

CHAPTER VI

Physico-chemical characterization and biological studies of newly synthesized metal complexes of an Ionic liquid-supported Schiff base: 1-{2-[(2-hydroxy-5-bromobenzylidene)amino]ethyl}-3-ethylimidazolium tetrafluoroborate*

6.1. Introduction

Ionic liquids (ILs) are organic salts that have low melting points below the boiling point of water and are stable in liquid state at 100 °C, even at room temperature. They can exhibit numerous desirable properties such as negligible vapor pressure [1], ability to dissolve various substrates; high electrical conductivity [2] and thermal stability [3-5]. ILs are considered as alternatives to volatile organic solvents (VOC) in various organic transformations. Due to low toxicity and biodegradability they have been termed as green solvents [6]. An unusual feature of ILs is the tenability of their physical and chemical properties by variation of cations and anions. Usually large organic cations and smaller anions are designed to carry on required functions [7]. Although most of the works on ILs highlight their use as reaction media in organic synthesis, these liquids are gradually drawing attention in the field of inorganic and material chemistry [8, 9]. The concept of functionalized ionic liquid (FILs), by introducing additional functional group as a part of cation or anion, has presently become a subject of interest [10-15]. There is huge possibility of chemical structure modifications through the incorporation of specific functionality. Such FILs are able to interact with a metal centre and contribute to an enhanced stability of metal salts [16]. Metal containing ILs are considered as promising new material that combine the feature of ILs with additional intrinsic magnetic, catalytic and spectroscopic properties depending on the incorporated metal ion [17].

Schiff bases, usually formed by the condensation of primary amine with an aldehyde are one of the most prevalent ligands in coordination chemistry [18]. Schiff-bases containing hetero-atoms such as nitrogen, oxygen and sulphur are of special interest due to their different ways of bonding with transition metal ions and unusual

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configuration [19]. They have been reported to exhibit a variety of biological actions due to the presence of azomethine linkage, which is responsible for different types of antibacterial, herbicidal and antifungal activities [20, 21]. Transition metal complexes of Schiff bases carrying nitrogen and other donor sites have a variety of applications including biological, medicinal analytical in addition to their vital role in organic synthesis and catalysis [22-26]. Hence, in this chapter, I have reported the synthesis of Co(II), Ni(II) and Cu(II) complexes of an ionic liquid supported Schiff base and their characterization using spectroscopic, analytical and magnetic data. Furthermore the applications of the Schiff base and its complexes as potential antibacterial agents have also been explored.

6.2. Experimental Section

6.2.1. *Materials and Methods*

All the reagents were of analytical grade and used without further purification. 1-ethylimidazole, 2-bromoethylamine hydrobromide and sodium tetrafluoroborate were procured from Sigma Aldrich, Germany. 5-bromo-2-hydroxybenzaldehyde, Co(II), Ni(II) and Cu(II) acetates 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-ethylimidazolium tetrafluoroborate, [2-aeim]BF₄ (**1c**) was synthesized by following a literature procedure [27]. The synthesis and physicochemical characterization of the FIL has been illustrated earlier in chapter II.

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 was recorded at room temperature on a FT-NMR (Bruker Avance-II 400 MHz) spectrometer by using DMSO-*d*₆ and D₂O as solvents. Chemical shifts are mentioned in ppm downfield of internal standard tetramethylsilane (TMS). Elemental microanalyses (C, H and N) were conducted by using Perkin-Elmer (Model 240C) analyzer. Metal content 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 prepared compounds was confirmed by thin layer chromatography (TLC) on silica gel plates and the plates

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were visualized with UV-light and iodine as and when required. The UV-Visible spectra were recorded in methanol with a JascoV-530 double beam Spectrophotometer at ambient temperature. Specific conductance was measured at (298.15 ± 0.01) K with a Systronic conductivity TDS-308 metre. Magnetic susceptibilities were measured at room temperature with a Sherwood Scientific Ltd magnetic susceptibility balance (Magway MSB Mk1). The melting point of the ligand and its complexes were determined by open capillary method. Antibacterial activities (*in vitro*) of the synthesized compounds were tested by disc diffusion method. All the bacteria strains were procured from MTCC, Chandigarh, and were cultured at the Department of Microbiology, Raiganj University, Raiganj, West Bengal, India.

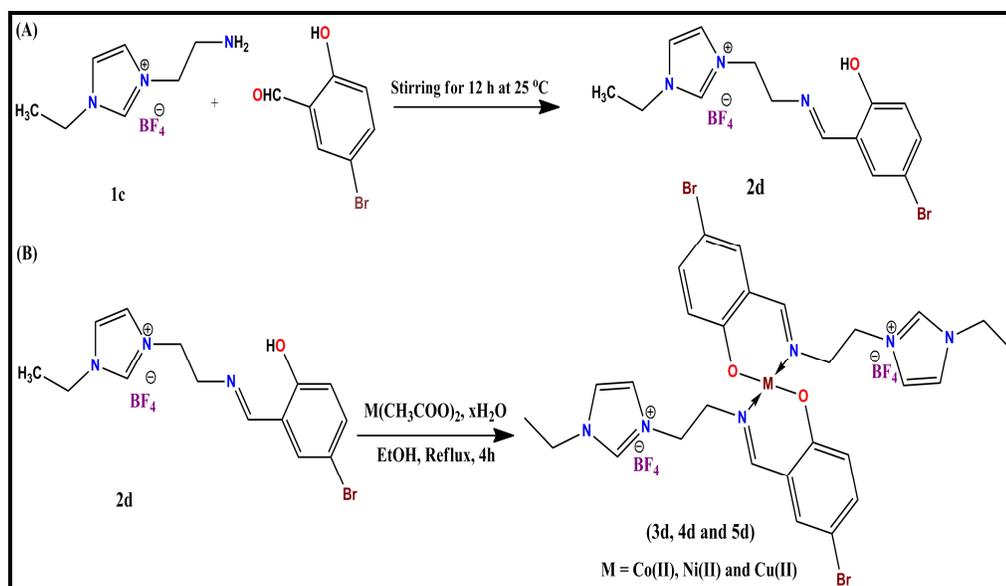
6.2.2. Synthesis of imidazolium ionic liquid-supported Schiff base, LH (2d)

