

CHAPTER III

Synthesis, characterization and antibacterial studies of Mn(II) and Co(II) complexes of an ionic liquid supported Schiff base: [1-{2-(2-hydroxybenzylideneamino)ethyl}-3-methyl-1*H* imidazolium] bromide*

3.1. Introduction

Ionic liquids (ILs) are generally based on inorganic or organic anions paired with large, usually asymmetric organic cations, have low melting points below 373 K although many are in fact liquid at/below ambient temperature [1, 2]. They are worthy of extensive investigation because of their unique physical and chemical properties such as nonvolatile, nonflammable, thermally stable and recyclable. In addition to the properties just mentioned, ILs exhibit a wide electrochemical window, high ionic conductivity, a broad temperature range of the liquid state and frequently possess excellent chemical inertness as well [3-5]. The hydrophobicity/hydrophilicity and other physical features of ionic liquids including density, melting point, conductivity, polarity, Lewis acidity, viscosity, enthalpy of vaporization can be altered by manipulating the structure of cations and anions [6] and issues such as their toxicity and biodegradability are now being researched to judge them as potentially green replacements for traditional molecular solvents [7]. To date, ILs have been used in organic synthesis, catalysis, industrial processing, electrochemistry, pharmaceuticals, biotechnology, nano-chemistry, analytical chemistry and separation technology. Ionic liquids shaped for a particular function are referred to functionalized ionic liquids (FILs). Recently, much attention has been paid to the preparation and application of FILs with special tasks, such as carrying hydroxyl, amino, sulfonic acid, carbonyl, *etc* [8-12]. The increasing popularity of the FILs lies in the fact that both the cationic and anionic parts can be altered and applied to a specific application. Again, the incorporation of functional groups can exhibit a particular capability to the ILs by increasing catalytic stability and reducing catalytic leaching [12, 13]. Imidazolium

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based systems play important roles in biochemical processes [14] for having varied pharmacological properties. Schiff bases and their metal complexes play a significant role in the field of coordination chemistry and have been studied extensively because of their remarkable chemical and physical properties. The azomethine linkage in the structures of Schiff bases has been ascribed for their biological actions like antibacterial and analytical activities [15, 16]. Particularly transition metal complexes of Schiff bases with oxygen and nitrogen donors are of particular interest, [17] because of their ability to possess unusual configuration and structure-related bioactivities [18, 19].

Hence in this chapter the synthesis and physico-chemical characterizations of an imidazolium ionic liquid-supported Schiff base, [1-{2-(2-hydroxybenzylideneamino)ethyl}-3-methyl-1*H* imidazolium] bromide and its Mn(II) and Co(II) complexes were reported. The synthesized Schiff base ligand and metal complexes were tested for *in vitro* antibacterial activity against two commonly known gram negative bacteria *Escherichia coli* and gram positive bacteria *Bacillus subtilis*.

3.2. Experimental Section

3.2.1. Materials and Methods

All the reagents were of analytical grade and used without further purification. 1-methyl imidazole and 2-bromoethylamine hydrobromide were procured from Sigma Aldrich, Germany. Salicylaldehyde, Mn(OOCCH₃)₂.4H₂O, Co(OOCCH₃)₂.4H₂O and all other chemicals were used as received from SD fine Chemicals, India. The solvents methanol, petroleum ether, chloroform, DMF and DMSO were used after purification by the standard methods describe in the literature. The amino functionalized ionic liquid, 1-(2-aminoethyl)-3-methylimidazolium bromide, [2-aemim]Br (**1a**) was synthesized by following a literature procedure [20]. The synthesis and physicochemical characterization of the ionic liquid have been described earlier in chapter II.

FT-IR spectra were recorded in KBr pellets with a Perkin-Elmer Spectrum FT-IR spectrometer (RX-1) operating in the region 4000 to 400 cm⁻¹. ¹H-NMR spectra were recorded at room temperature on a FT-NMR (Bruker Advance-II 400 MHz) spectrometer by using DMSO-*d*₆ and D₂O as solvents. Chemical shifts are quoted in ppm downfield of internal standard tetramethylsilane (TMS). Elemental micro-

analyses (C, H and N) were conducted by using Perkin–Elmer (Model 240C) analyzer. Metal contents were determined with the aid of AAS (Varian, SpectrAA 50B) by using standard metal solutions from Sigma-Aldrich, Germany. Mass spectra were recorded on a JMS-T100LC spectrometer. The purity of the synthesized compounds was checked by thin layer chromatography (TLC) on silica gel plates. The UV-Visible spectra were recorded in methanol with a JascoV-530 Spectrometer. Magnetic susceptibilities were measured at room temperature with a Sherwood Scientific Ltd magnetic susceptibility balance (Magway MSB Mk1). Molar conductance was measured with a Systronics conductivity TDS meter (Model- 308) with a cell (Type CD -30, cell constant $0.10 \pm 10\%$) at (298.15 ± 0.01) K. Antibacterial activities (*in vitro*) of the synthesized ligand and the complexes were studied by disc diffusion method against two bacteria, *viz.*, *Bacillus subtilis*. and *Escherichia coli*. with respect to the standard drug *Ampicilin*.

