NOVEL SCHIFF BASE METAL COMPLEXES OF 3-AMINO-4-HYDROXY BENZOIC ACID: SYNTHESIS AND INSTRUMENTAL CHARACTERIZATION

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Abstract:
New complexes of transition metals and Schiff base were synthesized with metals Cu (II), Fe (III) and Ni (II). By condensing 3-amino-4-hydroxy benzoic acid and 5-bromo-2-methoxy benzaldehyde, Schiff base ligand was prepared. Synthesized metal complexes and Schiff base ligand were characterized by using spectroscopic techniques and physico-chemical analysis i.e. electronic absorption (UV-Visible), FT-IR, ^{1}H-NMR & HRMS. UV-Visible spectra show red shift in metal complexes. Free ligand and its Cu (II), Fe (III) and Ni (II) complexes have different electronic absorptions spectra with certain alternations. FT-IR spectrums shows bidentate coordination of the ligand to the central metal ion. Estimated values of HRMS is in good agreement with calculated values for ligand. Molar conductance values demonstrated that metal complexes are non-electrolytic.

Keywords: Schiff base, 3-amino-4-hydroxy benzoic acid, synthesis, metal complex

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1. Introduction:

Schiff Base was firstly reported by Hugo Schiff about one hundred and sixty years ago. From the previous century to the present, Schiff bases have been crucial ligands in coordination chemistry, which is the most widely used compounds in applied chemistry [1]. These Schiff bases have wide applications in the field of pharmaceuticals, dye, polymers, catalyst and organic synthesis [2]. Active carbonyl compounds condensing with the primary amine forms the Schiff base ligand. Schiff bases consist of azomethine (R^1-C=N-R^2) group, R^1 & R^2 = aryl, heterocyclic, cyclic or alkyl group [3]. Over recent years, Interest has been shown in the design and preparation of new Schiff base ligands and their metal complexes because of their outstanding characteristics, close structural resemblance to naturally occurring biological substances, simplified preparation and synthetic flexibility that allows for the design of appropriate structural properties [4]. Schiff base metal complexes shows remarkable applications in the medicinal field. They shows anti-cancer, anti-leukaemia, anti-HIV activities. [5]. Schiff bases are frequently used in analytical calculations. As necessary components of the measurement systems, organic reagents are required for the operation of many modern analytical equipment. To improve selectivity and sensitivity, they are utilised, for instance in optical [6], electrochemical sensors [7] and in a variety of chromatographic techniques [8]. Present study focused on the synthesis and spectral studies of the novel complexes of transition metals prepared with Schiff base ligand synthesized from 3-amino-4- hydroxy benzoic acid and 5-bromo-2-methoxy benzaldehyde.

2. Materials and Methods:

Chemicals required for synthesis of ligand and complexes were purchased from Thermo Fischer Scientific Company Ltd. of AR grade. FT-IR analysis was done on Perkin Elmer, ^{1}H- NMR on Brucker advance neo 500 MHz spectrometer and UV-Visible spectrum was done on Shimadzu double beam spectrophotometer.

2.1 Preparation of ligand:

A mixture of 3-amino-4-hydroxy benzoic acid (0.002 M) and 5-bromo-2-methoxy benzaldehyde (0.002 M) were dissolved in absolute ethanol and by stirring on magnetic stirrer for 30 min, light Cream coloured product is obtained. Wash with absolute ethanol and dried. Melting point was recorded. Figure 1 depicts the plan for ligand preparation.

Colour: Light Cream, Yield: 72-75 %, Elemental analysis, found (calcd.) for $C_{15}H_{12}BrNO_4$; C, 51.38 (51.45); H, 3.40 (3.45); N, 3.97 (4.00); FT-IR data (KB, cm^{-1}); 3430 υ(O-H), 1600 υ (C =N), 1590 υ (C=C), 1700 υ (C=O of COOH) ^{1}H-NMR; δ 8.92 (1H,(S), HC=N), δ 12.58 (1H, (S), -COOH), δ 9.94 (1H, (S), Ar-OH), δ 7.65 to 7.73 (6H, (M), Aromatic), δ 3.91 (3H, (S), -OCH3). UV-Vis (DMF, nm); 256, 269, 322.