The ionic liquid-supported Schiff base (LH) was synthesized by following a literature procedure [28]. A mixture of 5-bromo-2-hydroxybenzaldehyde (2.01 g, 10 mmol) and [2-aeim]BF₄ (2.27 g, 10 mmol) in methanol was stirred at room temperature for 12 h. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with ethanol. The precipitate was filtered, washed with cold ethanol and dried to afford the expected ligand as light yellow solid. 3.03 g (yield 75 %). M.p.: 98-100 °C; Anal. Calc. for C₁₄H₁₇N₃OBBrF₄ (410): C, 41.01; H, 4.18; N, 10.25. Found: C, 40.91; H, 4.11; N, 10.21 %. FT-IR (KBr, cm⁻¹): 3449 (O-H), 1673 (C=N), 1276 (C-O), 1114 (B-F). ¹H NMR: (400 MHz, DMSO-*d*₆): δ 2.49 (s, 3H, CH₃), 3.82 (t, 1H, N-CH₂), 3.99 (t, 1H, N-CH₂), 4.52 (t, 1H, N-CH₂), 6.91–6.85 (m, 3H, Ar-H), 7.33 (s, 1H, NCH), 7.42 (s, 1H, NCH), 8.50 (s, 1H, N=CH), 7.73 (s, 1H, N(H)CN), 9.10 (s, 1H, OH). ¹³C NMR (400 MHz, DMSO-*d*₆): δ 137.31, 135.59, 123.76, 123.09, 122.41, 122.25, 119.63, 53.91, 48.52, 48.14, 44.99, 43.71, 41.15, 35.90. UV-Vis (Methanol) $\lambda_{\text{max/nm}}$: 218, 250, 336. ESI-MS (CH₃OH, m/z): 322 ([M-H-BF₄]⁺, M= [C₁₄H₁₇N₃OBr]⁺).

6.2.3. Synthesis of the metal complexes (3d, 4d and 5d)

To a ethanolic solution (20 mL) of LH (2d) (0.410 g, 1 mmol) in a round bottomed flask equipped with a condenser, metal acetate salt of Co(II), Ni(II) and Cu(II), *viz.*, (0.5 mmol) dissolved in ethanol was added gradually. The reaction mixture was refluxed for 4 h until the starting materials were completely consumed as monitored by TLC. On completion of the reaction, solvents were evaporated and the

reaction mixture was cooled to room temperature. The precipitate was collected by filtration, washed successively with cold ethanol (10 mL \times 3). Finally it was dried in vacuum desiccators to obtain the solid product. The complexes are soluble in *N,N*-dimethylformamide, dimethylsulphoxide, acetonitrile, methanol and water. A schematic representation of the synthesis procedure is shown in Scheme 6.1.



Scheme 6.1. Synthesis of the ionic liquid supported Schiff base, 1-{2-[(2-hydroxy-5-bromobenzylidene)amino]ethyl}-3-ethylimidazolium tetrafluoroborate (**2d**), and its metal complexes (**3d**, **4d** and **5d**) from (**2d**).

6.2.2.1. Co(II) complex (3d): Brown solid; 0.62 g (yield, 71 %) M. p.: 128-130°C; Anal. Calc. for $\text{C}_{28}\text{H}_{32}\text{CoB}_2\text{Br}_2\text{F}_8\text{N}_6\text{O}_2$ (877): C, 38.35; H, 3.68; N, 9.58; Co, 6.72. Found: C, 38.16; H, 3.53; N, 9.32, Co, 6.42 %. FT-IR (KBr, cm^{-1}): 3442 (O-H), 1629 (C=N), 1316 (C-O), 1019 (B-F), 633 (M-O), 523 (M-N). UV-Vis (Methanol) $\lambda_{\text{max/nm}}$: 220, 338, 394. ESI-MS (CH_3OH , m/z): 701 $[\text{M}-2\text{BF}_4]^+$, $\text{M} = [\text{C}_{28}\text{H}_{32}\text{CoBr}_2\text{N}_6\text{O}_2]^+$.

6.2.2.2. Ni(II) complex (4d): Light green solid; 0.60 g (yield, 69%). M. p. 140-142 °C; Anal. Calc. for $\text{C}_{28}\text{H}_{32}\text{NiB}_2\text{Br}_2\text{F}_8\text{N}_6\text{O}_2$ (876.7): C, 38.36; H, 3.68; N, 9.58; Ni, 6.69. Found: C, 38.11; H, 3.50; N, 9.37, Ni, 6.33 %. FT-IR (KBr, cm^{-1}): 3437 (O-H), 1627 (C=N), 1314 (C-O), 1018 (B-F), 634 (M-O), 535 (M-N). UV-Vis

(Methanol) $\lambda_{\text{max}}/\text{nm}$: 219, 340, 400. ESI-MS (CH_3OH , m/z): 702 ($[\text{M}+2\text{H}-2\text{BF}_4]^+$, $\text{M} = [\text{C}_{28}\text{H}_{32}\text{NiBr}_2\text{N}_6\text{O}_2]^+$).

6.2.2.3. Cu(II) complex (5d): Dark green solid; 0.64 g (yield, 73 %). M. p. 147-149 °C; Anal. Calc. for $\text{C}_{28}\text{H}_{32}\text{CuBr}_2\text{F}_8\text{N}_6\text{O}_2$ (881.56): C, 38.15; H, 3.66; N, 9.53; Cu, 7.21. Found: C, 38.07; H, 3.49; N, 9.31, Cu, 6.99%. FT-IR (KBr, cm^{-1}): 3448 (O-H), 1625 (C=N), 1317 (C-O), 1014 (B-F), 648 (M-O), 559 (M-N). UV-Vis (Methanol) $\lambda_{\text{max}}/\text{nm}$: 222, 342, 396. ESI-MS (CH_3OH , m/z): 705.74 $[\text{M}-2\text{BF}_4]^+$, $\text{M} = [\text{C}_{28}\text{H}_{32}\text{CuBr}_2\text{N}_6\text{O}_2]^+$.

6.4.4. Antibacterial assay

Antibacterial activities of the synthesized compounds were tested *in vitro* against the four Gram negative bacteria (*E. coli*, *P. aeruginosa*, *P. vulgaris* and *E. aerogenes*) and two Gram positive bacteria (*S. aureus* and *B. cereus*) strains using agar disc diffusion method [29, 30] by NCCLS (National Committee for Clinical Laboratory Standards, 1997). The nutrient agar (Hi-Media Laboratories Limited, Mumbai, India) was autoclaved at 121 °C and 1 atm for 15-20 minutes. The sterile nutrient media was kept at 45-50°C, after that 100 μL of bacterial suspension containing 10^8 colony-forming units (CFU)/mL were mixed with sterile liquid nutrient agar and poured into the sterile Petri dishes. Upon solidification of the media, filter disc (5 mm diameter) was individually soaked with different concentration (10, 20, 30, 40 and 50 $\mu\text{g}/\text{mL}$) of each sample solution and placed on the nutrient agar media plates. The different concentrations were made by diluting with DMSO. The plates were incubated for 24 hours at 37°C. The diameter of the zone of inhibition (including disc diameter of 5 mm) was measured. Each experiment was performed three times to minimize the error and the mean values were accepted.