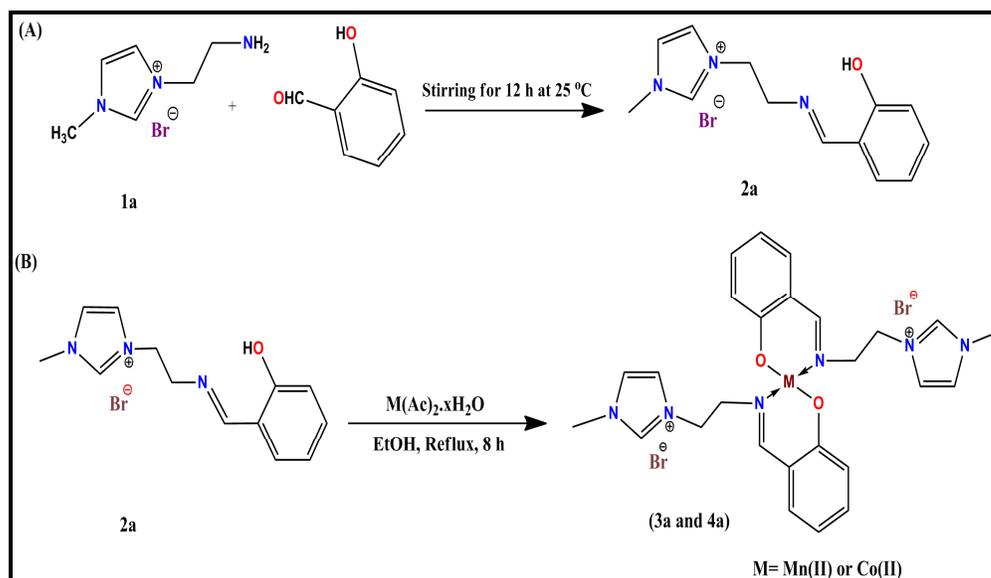
3.2.2. Synthesis of imidazolium ionic liquid-supported Schiff base, LH (2a)

A mixture of salicylaldehyde (1.22 g, 10 mmol) and [2-aemim]Br (2.06 g, 10 mmol) was stirred at room temperature for 12 h without a solvent, followed by washing with diethyl ether (3×30 mL) and vacuum evaporation which gave the product as brown oil: 2.11g (yield: 68%). Anal. Calcd. for $C_{13}H_{16}N_3OBr$ (310): C, 50.34; H, 5.20; N, 13.55. Found: C, 50.11; H, 5.09; N, 13.20 %; FT-IR (KBr, cm^{-1}): 3429 (O-H), 3143, 1626 (C=N), 1579, 1454 (C-O), 1279, 623 (C-Br); 1H -NMR: (400 MHz, DMSO- d_6): δ 3.95 (s, 3H, CH_3), 4.68 (t, 1H, N- CH_2), 4.58 (t, 1H, N- CH_2), 7.83–7.72 (m, 4H, Ar-H), 6.98 (s, 1H, NCH), 6.95 (s, 1H, NCH), 9.20 (s, 1H, N=CH), 9.29 (s, 1H, N(H)CN), 8.31 (s, 1H, OH). ^{13}C -NMR: (400 MHz, DMSO- d_6): δ 136.98, 136.36, 135.07, 124.58, 123.93, 123.13, 122.55, 119.58, 53.46, 52.77, 50.93, 36.38 and 35.86. ESI-MS (CH_3OH , m/z) 230, $[(M-Br)^+, M = (C_{13}H_{16}N_3O)^+]$.

3.2.3. Synthesis of the metal complexes (3a and 4a)

To an ethanolic solution (20 mL) of ligand, LH (0.50 g, 1.30 mmol), metal acetate, *viz.*, $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.173 g, 0.65 mmol) or $Co(CH_3COO)_2 \cdot 4H_2O$ (0.16 g, 0.65 mmol) dissolved in ethanol was added and the mixture was refluxed for 8 h until the starting materials were completely consumed as monitored by TLC. On completion of the reaction, solvent was evaporated and the reaction mixture was cooled to room temperature.

The precipitate was filtered, washed with ethanol (10 mL \times 3) and dry ether (10 mL \times 3), respectively and finally dried in a desiccator to obtain the solid product. The complexes are soluble in *N,N*-dimethylformamide, dimethylsulphoxide, acetonitrile and methanol. A schematic representation of the synthesis was shown in Scheme 3.1.



Scheme 3.1. Synthesis of the ionic liquid-supported Schiff base, [1-{2-(2-hydroxybenzylideneamino)ethyl}-3-methyl-1*H* imidazolium] bromide (**2a**), and M(II) complexes (**3a** and **4a**) from (**2a**).

3.2.2.1. Mn(II) complex (3a): Brown solid; 0.59 g (yield, 67 %). Anal. Calc. for $C_{26}H_{30}MnN_6O_2Br_2$ (673): C, 46.38; H, 4.49; N, 12.48; Mn, 8.16. Found: C, 46.22; H, 4.43; N, 12.36; Mn, 8.06; FT-IR (KBr, cm^{-1}): 3398 (O-H), 1616 (C=N), 1444 (C-O), 756 (Br), 565 (M-O), 460 (M-N). UV-Vis (Methanol) λ_{max}/nm : 211, 255, 314. ESI-MS (CH_3OH , m/z): 513 ($[M-2Br]^+$, $M = [C_{26}H_{30}MnN_6O_2]^+$).

