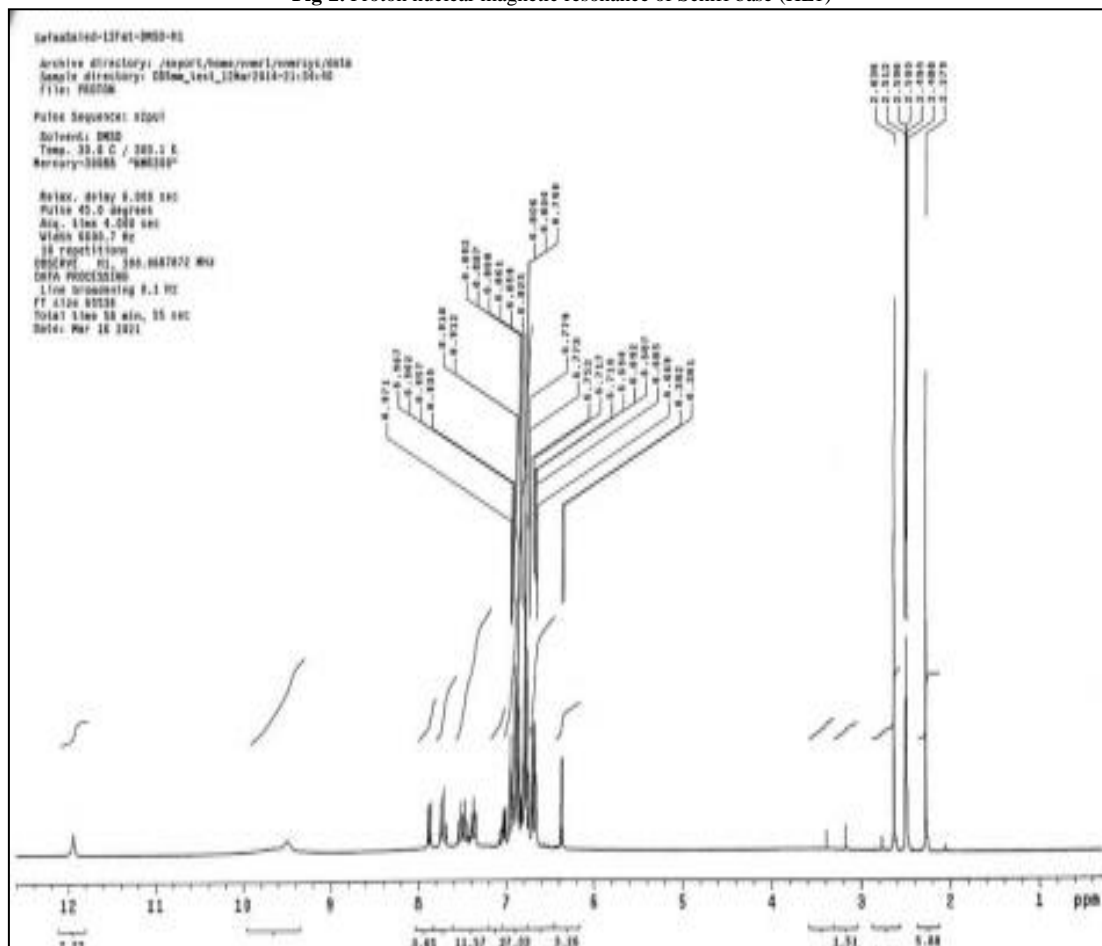