6.3. Results and Discussion

All the isolated compounds were stable at room temperature to be characterized by different analytical and spectroscopic methods.

6.3.1. FT-IR spectral studies

The assignments of the IR bands of the synthesized Co(II), Ni(II) and Cu(II) complexes have been made by comparing with the bands of ligand (LH) to determine the coordination sites involved in chelation. Only the distinct and characteristic peaks have been discussed. FT-IR spectra of the ligand exhibited a strong broad absorption

band at $3450.61\text{-}3236\text{ cm}^{-1}$; this band was assigned to the hydrogen bonded -OH of the phenolic group with H-C(=N) group of the ligand (OH...N=C) [31, 32]. All the complexes showed broad diffuse band at $3437\text{-}3448\text{ cm}^{-1}$ that may be attributed to the presence of the solvated water or ethanol molecules. However, these bands appear stronger compare to that of the ligand due to the moisture content of the ligand subject to the intrinsic nature of the anion tetrafluoroborate [33-35]. The band for phenolic C-O of free ligand was observed at 1276 cm^{-1} . Upon complexation, this band was shifted to higher wave number $1314\text{-}1317\text{ cm}^{-1}$ for all the complexes. This fact suggested the involvements of phenolic C-O in the coordination process [36]. This interpretation is further confirmed by the appearance of M-O band at $633\text{-}638\text{ cm}^{-1}$ in the spectra of the metal complexes. The intense band at 1673 cm^{-1} that corresponds to azomethine group (-C=N) in the free ligand was shifted to the lower frequencies in the range $1625\text{-}1629\text{ cm}^{-1}$ in case of the metal complexes, indicating the participation of azomethine group (-C=N) in the coordination sphere [37]. This was further emphasized by the appearance of a new weak to medium intensity absorption band in the region $523\text{-}559\text{ cm}^{-1}$ that could be attributed to M-N stretching vibration for the metal complexes [38]. The bands in the range of $1014\text{-}1114\text{ cm}^{-1}$ for the spectra of the ligand and metal complexes were assigned for B-F stretching frequency. IR spectra of the ligand, LH (**2d**) and its metal complexes (**3d**, **4d** and **5d**) are given in Figs 6.1-6.4.

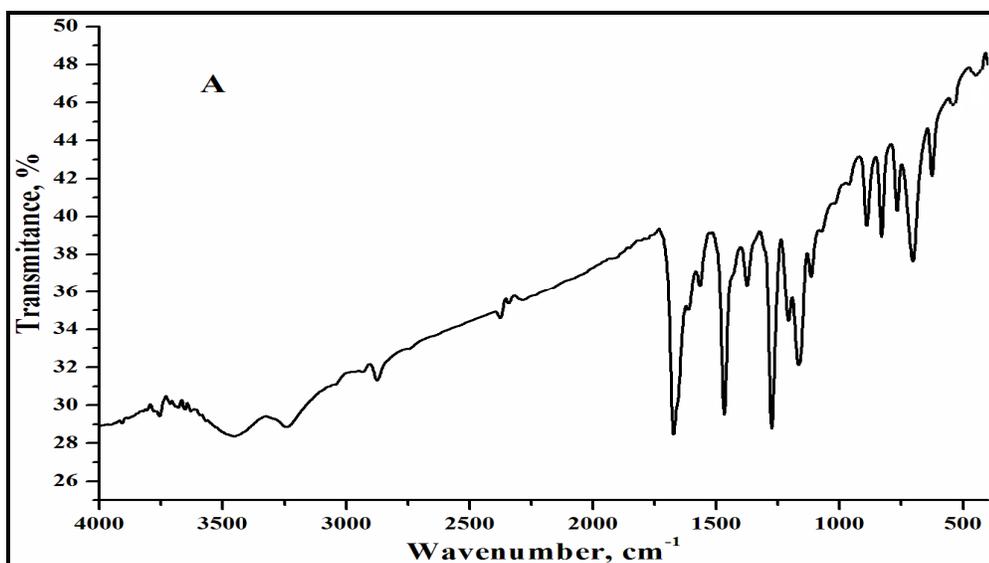


Fig 6.1. FT-IR spectrum of LH (**2d**).

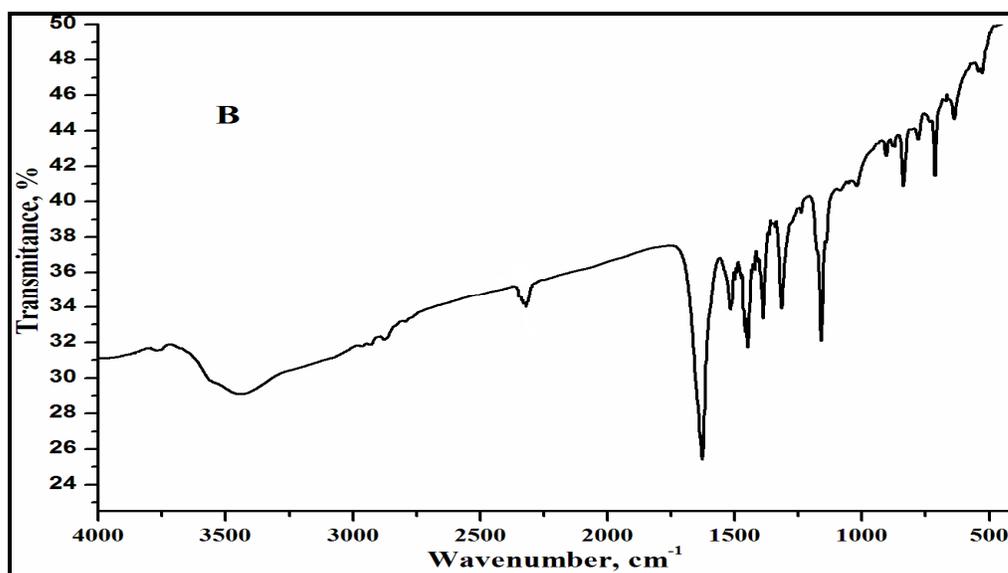


Fig 6.2. FT-IR spectrum of Co(II) complex (3d).