3.2.2.2. Co(II) complex (4b): Dark brown solid; 0.60 g (yield, 68 %). Anal. Calc. for $C_{26}H_{30}CoN_6O_2Br_2$ (677.30): C, 46.11; H, 4.46; N, 12.41; Co, 8.20. Found: C, 46.02; H, 4.33; N, 12.39; Co, 8.10; FT-IR (KBr, cm^{-1}): 3423 (O-H), 1601 (N-H), 1449 (C-O), 761 (Br), 590 (M-N), 475 (M-O). UV-Vis (Methanol) λ_{max}/nm : 220, 248, 403. ESI-MS (CH_3OH , m/z): 517 ($[M-2Br]^+$, $M = [C_{26}H_{30}MnN_6O_2]^+$).

3.3. Results and Discussion

The complexes are moisture sensitive, stable in vacuum desiccator and soluble in *N, N*-dimethylformamide, dimethylsulphoxide, acetonitrile and methanol. All the isolated compounds were found to be hygroscopic in nature and were characterized by different analytical and spectroscopic methods.

3.3.1. FT-IR spectral studies

FT-IR spectra of the complexes (**3a** and **4a**) were compared to that of the free ligand in order to determine the coordination sites involved in the complexation. The ligand showed a strong broad band at 3429-3143 cm^{-1} ; this band was attributed to the hydrogen bonded -OH of the phenolic group with H-C(=N) group of the ligand (OH...N=C) [21]. The broad band appeared in the range 3398-3423 cm^{-1} in the spectra of Mn(II) and Co(II) complexes, respectively were due to absorption of water molecules as reported *Gruzdev* et al [22]. The band at 1454 cm^{-1} was observed for phenolic -CO of the free ligand shifted to lower frequency region 1444-1449 cm^{-1} for the complexes [23] on chelation. In the ligand a band corresponding to the azomethine group (-C=N) was found at 1626 cm^{-1} . On complexation, this band gets shifted to the range of 1616-1601 cm^{-1} . This indicated the involvement of N-atom of azomethine (-C=N) group in the complex formation [24]. Therefore IR spectra suggested that the ligand (**2a**) coordinated to metal ions (Mn^{2+} and Co^{2+}) through the N- atom of azomethine (-C=N) group and the O-atom of phenolic (O-Ar) group. The peak at the range of 756-761 cm^{-1} in the spectra of complexes, was assigned for bromide. The new bands appearing in the regions 565-590 cm^{-1} and 460-475 cm^{-1} in the spectra of **3a** and **4a** complexes could be assigned to M-O and M-N stretching frequencies, respectively [25]. FT-IR spectra of the Schiff base, LH (**2a**) and its Mn(II) and Co(II) complexes (**3a** and **4a**) are given in Figs 3.1-3.3.

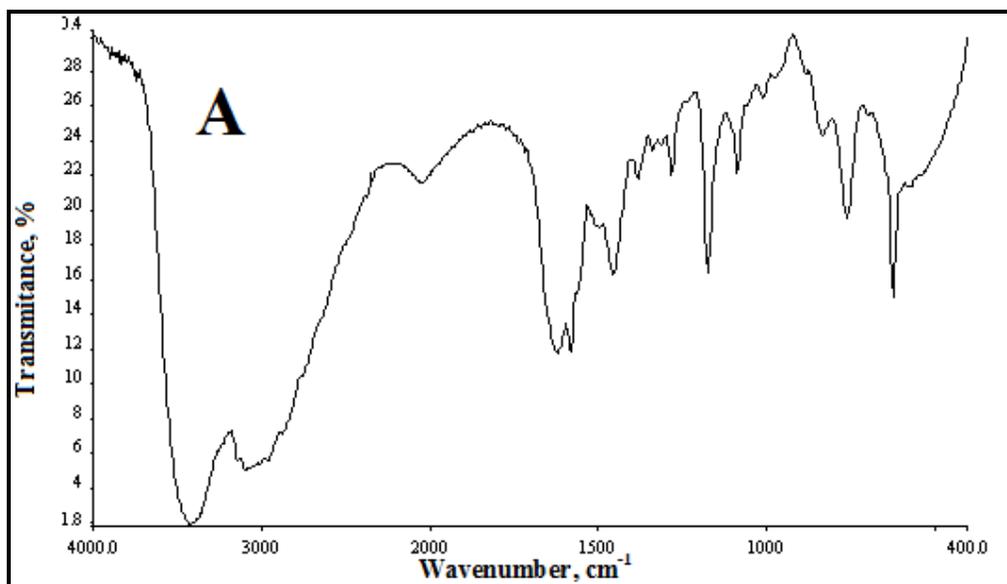


Fig 3.1. FT-IR spectrum of LH (2a).