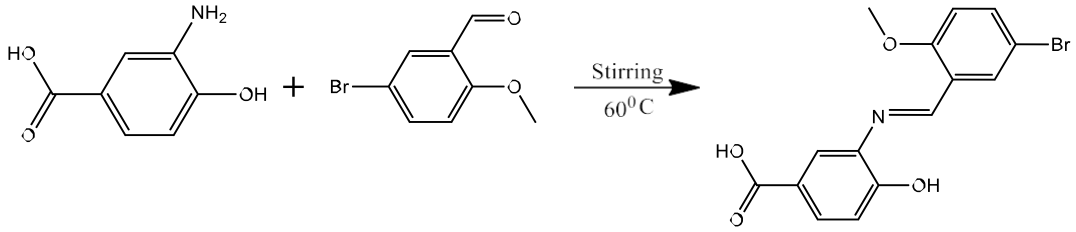

Figure. 1 Schiff base ligand scheme for (E)-4-hydroxy-3-((5-bromo-2-methoxy benzylidene) amino) benzoic acid.

2.2 Preparation of Metal Complexes:

Metal complexes of transition metals were synthesized by adding metal nitrate [Cu (II), Fe (III) and Ni (II)] 0.002 M in absolute ethanol to the Schiff base ligand (0.002 M) in same solvent. By Stirring this solution on magnetic stirrer for half hour at 60^0C precipitate was obtained which then collected by filtration and wash with several times with methanol and ethanol.

3. Result and Discussion:

Spectroscopic methods were used to characterise the synthesised Schiff base and its complexes. IR spectroscopic analysis was done on Perkin Elmer spectrometer, UV-Visible analysis was done on Shimadzu double beam spectrometer, ^{1}H-NMR was done on Brucker advance neo 500 MHz spectrometer.

3.1IR Spectra:

Study of infrared spectra gives significant information of ligand and its bonding present in the metal complexes. The binding mode of ligand with central metal ion in complexes was determined by FT-IR spectral analysis. The free Schiff base ligand's FT-IR spectrum was compared to that of metal complexes. The ligands' coordination with the central metal ion is accounted by shift in bands. In infrared spectral studies band frequencies of functional group those are participated in coordination are focused and discussed. Band frequencies assigned to different functional groups are empirical and are based on the references.

a) IR Spectra of Ligand:

The existence of band in the ligand spectrum at 1600 cm^{-1} for υ(C=N), confirms the imine formation. At 1700 cm^{-1} a strong band found attributed to υ(C=O) carbonyl group, intense broad band found at 3430 cm^{-1} attributed to hydroxyl group υ(-OH), and a strong band found at 1590 cm^{-1} attributed to υ(-C=C-). Schiff base preparation has been supported by the infrared data. The peaks in FT-IR spectra is closely matched with literature [9].

b) IR Spectra of Cu(II)L Complex:

The complex Cu(II)L formation is supported by infrared spectra which shows a band of frequency 1671cm^{-1} attributed to imine group υ(C=N). The vibrational frequency of this band is higher than that of the ligand. Band found at 3401cm^{-1} is associated with υ(-OH). A new band found in spectrum of complex at 466 cm^{-1} is attributed to metal-oxygen bond υ(M-O) which confirms coordination by ligand through oxygen with centred metal ion [10].

c) IR Spectra of Fe (III)L Complex:

For the azomethine vibration, the Fe(III)L complex show a strong band of 1673 cm^{-1}, a wide band found at 3399 cm^{-1} for a hydroxyl group υ (-OH). A new band found in spectrum of complex at 464 cm^{-1} is attributed to metal-oxygen bond υ(M-O) which confirms coordination by ligand through oxygen with centred metal ion.

IR Spectra of Ni (II)L Complex:

The Ni(II)L complex infrared spectrum shows band at 1671cm^{-1} that is the azomethine functional group vibration and a band at 3401cm-1 that is the υ(-OH) group vibration, is shifted to a lower frequency than the ligand. A new band found in spectrum of complex at 471 cm^{-1} is attributed to metal-oxygen bond υ(M-O) which confirms coordination by ligand through oxygen with centred metal ion.

The infrared spectrums of prepared Schiff base and its Cu(II), Fe(III) and Ni(II) complexes are shows in figures from 2 to 5.