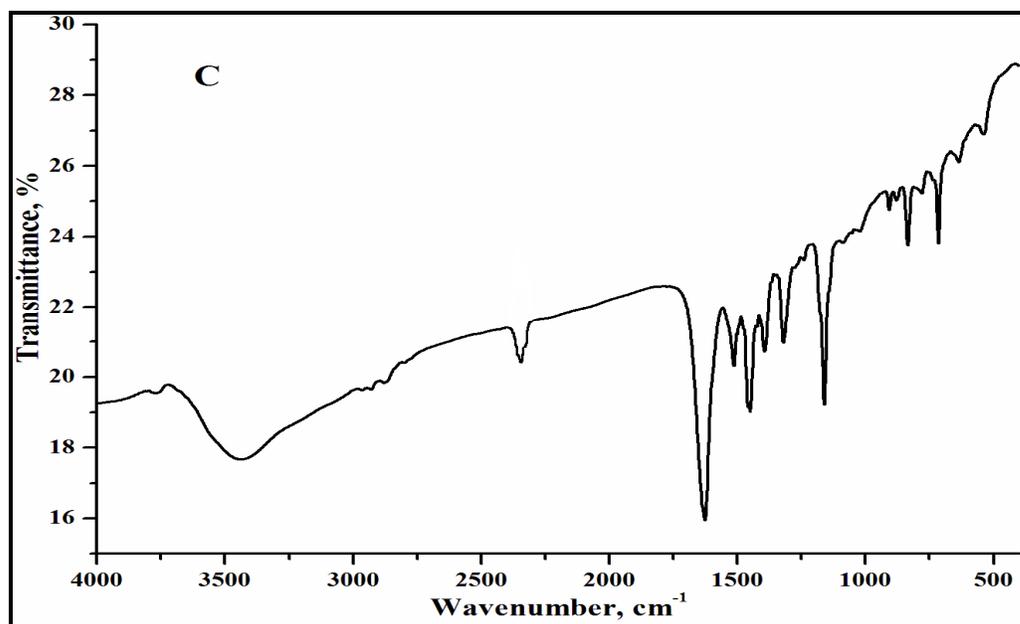


Fig 6.3. FT-IR spectrum of Ni(II) complex (4d).

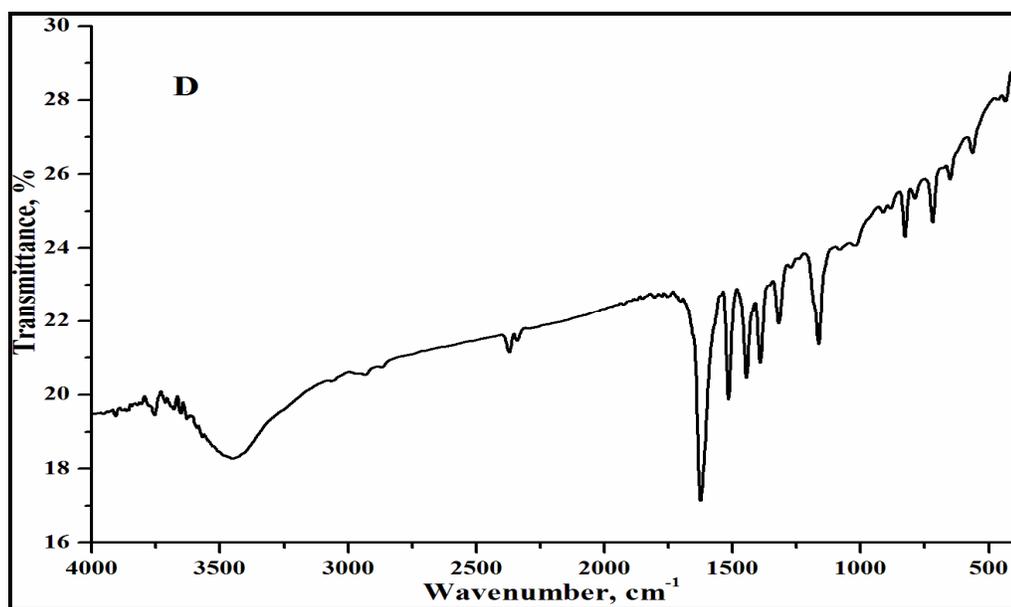


Fig 6.4. FT-IR spectrum of Cu(II) complex (**5d**).

6.3.2. Mass spectral studies

To get information regarding the structure of the synthesized compounds at the molecular level, electrospray ionization (ESI) mass spectrometry was performed using methanol as solvent. The ligand (LH) exhibited a peak (m/z) at 322 which could be assigned to $[M-H-BF_4]^+$ ion, $[M= C_{14}H_{17}N_3OBr]^+$ [39]. The Co(II) complex (**3d**) displayed a peak (m/z) at 701.49 which was due to the $[M-2BF_4]^+$ ($M= [C_{28}H_{32}CoBr_2N_6O_2]^+$) ion. A peaks (m/z) at 701.62 in the ESI-MS spectrum of Ni(II) complex (**4d**) was assigned for the $[M+H-2BF_4]^+$ ($M= [C_{28}H_{32}NiBr_2N_6O_2]^+$) ion. The Cu(II) complex (**5d**) exhibited a peak (m/z) at 705.74 which was attributed to $[M-2BF_4]^+$ ($M= [C_{28}H_{32}CuBr_2N_6O_2]^+$) ion [40]. The mass spectra of the ligand and complexes were in good agreement with the respective structures as revealed by the elemental and other spectral analyses. The ESI-MS spectra of the ligand and complexes are shown in Figs 6.5-6.8.