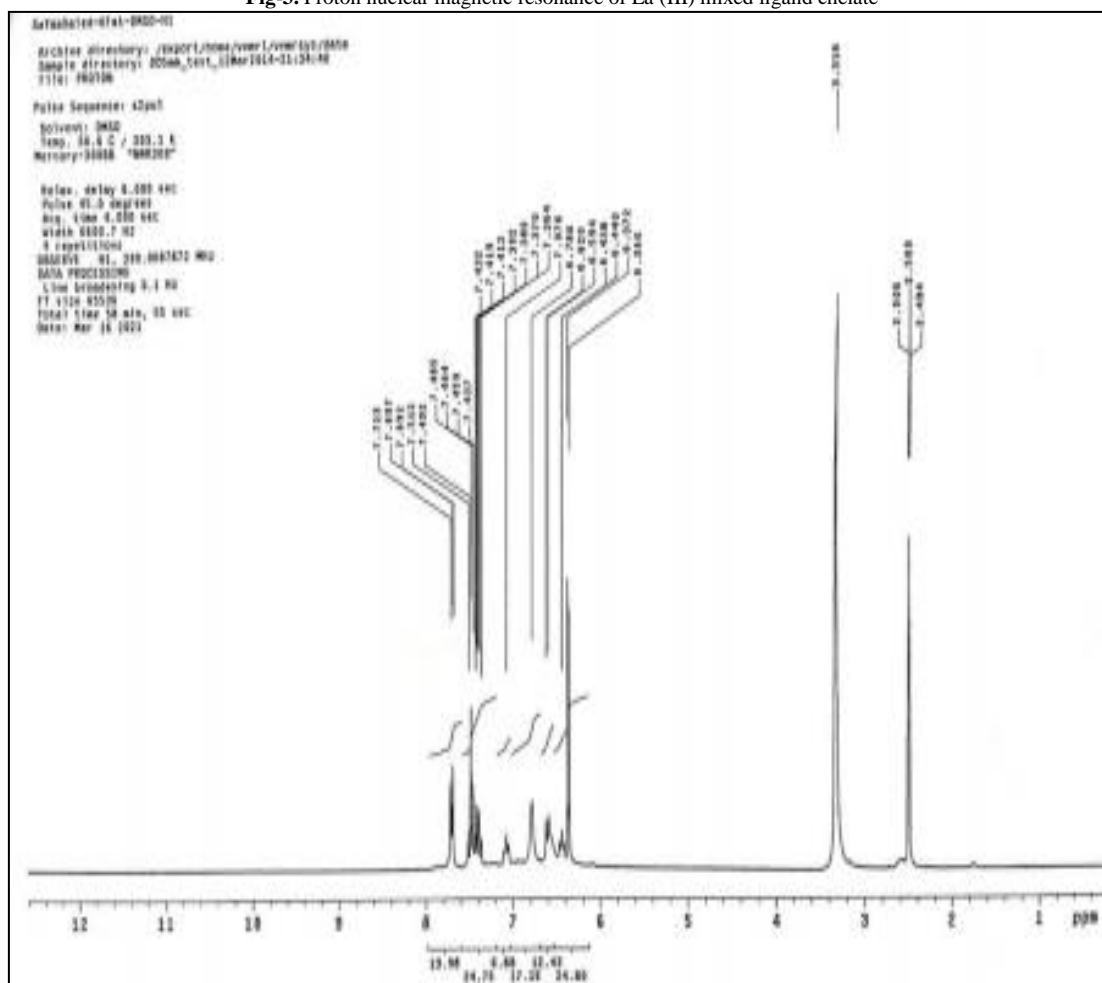