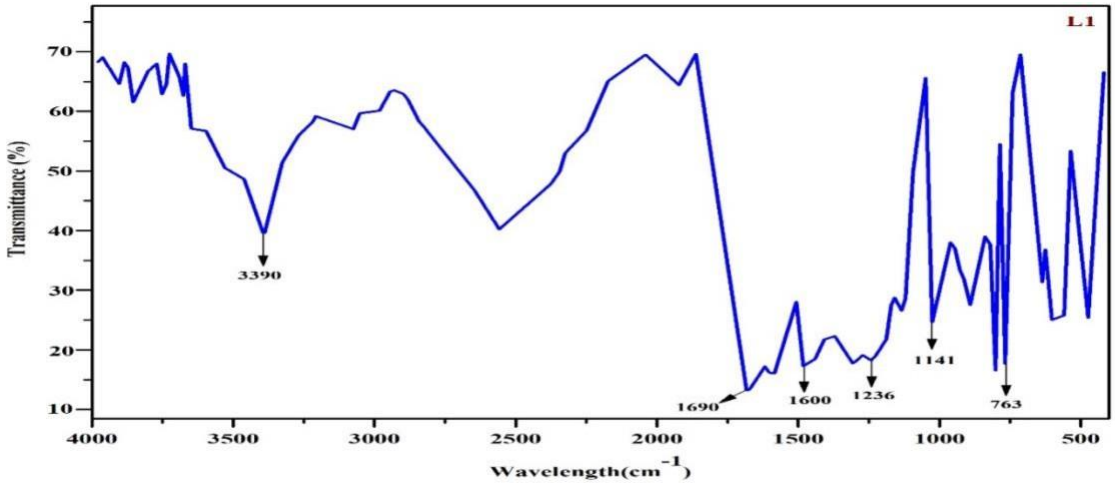

Fig. 2 Schiff base infrared spectrum

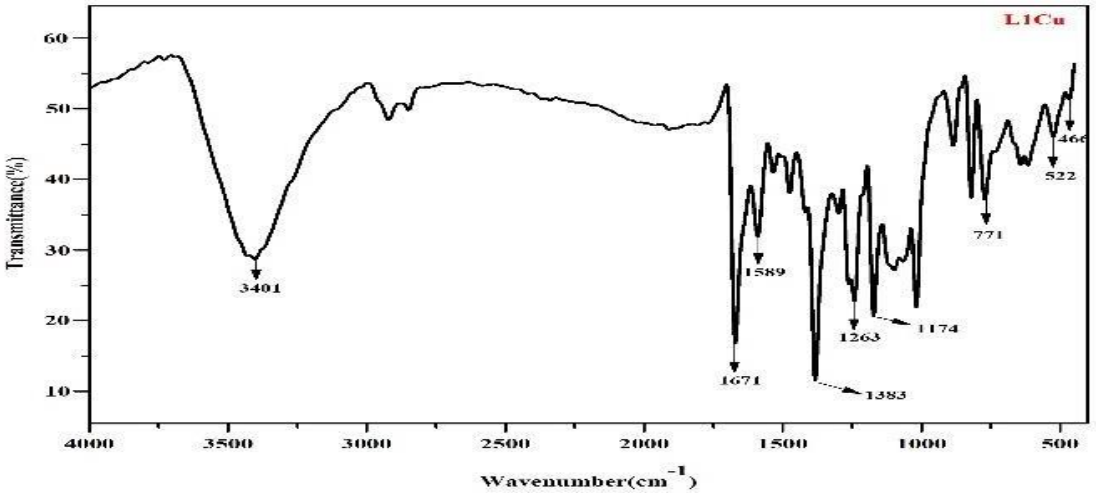

Fig. 3 Cu(II)L complex infrared spectrum

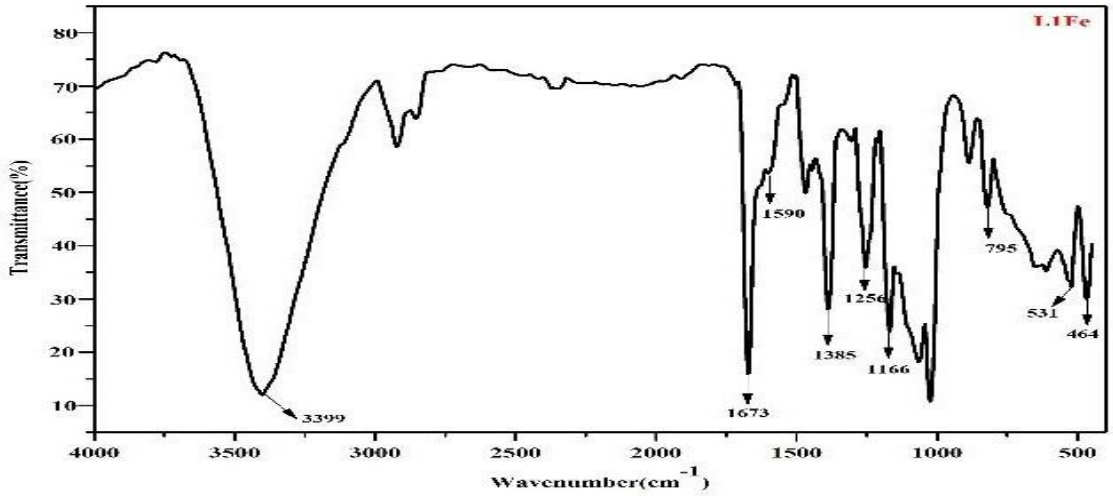

Fig. 4 Fe(III)L complex infrared spectrum

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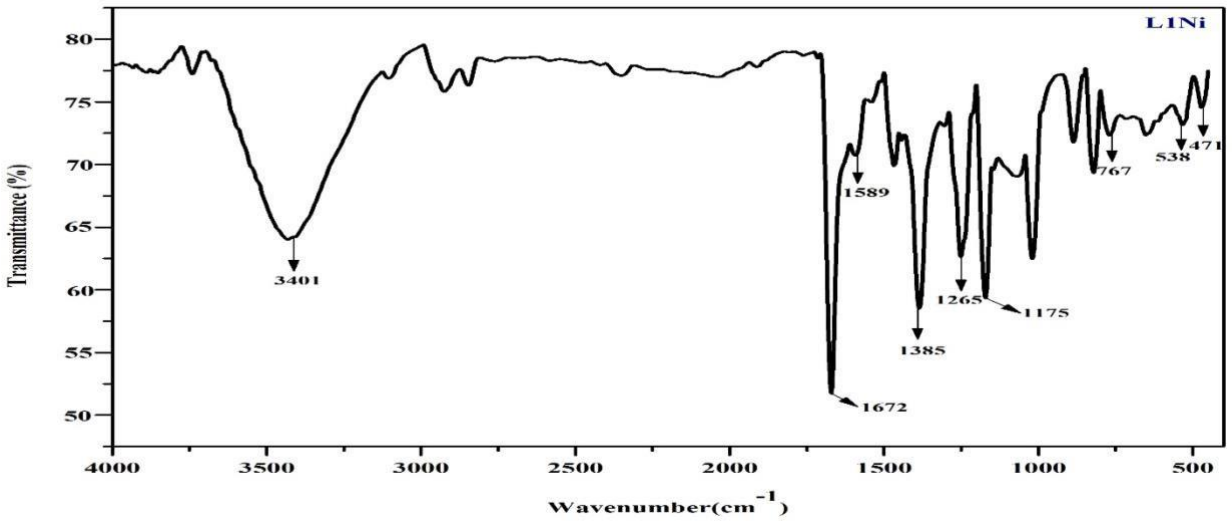

Fig. 5 Ni(II)L complex infrared spectrum

3.2

3.3UV-Visible Spectra:

Ligand shows electronic absorption at 256, 269 (π⟶π*) and 322 nm (η⟶π*). Cu (II) Complex shows absorption peaks at 268 nm (π⟶π*), 327 and 432 nm(η⟶π*). Fe (III) Complex shows peaks at 260, 268 (π⟶π*) and 332, 436 nm (η⟶π*), Ni(II) Complex displays absorption peaks at 269 nm (π⟶π*) and 313, 408 nm (η⟶π*). It is found that metal complexes and ligand have different electronic spectra and red shift observed in metal complexes which confirms complexes formation. Some of the alterations in frequencies and intensities of the free ligand. Metal complexes typically display the distinctive bands of Schiff base ligand. Complexes have similarities in their electronic spectra, suggesting that their structures are similar. Figures (6 to 9) displays the electronic absorption spectra of the ligand and complexes.