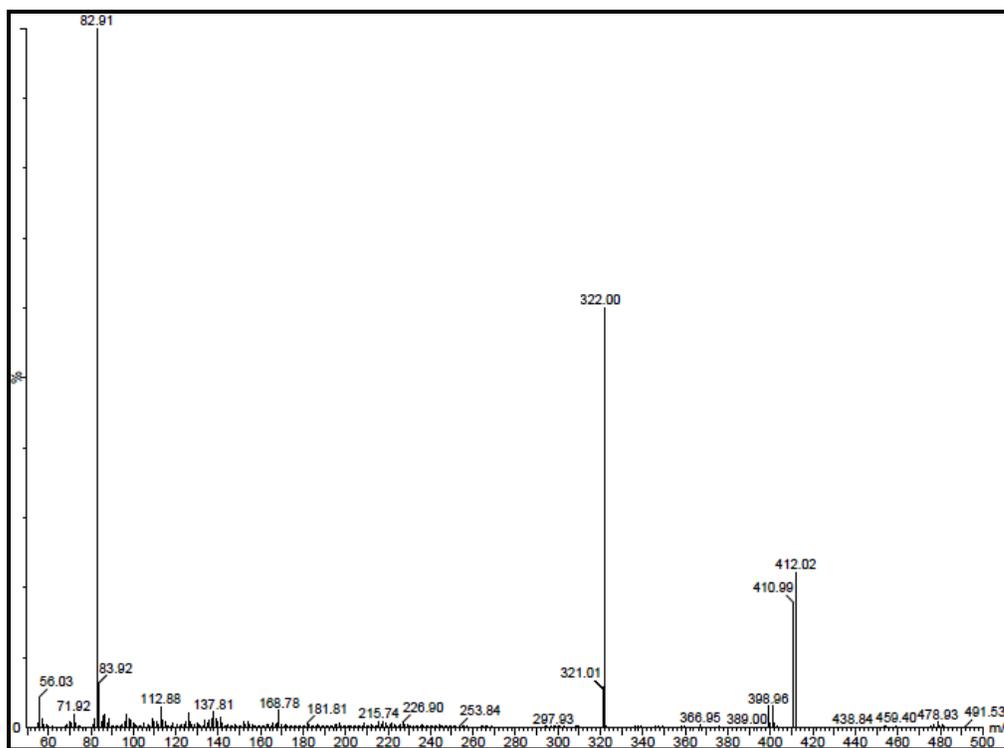


Fig 6.5. ESI-MS spectrum of LH (2d).

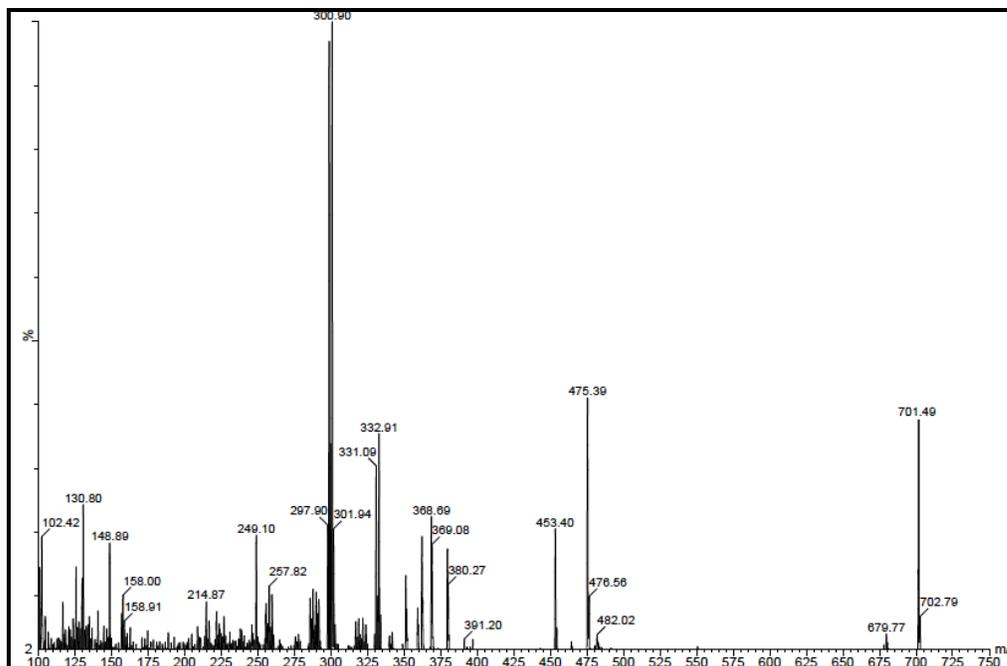


Fig 6.6. ESI-MS spectrum of Co(II) complex (3d).

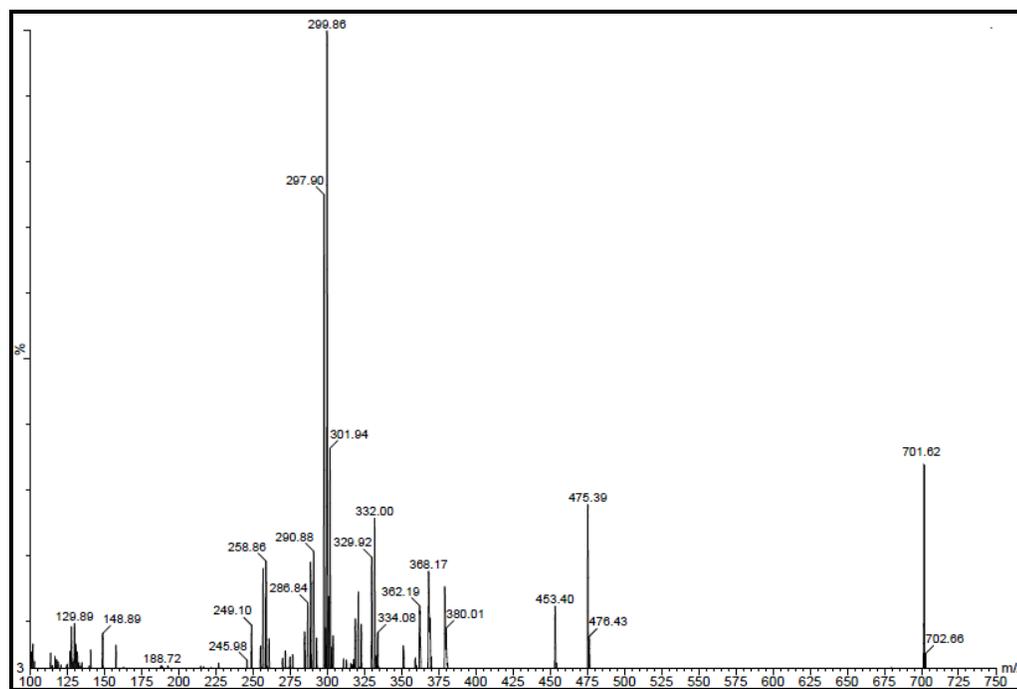


Fig 6.7. ESI-MS spectrum of Ni(II) complex (4d).