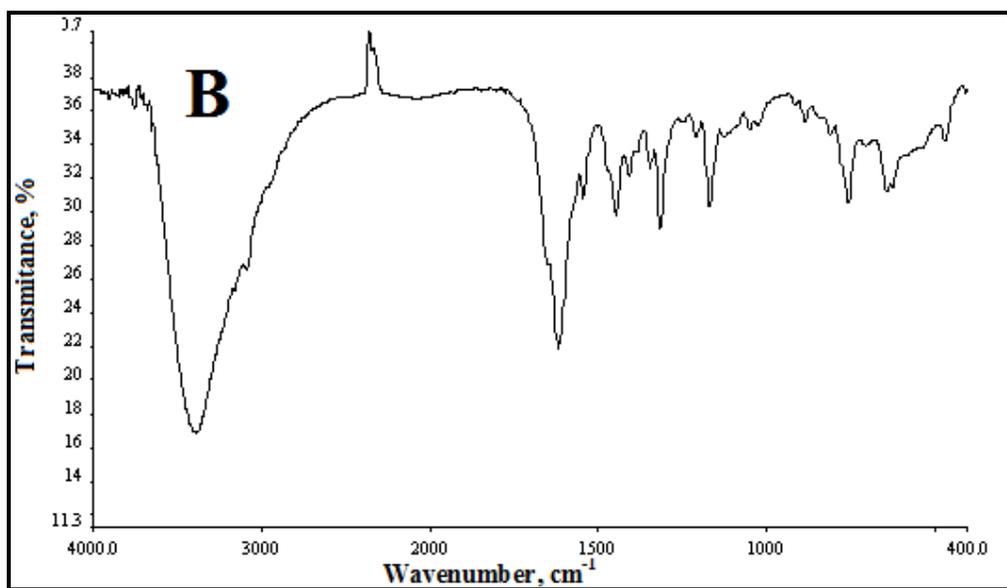


Fig 3.2. FT-IR spectrum of Mn(II) complex (3a).

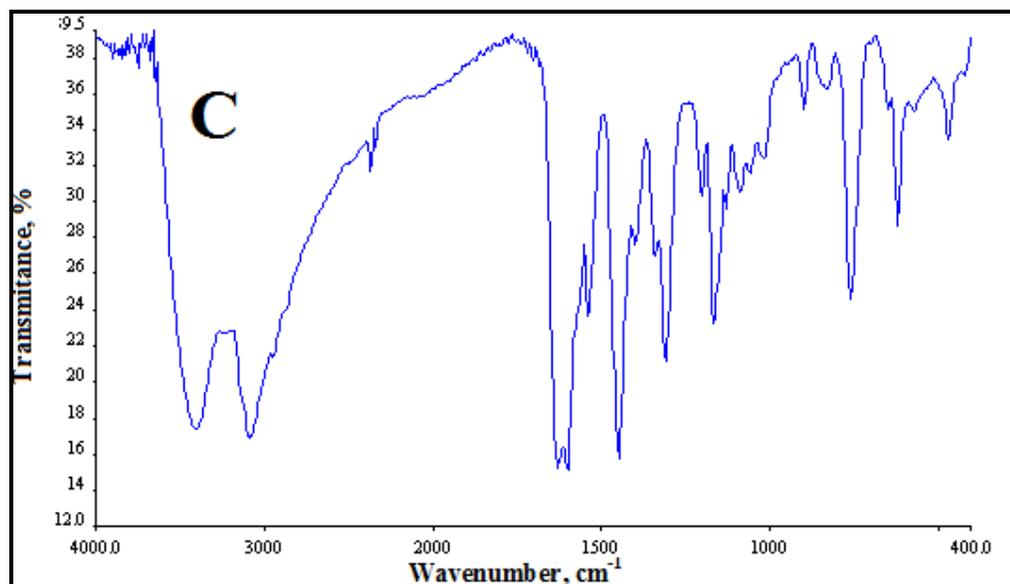


Fig 3.3. FT-IR spectrum of Co(II) complex (**4a**) .

3.3.2. Mass spectral studies

The mass spectra of the ligand (**2a**) showed a molecular ion peaks (m/z) at 230, which was assigned to M^+ , $[C_{13}H_{16}N_3O]^+$ ion peak. The Mn(II) complex (**3a**) exhibited a peak (m/z) at 513 which was due to $[M-2Br]^+$ ($M = [C_{26}H_{30}MnN_6O_2]^+$) ion. A peaks (m/z) at 517 in the ESI-MS spectrum of Co(II) complex (**4a**) attributed to the at $[M-2Br]^+$ ($M = [C_{26}H_{30}CoN_6O_2]^+$).ion. The different molecular ion peaks, observed in the mass spectra of the Mn(II) and Co(II) complexes, were assigned to different fragmentations of the metal complexes by successive rupture of different bonds in order to form stable ions. The ESI-MS spectra of the ligand and complexes are shown in Figs 3.4-3.6.