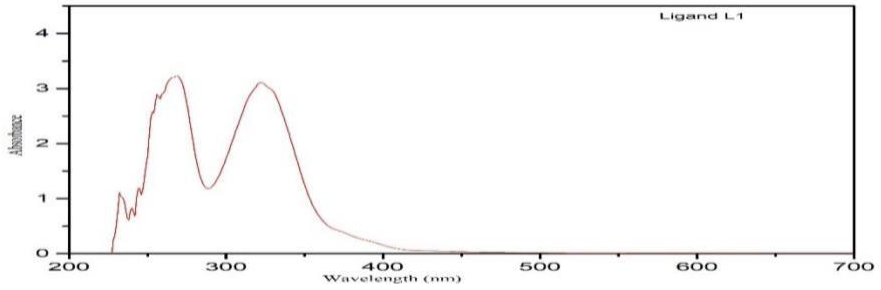

Fig.6 Schiff base ligand electronic absorption spectra

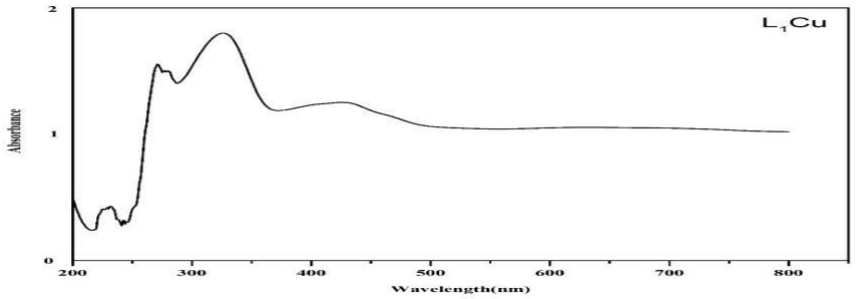

Fig. 7 Cu (II) complex electronic absorption spectra

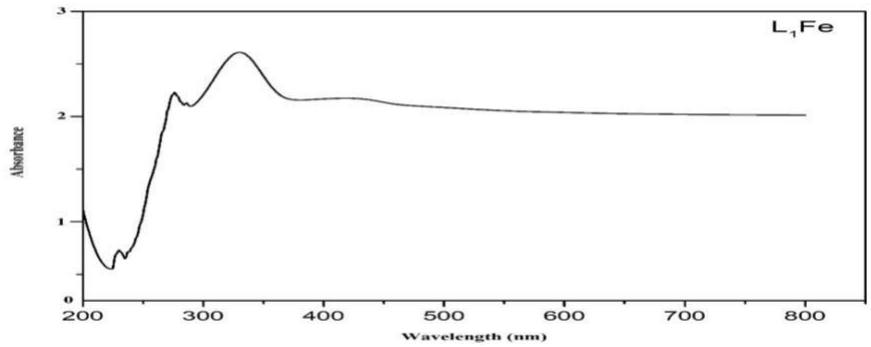

Fig. 8 Fe (III) complex electronic absorption spectra

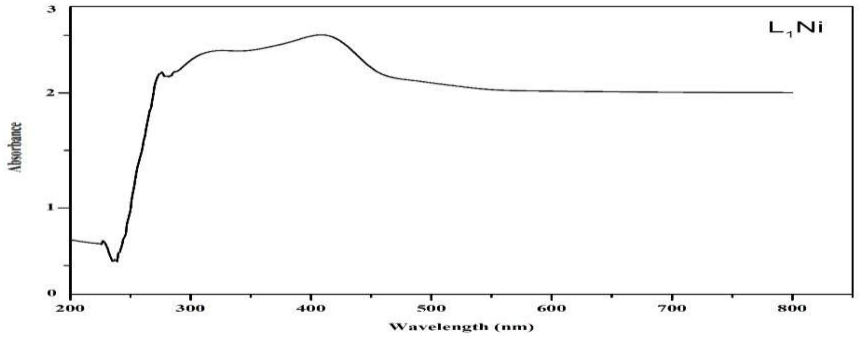

Fig. 9 Ni (II) complex electronic absorption spectra

3.4 ^{1}H-NMR Spectra

Figure 10 displays the synthesized ligand's 1H-NMR spectra. Singlet peak for azomethine proton observed at δ 8.92 ppm. Also, a singlet was observed at δ 12.58 ppm due to the proton of the carboxylic acid (-COOH) and a multiplet due to the aromatic protons (6H) seen in the range of δ 7.65-7.73 ppm. Additionally, a singlet at 3.91 ppm, for the methoxy (-OCH 3) group, was also identified. The NMR data shown below validate the synthesis of the ligand.