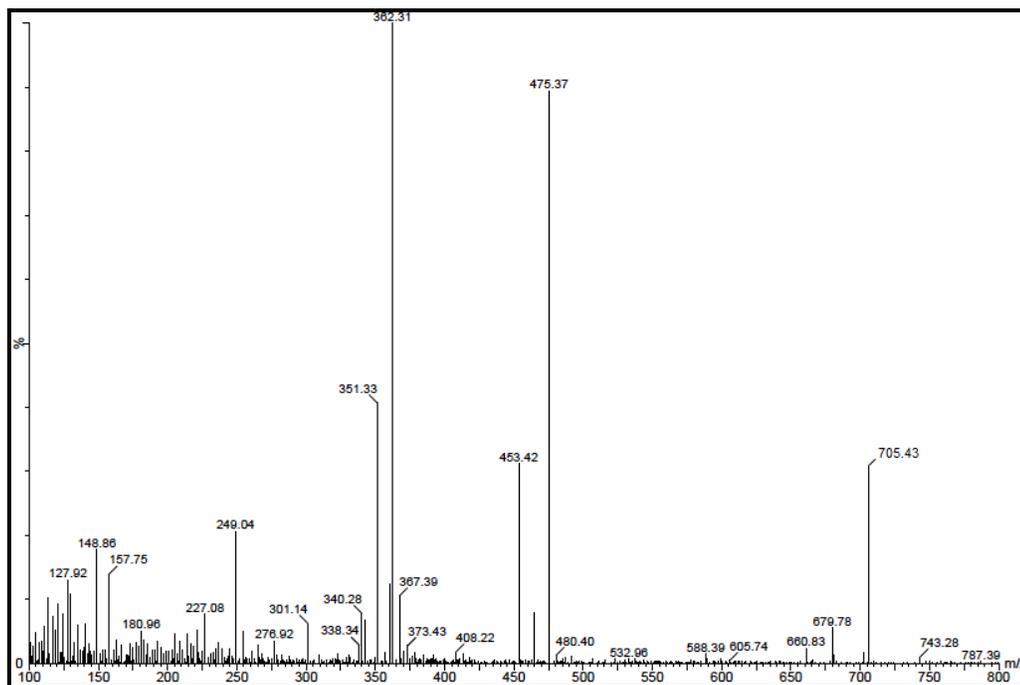


Fig. 6.8. ESI-MS spectrum of Cu(II) complex (5d)

6.3.3. ^1H and ^{13}C -NMR spectral studies

^1H -NMR and ^{13}C -NMR spectra of Schiff base were recorded in $\text{DMSO-}d_6$ (Shown in Fig 6.9 and Fig 6.10). ^1H -NMR of the ligand (LH) showed singlet at δ 8.50 ppm assignable to proton of the azomethine group ($-\text{CH}=\text{N}-$) presumably due to the effect of the *ortho*-hydroxyl group in the aromatic ring. A singlet at δ 9.10 ppm could tentatively be attributed to hydroxyl proton. The LH (**2d**) displayed downfield shift of the $-\text{OH}$ proton was due to intramolecular ($\text{O-H}\cdots\text{N}$) hydrogen bond [41]. ^{13}C -NMR spectra of ligand exhibited peaks at δ 137.31 and 135.59 presumably due to the phenolic (C-O) and imino ($-\text{CH}=\text{N}$) carbon atoms (due to Keto-imine tautomerism). The chemical shifts of the aromatic carbons appeared at δ 123.76, 123.09, 122.41, 122.25 and 119.53.

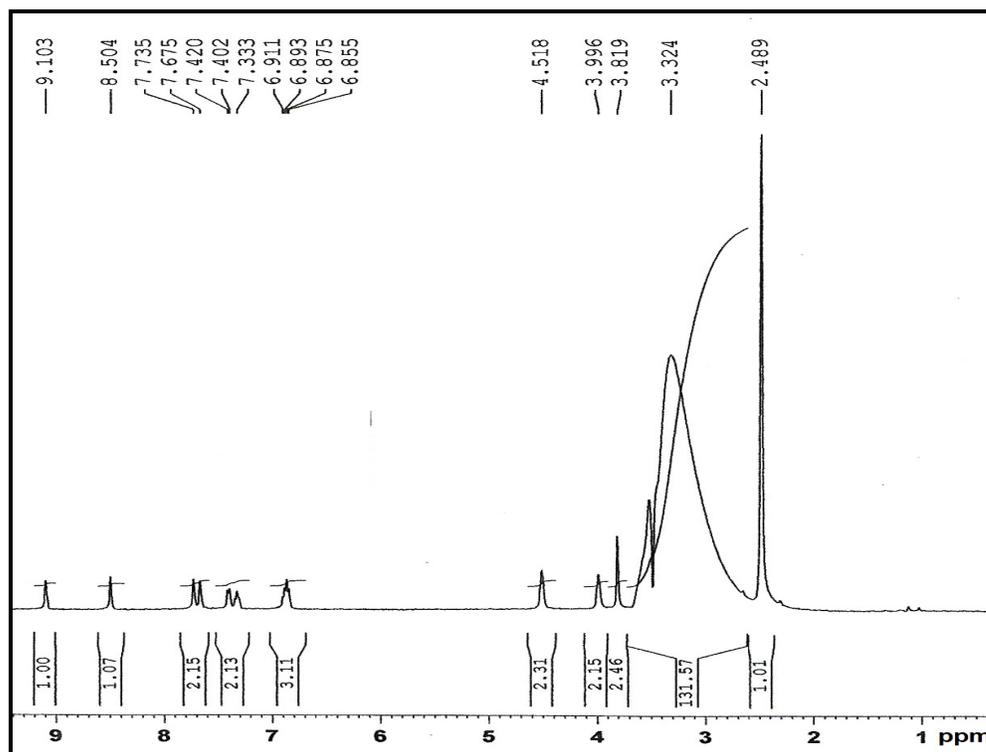


Fig 6.9. ^1H -NMR spectrum of LH (**2d**).