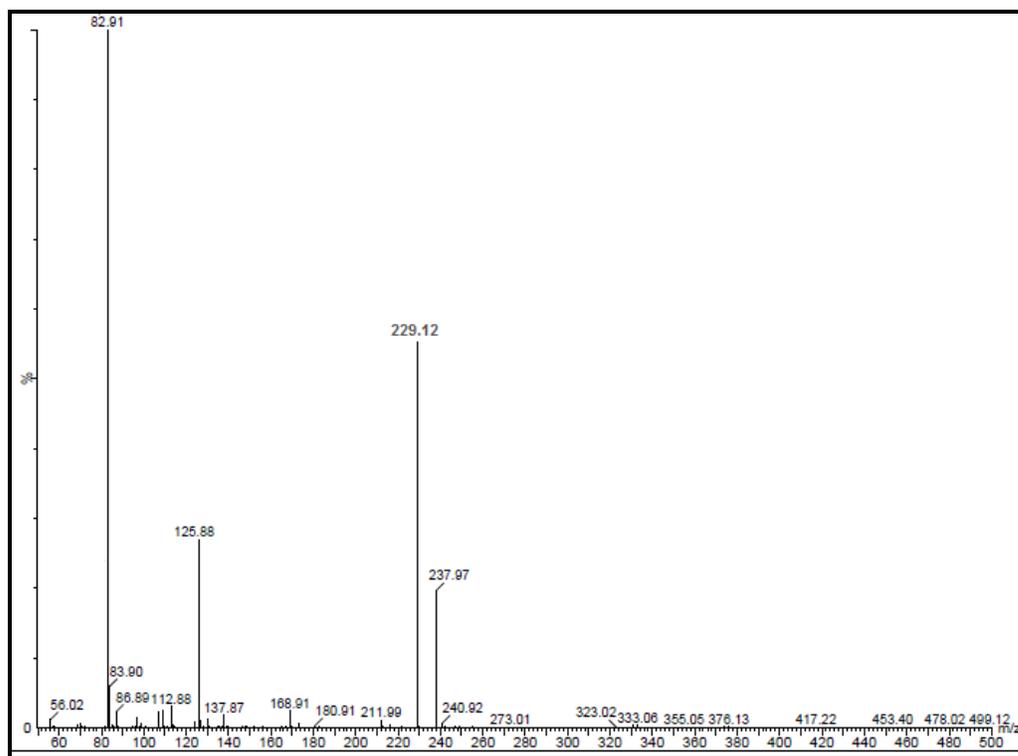


Fig 3.4. ESI-MS spectrum of LH (2a).

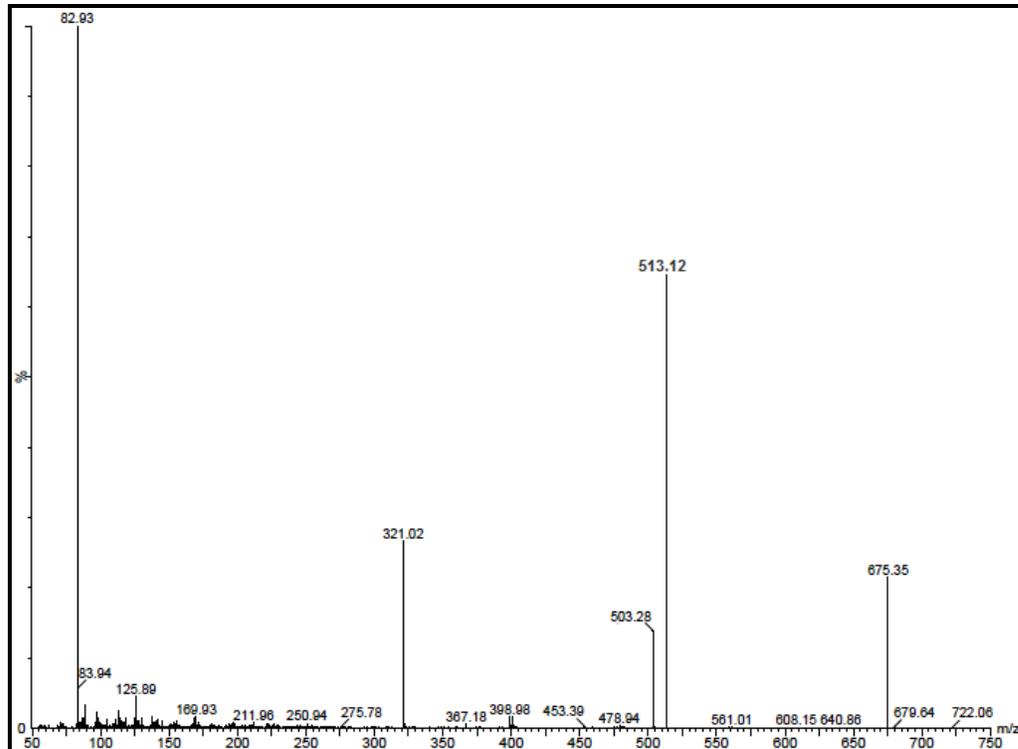


Fig 3.5. ESI-MS spectrum of Mn(II) complex (3a).

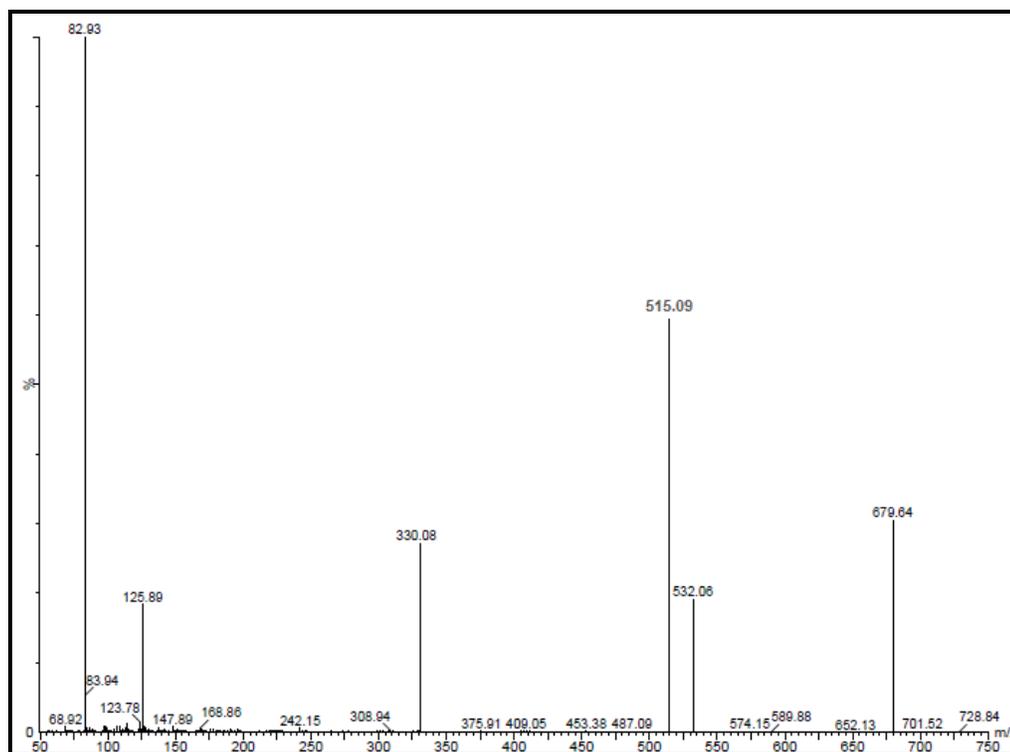


Fig 3.6. ESI-MS spectrum of Co(II) complex (**4a**).