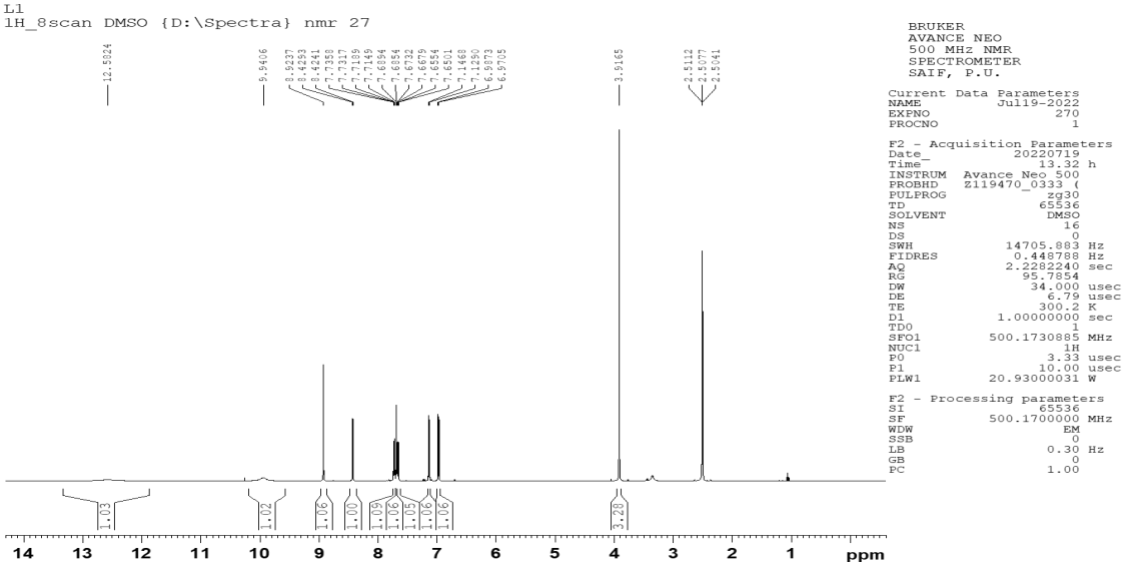

Figure.10 ^{1}H-NMR Spectrum of Schiff base ligand (L)

3.5 HRMS:

The measured HRMS values for Schiff base ligand exhibit a strong correlation with the theoretical values. M+H = 350.0027 was calculated, and M+H = 350.0028 was the observed value. HRMS of Schiff base ligand is shown in the fig. 11.

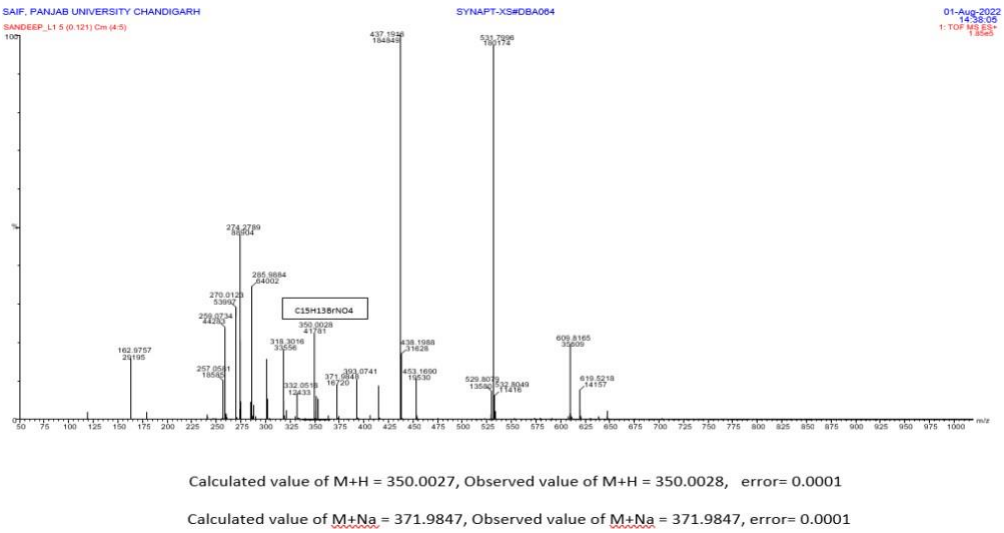

Fig. 11 HRMS of Schiff base ligand.

4. Conclusion:

Condensation of 3-amino-4-hydroxy benzoic acid and 5-bromo-2-methoxy benzaldehyde gives formation of an imine bridge between amine and aldehyde. Ligand coordination confirmed by new bands observed in IR spectra corresponds to metal-oxygen bond υ(M-O) which indicates coordination of ligand through oxygen with central transition metal ion in the complex. UV-Visible Spectra shows red shift in metal complexes which confirms complexes formation. Sophisticated instrumental characterisations are in good agreement with the proposed structures.

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6. CONFLICTS OF INTEREST: There are no conflicts of interest, according to the authors.

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