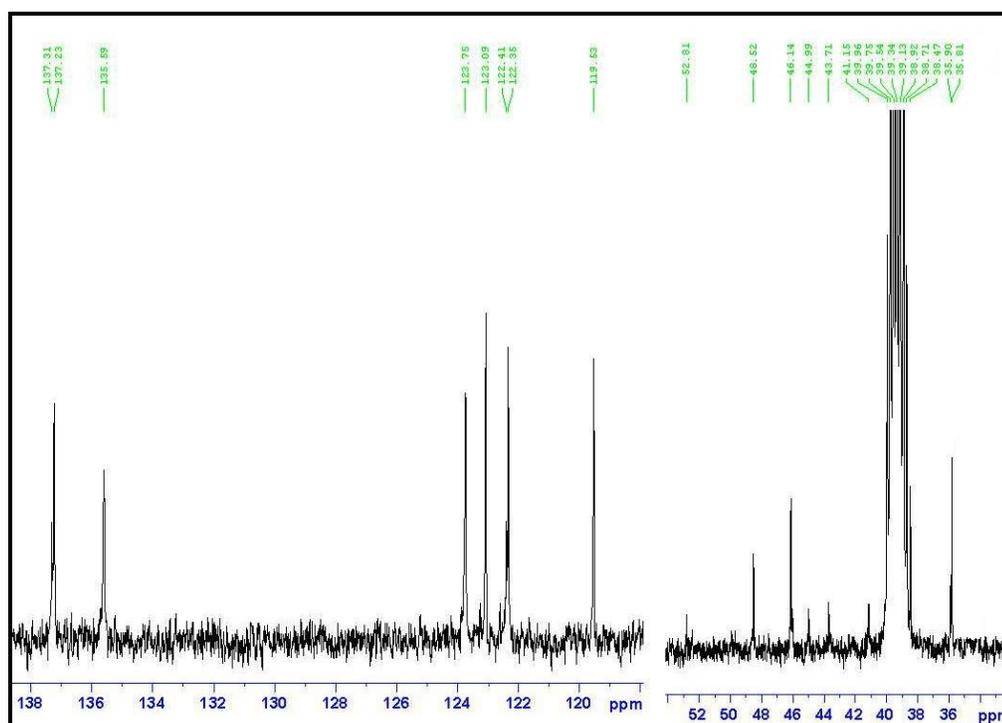


Fig 6.10. ^{13}C -NMR spectrum of LH (**2d**).

6.3.4. Molar conductance measurements

The molar conductance of the complexes (A_m) was determined by using the relation $A_m = 1000 \times \kappa / c$, where c and κ stands for the molar concentration of the metal complexes and specific conductance, respectively. The complexes (1×10^{-3} M) were dissolved in *N, N*-dimethylformamide (DMF) and their specific conductance was measured at (298.15 ± 0.01) K. The conductance values were in the range of 134, 131 and $130 \text{ S cm}^{-1} \text{ mol}^{-1}$ respectively for the metal complexes (**3d**, **4d** and **5d**), indicating their 1:2 electrolytic behaviour.

6.3.5. Electronic absorption spectral and magnetic moment studies

The UV-Visible spectra of the ligand and the metal complexes (as depicted in Fig 6.11.) were recorded at ambient temperature using methanol as solvent. The electronic spectrum of LH (**2d**) exhibited three absorption bands at 336, 250 and 218 nm due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and transitions involved with the imidazolium moiety, respectively [42, 43]. For the complexes, the bands that appeared below 350 nm were ligand centred transitions ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$). The Co(II) complex (**3d**) displayed a band at 394 nm which could be assigned to the combination of ${}^2\text{B}_{1g} \rightarrow {}^1\text{A}_{1g}$ and ${}^1\text{B}_{1g}$

\rightarrow^2E_g transitions and supporting square planar geometry [44, 45]. The complex (**3d**) showed magnetic moment of 2.30 B.M. due to one unpaired electron. The Ni(II) complex (**4d**) was diamagnetic and the band around 400 nm due to $^1A_{1g} \rightarrow ^1B_{1g}$ transition is consistent with low spin square planar geometry [46]. UV-visible spectra of Cu(II) complex (**5d**) showed $d \rightarrow \pi^*$ metal-ligand charge transfer transition (MLCT) in the region 396 nm had been assigned to the combination of $^2B_{1g} \rightarrow ^2E_g$ and $^2B_{1g} \rightarrow ^2B_{2g}$ transitions in a distorted square planar environment [47, 48]. The experimental magnetic moment for Cu(II) complex (**5d**) was 1.82 B.M. consistent with the presence of an unpaired electron [49].

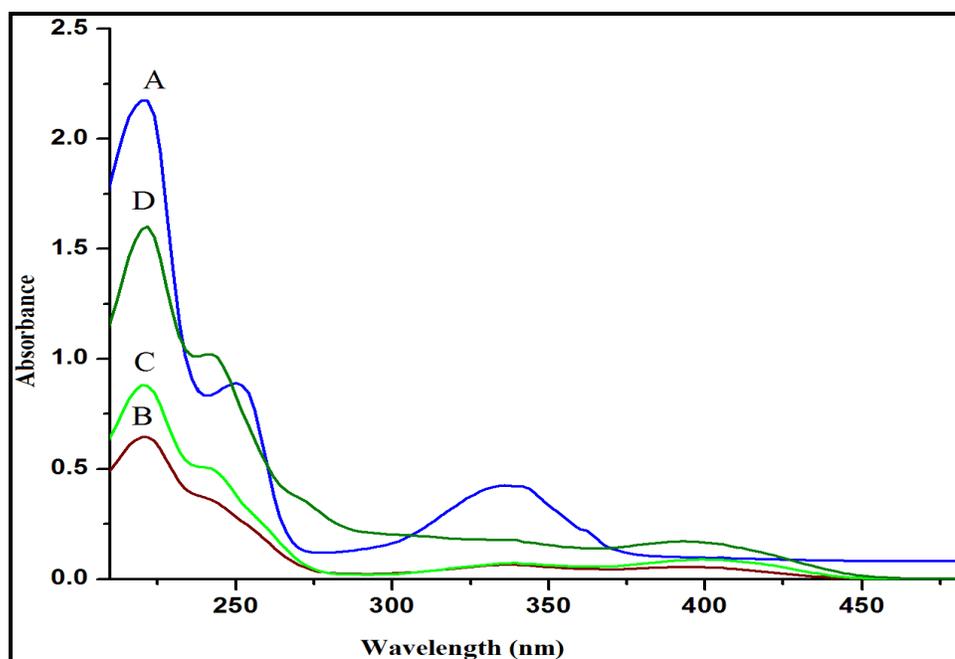


Fig 6.11. UV-visible spectra in methanol (concentration of the solutions 1×10^{-4} M): (A) LH (**2d**); (B) Co(II) complex (**3d**); (C) Ni(II) complex (**4d**) and (D) Cu(II) complex (**5d**).