3.3.3. ^1H and ^{13}C -NMR spectral studies

^1H -NMR and ^{13}C -NMR spectra of Schiff base (**LH**) were recorded in $\text{DMSO-}d_6$ (Shown in Fig 3.7 and Fig 3.8.). ^1H -NMR of the LH (**2a**) showed singlet at 9.20 ppm assignable to proton of the azomethine group ($-\text{CH}=\text{N}-$) probably due to the effect of the *ortho*-hydroxyl group in the aromatic ring. A singlet at 8.31 ppm can tentatively be attributed to hydroxyl proton. The LH (**2a**) showed downfield shift of the $-\text{OH}$ proton was due to intramolecular ($\text{O}-\text{H}\cdots\text{N}$) hydrogen bond [26]. ^{13}C -NMR spectra of ligand exhibited peaks at δ 136.98 and 136.36 presumably due to the phenolic ($\text{C}-\text{O}$) and imino ($-\text{CH}=\text{N}$) carbon atoms (due to Keto-imine tautomerism). The chemical shifts due to the aromatic carbons appeared at δ 124.58, 123.13, 122.55 and 119.58.

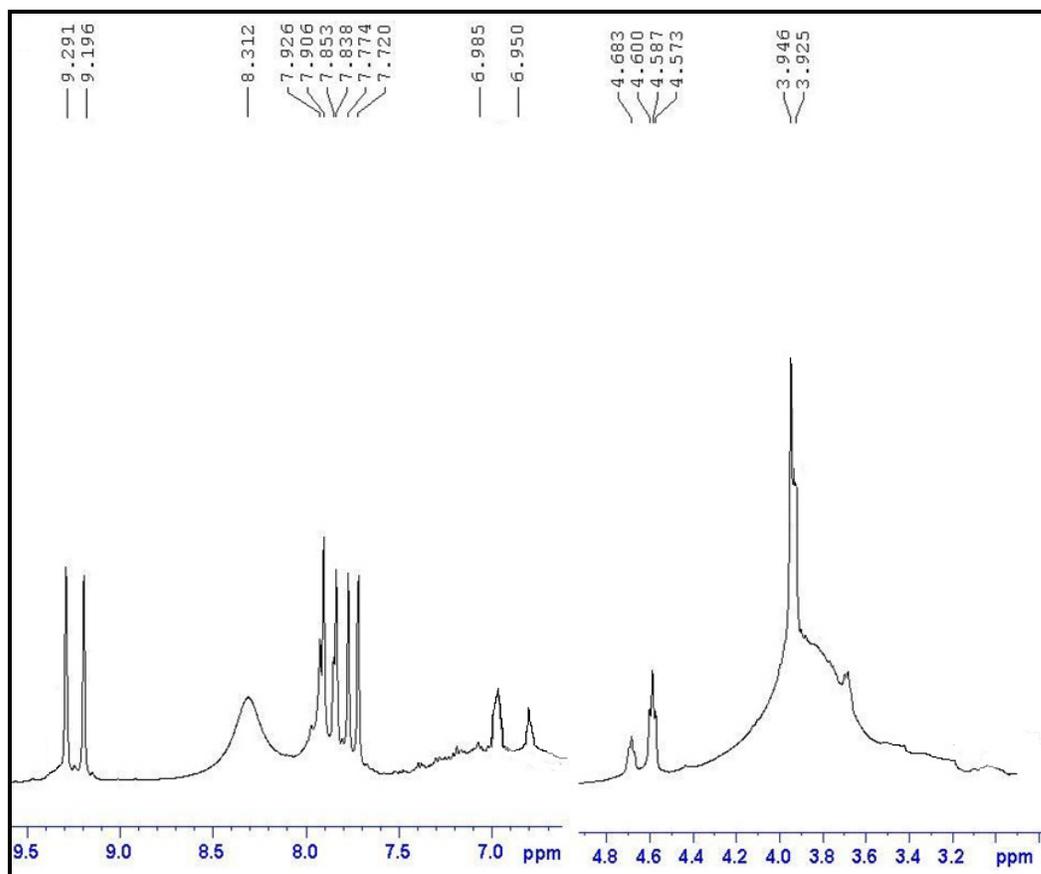


Fig 3.7. ¹H-NMR spectrum of LH (2a).

3.3.4. Molar conductance measurements

The molar conductance of the complexes (**3a** and **4a**) (Λ_m) were obtained from the relation $\Lambda_m = 1000 \times \kappa/c$, where c and κ stand for the molar concentration and specific conductance of the metal complexes, respectively. The complexes (1.8×10^{-3} M) were dissolved in *N,N*-dimethylformamide and their specific conductivities were measured at 25 °C. The molar conductances were found to be in the range 212-238 $\Omega^{-1} \text{ cm}^{-1} \text{ mol}^{-1}$ indicating their 1:2 electrolytic behaviour [27].