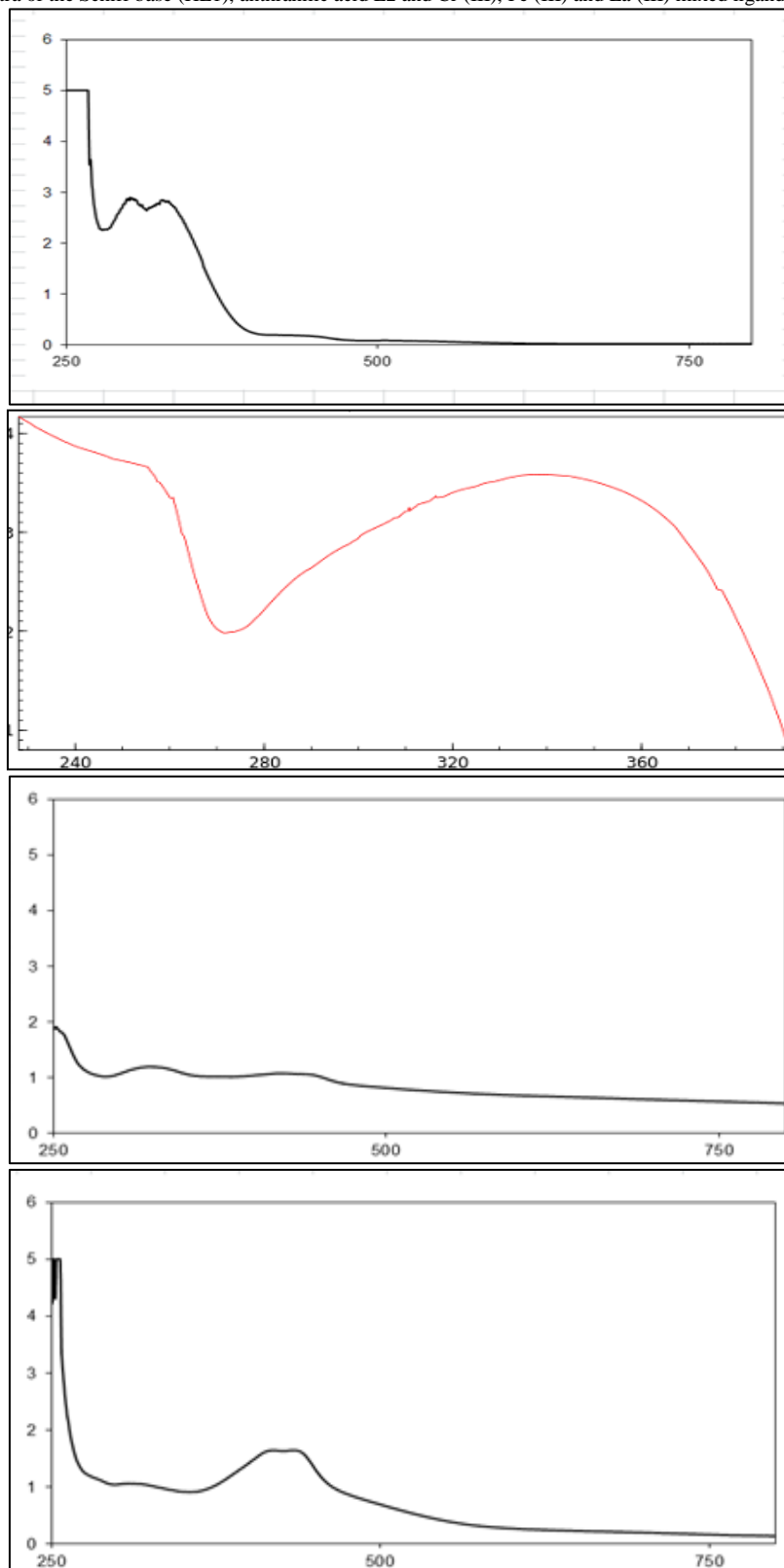
Fig-3. Proton nuclear magnetic resonance of La (III) mixed ligand chelate