6.3.6. Antibacterial activities

Minimum inhibitory concentration was measured by Broth Micro dilution susceptibility method. Serial dilutions of sample solutions were made in nutrient broth medium. Then 1 mL of standard (0.5 *McFarland*) bacteria suspension was inoculated

Table 6.1. Antibacterial activity data of Schiff base (**2d**) and its metal complexes (**3d**, **4d** and **5d**) against *E. Coli*, *S. aureus* and *B.cereus*.

Specimen	Concentration ($\mu\text{g/mL}$)														
	<i>E. coli</i>					<i>S. aureus</i>					<i>B.cereus</i>				
	10	20	30	40	50	10	20	30	40	50	10	20	30	40	50
LH (2d)	7	9	12	14	16	7	10	12	15	18	8	10	12	15	17
Co(II) complex (3d)	-	-	6	7	8	-	6	7	7	9	-	7	8	9	10
Ni(II) complex (4d)	6	8	9	10	12	6	8	9	12	14	-	-	-	6	7
Cu(II) complex (5d)	-	6	7	8	9	-	6	7	7	9	-	7	8	9	10

Table 6.2. Antibacterial activity data of Schiff base (**2d**) and its metal complexes (**3d**, **4d** and **5d**) against *P. aeruginosa*, *P. vulgaris* and *E. aerogenes*.

Specimen	Concentration ($\mu\text{g/mL}$)														
	<i>P. aeruginosa</i>					<i>P. vulgaris</i>					<i>E. aerogenes</i>				
	10	20	30	40	50	10	20	30	40	50	10	20	30	40	50
LH (2d)	9	12	17	20	21	10	12	14	15	19	-	-	-	6	6
Co(II) complex (3d)	-	-	7	8	10	6	8	9	10	15	7	8	12	14	14
Ni(II) complex (4d)	-	6	7	9	11	7	8	9	9	10	7	10	11	11	13
Cu(II) complex (5d)	-	-	6	7	7	-	-	6	6	8	-	-	-	-	6

into each of these tubes. A similar nutrient broth tube without sample was also inoculated and used as control. The tubes were kept at 37 °C for 24 hours. The lowest concentration of sample which inhibited bacterial growth was considered as minimum inhibitory concentration. Final confirmation was done by streaking on nutrient agar medium. The samples under study showed promising result against all the bacterial strains. (Data was given in Table 6.1 and Table 6.2) From the inhibitory values it was clear that the ligand (**2d**) was most effecting against five organisms (MIC 10 $\mu\text{g/mL}$)

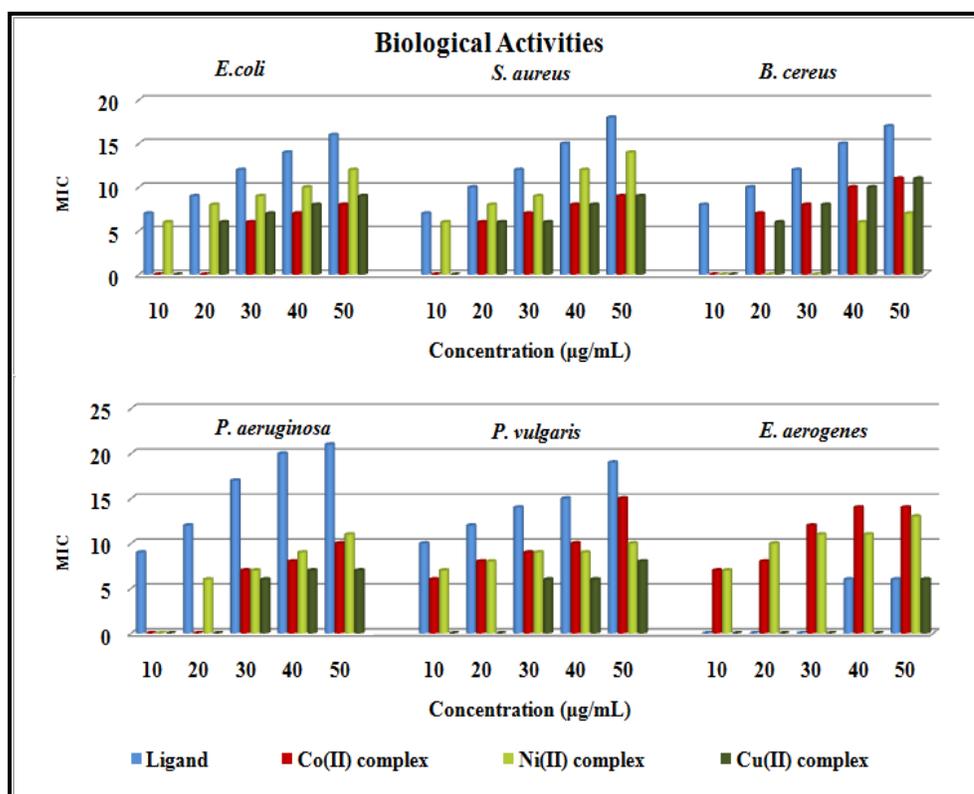


Fig 6.12. Inhibition zones for the LH (**2d**), Co(II) complex (**3d**), Ni(II) complex (**4d**) and Cu(II) complex (**5d**).

except *E. aerogenes*. Co(II) complex (**3d**) was most effective against *P. vulgaris* and *E. aerogenes*. Ni(II) complex (**4d**) was observed very active against *E. coli*, *S. aureus*, *P. aeruginosa* and *E. aerogenes* (MIC 10 $\mu\text{g/mL}$). The Cu(II) complex (**5d**) was most effective against *E. coli*, *S. aureus*, *B. cereus* (MIC value 20 $\mu\text{g/mL}$) and against *P. aeruginosa*, *P. vulgaris* (MIC value 30 $\mu\text{g/mL}$). The result was shown in Fig 6.12.

6.4. Conclusion

Herein this chapter the synthesis and physico-chemical characterization of Co(II), Ni(II) and Cu(II) complexes bearing an ionic liquid-supported Schiff base ligand 1-{2-[(2-hydroxy-5-bromobenzylidene)amino]ethyl}-3-ethylimidazolium tetrafluoroborate have been reported. The Schiff base and metal complexes were characterized by spectral and analytical methods. The spectral and magnetic susceptibility measurements suggested that the bidentate ligand coordinated to the central metal ion through the azomethine nitrogen and phenolic oxygen atoms,

yielding square planar complexes. The synthesized complexes and ligand showed reasonable antibacterial activity against the tested gram positive/negative bacteria.

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