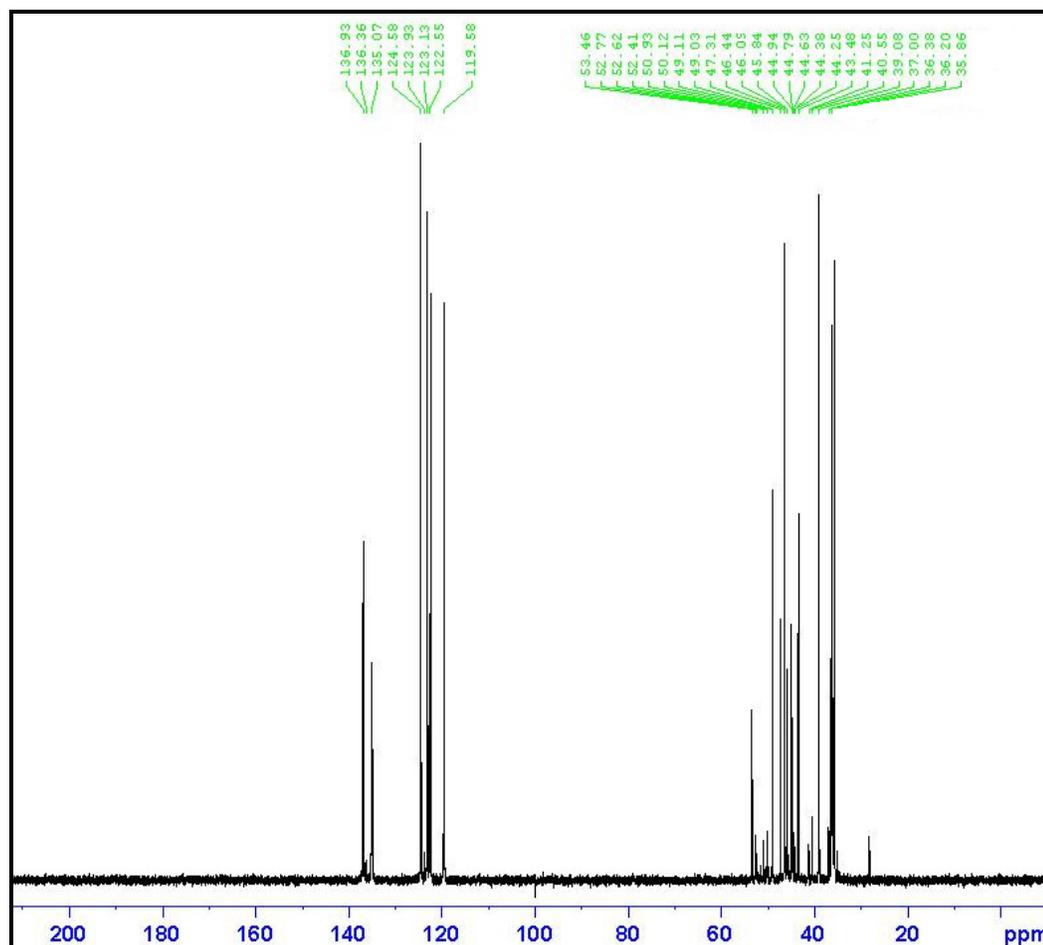


Fig 3.8. ^{13}C -NMR spectrum of LH (**2a**).

3.3.5. Electronic absorption spectral and magnetic moment studies

UV-Visible spectra of the Schiff base (**2a**) and its metal complexes (Given in Fig 3.9) were recorded in methanol at ambient temperature. The electronic absorption spectrum of ligand showed three absorption bands at 318, 255 and 214 nm, respectively due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ transitions and transitions involved with the imidazolium moiety [28, 29]. Mn(II) complex (**3a**) showed three absorption bands at 314, 255 and 211 nm; that was the ligand band at 318 nm showed hypsochromic shift probably due to coordination with Mn^{2+} (d^5) ion. Co(II) complex (**4a**) also displayed three absorption bands at 220, 248 and 403 nm due to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$, ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transitions, respectively. Thus UV-Visible spectra of both the complexes (**3a** and **4a**) suggested no Jahn-Teller distortion and tetrahedral geometry was proposed for both the complexes [30].