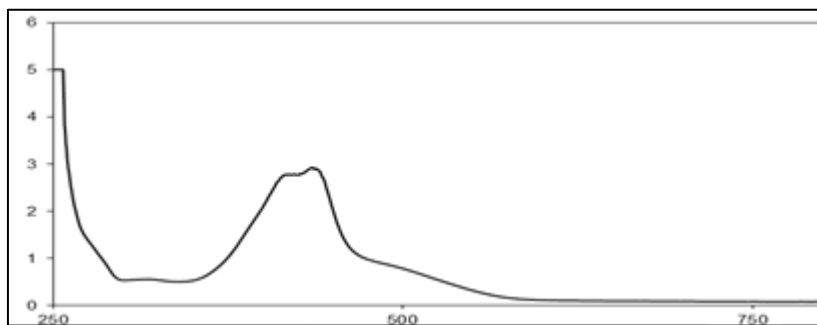


4.4. Electronic Spectra and Magnetic Moments

The ultraviolet spectrum of Schiff base (figure 4) was recorded at ambient temperature in 10^{-3} M DMF solvent shows two bands at 289 nm (34602cm^{-1}) and 310nm (32258cm^{-1}) attributed to $\pi\text{-}\pi^*$ (phenyl ring) and $n\text{-}\pi^*$ transitions, Ballhausen [16], Greenwood and Earnshaw [17]. The electronic spectrum of CrL1L2 complex shows two bands at 310 nm (32258cm^{-1}) and 408 nm (24509cm^{-1}) assigned to ${}^4\text{A}_2\text{g}(\text{F})\text{-}{}^4\text{T}_1\text{g}(\text{F})$ and ${}^4\text{A}_2\text{g}(\text{F})\text{-}{}^4\text{T}_2\text{g}(\text{F})$ transitions, Miessler and Tarr [18]. Magnetic moment of 3.95 B.M was obtained for Cr(III)L1L2 complex, which consistent with an octahedral geometry, Ingale, *et al.* [19]. The electronic spectrum of FeL1L2 complex exhibits one band at 377nm (26525cm^{-1}) which assigned to ${}^6\text{A}_1\text{g}\text{-}{}^4\text{T}_1\text{g}$ transition, Gupta, *et al.* [20]. Iron(III) ion in an octahedral environment has a d^5 configuration with a spin only magnetic moment of 6.01 B.M. The electronic spectrum of La(III)L1L2 complex reveals two bands at 377nm(26525cm^{-1}) and 394nm(25380cm^{-1}) assigned to $\pi\text{-}\pi^*$, $n\text{-}\pi^*$ and LMCT transitions [21] Fig-4.

Fig-4. Electronic spectra of the Schiff base (HL1), anthranilic acid L2 and Cr (III), Fe (III) and La (III) mixed ligand complexes, respectively

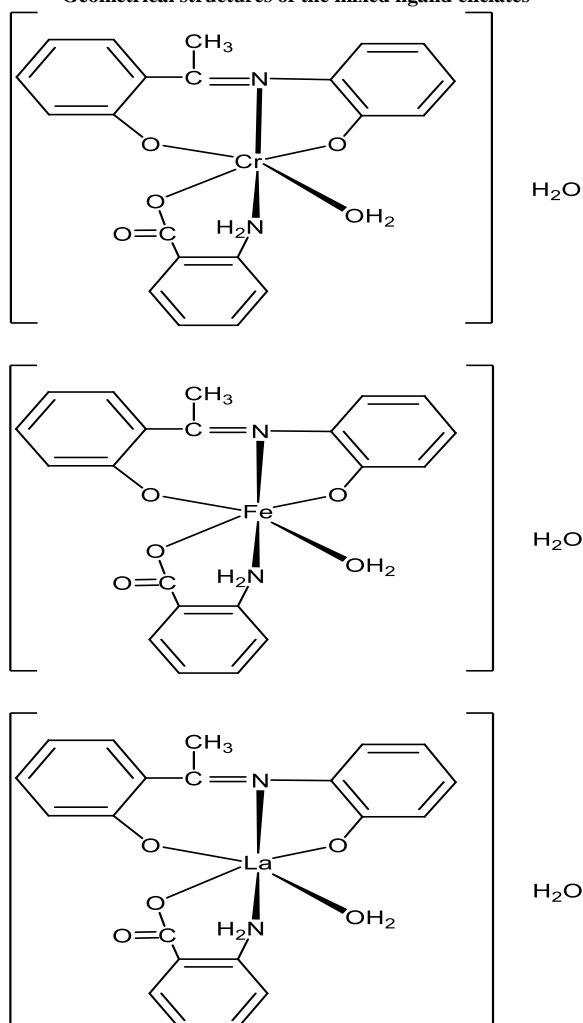




5. Conclusion

The analytical and spectral data of the Schiff base, anthranilic acid and their mixed ligand complexes suggest the formation of the expected Schiff base and the mixed ligand complex have 1:1:1[M:L1:L2] ratio. An octahedral geometry was pointed out for all the mixed ligand complexes.

Geometrical structures of the mixed ligand chelates



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