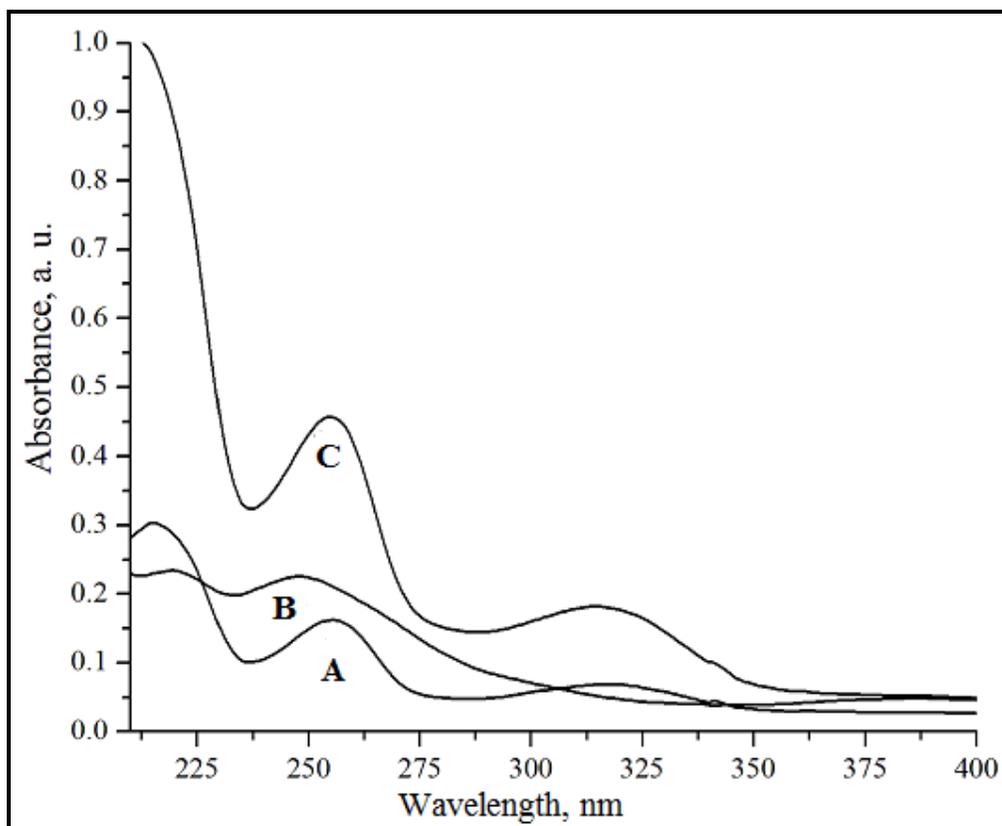


Fig 3.9. UV-visible spectra in methanol (concentration of the solutions 1×10^{-4} M):
 (A) LH (**2a**); (B) Mn(II) complex (**3a**) and (C) Co(II) complex (**4a**).

This fact was also substantiated by the results obtained from FT-IR, ESI-MS, UV-Visible spectra and the measured magnetic moments (5.86 and 4.67 B.M, respectively for **3a** and **4a** complex).

3.3.6. Antibacterial activities

The Schiff base ligand (**2a**) and their metal complexes (**3a** and **4e**) were studied against the gram negative bacteria *Escherichia coli* and gram positive bacteria *Bacillus subtilis*. to assess their potentials as antibacterial agents. Stock solutions of synthesised compounds were prepared by dissolving the compounds in water and serial dilutions of the solutions were made in sterile distilled water for different concentrations to determine the minimum inhibition concentration (MIC). The concentrations of the tested compounds were 31.25, 62.5, 125 and 250 $\mu\text{g mL}^{-1}$ in comparison to the standard drug *Ampicilin*. The nutrient agar medium was poured into 0.5 mL culture contained in Petri dishes and well diffusion technique [31, 32] was

performed. Petri dishes were placed in an incubator at 37 °C for 24 h. No significant inhibition zones surrounding the well were observed against the complexes (minimum

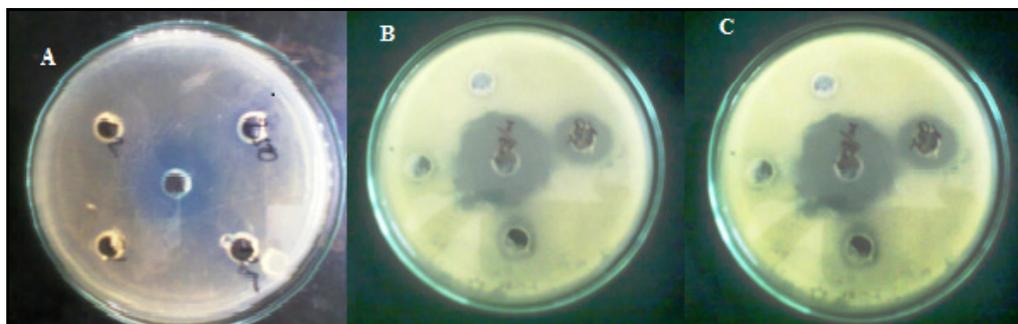


Fig 3.10. Inhibition zones for anti-bacterial activities: A, LH (**2a**); B, the Mn(II) complex (**3a**); C, the Co(II) complex (**4a**) against *Escherichia Coli*.

inhibition concentration against *Escherichia coli* was shown in Fig 3.10), but the ligand showed very low antibacterial activities with well diameters in the range of 1.0-1.2 mm at the concentration $250 \mu\text{g mL}^{-1}$ against the bacteria studied.

3.4. Conclusion

Here in this work, the synthesis and physico-chemical characterization of an imidazolium ionic liquid-supported Schiff base, *i.e.*, 1-{2-(2-hydroxybenzylideneamino)ethyl}-3-methylimidazolium bromide, and its Mn(II) and Co(II) complexes were described. Different analytical and spectral studies revealed that the Schiff base acts as bidentate ligand that coordinated through the azomethine nitrogen and phenolic oxygen atoms to Mn(II) and Co(II) ions and thus formed tetrahedral 1:2 (M:L) complexes. The synthesized compounds were tested for their antibacterial activities against the bacteria *Escherichia coli* and *Bacillus subtilis*. The observed minimum inhibition (MIC) concentration, suggested that the synthesized complexes have no significant antibacterial activities against the bacteria *Escherichia coli* and *Bacillus subtilis*.

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