

Chapter

Imidazolium Ionic Liquid-Supported Schiff Base and Its Transition Metal Complexes: Synthesis, Physicochemical Characterization and Exploration of Antimicrobial Activities

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Abstract

New Co(II), Ni(II) and Cu(II) metal complexes from an imidazolium ionic liquid supported Schiff base, 1-{2-(2-hydroxy-5-nitrobenzylideneamino)ethyl}-3-ethylimidazolium tetrafluoroborate were synthesized and characterized by different analytical and spectroscopic techniques such as elemental analysis (CHN analysis), UV-Visible, ^1H NMR, ^{13}C NMR, FT-IR, powder X-ray diffraction, mass-spectra, magnetic susceptibility measurements and molar conductance data. From these spectroscopic and analytical data, tetra coordinated 1:2 metal-ligand stoichiometry was suggested for the metal complexes. The molar conductance data of the complexes revealed their electrolytic nature (1:2). The synthesized complexes along with the ligand were screened for *in vitro* antibacterial applications against Gram-negative and Gram-positive bacteria to assess their inhibition potentials. The complexes were proved very effective against the tested organisms.

Keywords: ionic liquid-based Schiff base, Co(II) complex, Ni(II) complex, Cu(II) complex

1. Introduction

Ionic liquids (ILs) may be defined as “ionic materials,” with low melting points (below 100°C) generally composed of inorganic or organic anions paired with large, usually asymmetric organic cations. Ionic liquids (ILs) pose a plethora of unique physicochemical and solvation characteristics that can be tuned for specific applications and often producing interesting results when employed instead of traditional molecular solvents [1, 2]. In addition, most ILs show negligible vapor pressure [3] as well as high thermal stability [4–6]. Due to these attractive features they are termed as neoteric solvents or green solvents. In recent years, ILs were extensively studied for their wide electrochemical window, high ionic conductivity [7] and a broad temperature range of the liquid state. Moreover, the physical properties of ILs including density, melting point, polarity, Lewis acidity, viscosity and enthalpy of vaporization can all be tuned

by changing their cation and anion pairing [8]. IL-based solvent system typically exhibits enhanced reaction kinetics resulting in the efficient use of time and energy [1]. Due to these properties, ILs are treated as a new generation of solvents for catalysis, ecofriendly reaction media for organic synthesis and a successful replacement for conventional media in chemical processes [1, 9]. Recently, many researchers have focused on the synthesis of new ionic liquids called functionalized ionic liquids (FILs) with different functional groups in the cationic moiety [10–15]. Such functionalization of the cation can easily be done in a single reaction step and thus both the cationic and anionic moieties of the FILs can be altered as required for specific applications like increased catalytic stability and reduced catalyst leaching, etc. [16, 17].

Of note Schiff base being a salient class of multidentate ligand has played a key role in coordination chemistry. They exhibit varied denticities, chelating capability [18–20], functionalities [21] and diverse range of biological, pharmacological and antitumor activities. Schiff-bases containing hetero-atom such as N, O, and S are drawn special interest for their varied ways of coordination with different transition metal ions and having unusual configurations [22–24]. The present chapter describes the syntheses and physicochemical characterizations of an IL-supported Schiff base, 1-{2-(2-hydroxy-5-nitrobenzylideneamino)ethyl}-3-ethylimidazolium tetrafluoroborate and its Co(II), Ni(II) and Cu(II) complexes. The ligand and its metal complexes were screened for their *in vitro* antibacterial activities against Gram-negative bacteria *Escherichia coli*, *Pseudomonas aeruginosa*, *Proteus vulgaris*, *Enterobacter aerogenes* and Gram-positive bacteria *Staphylococcus aureus* and *Bacillus cereus*. The complexes and the ligand were found most effective against the tested Gram-negative/positive bacteria.

2. Materials and physical measurements

Analytical grade chemicals were used for synthesis without further purification. 1-ethyl imidazole, 2-bromoethylamine hydrobromide, 5-nitro-2-hydroxybenzaldehyde and NaBF₄ (sodium tetrafluoroborate) were purchased from Sigma Aldrich, Germany. Metal acetates and other reagents were used as obtained from SD Fine Chemicals, India. CH₃OH, petroleum ether, CHCl₃, DMF and DMSO were used after purification by standard methods described in the literature. FT-IR spectra were recorded by KBr pellets on a Perkin-Elmer Spectrum FT-IR spectrometer (RX-1). ¹H NMR and ¹³C NMR spectra were recorded on a FT-NMR (Bruker Avance-II 400 MHz) spectrometer by using D₂O and DMSO-*d*₆ as solvents. Powder X-ray diffraction (XRD) data were obtained on INEL XRD Model Equinox 1000 using Cu K α radiation ($2\theta = 0-90^\circ$). Elemental microanalysis (CHN analysis) was performed on Perkin-Elmer (Model 240C) analyzer. Metal content was obtained from AAS (Varian, SpectrAA 50B) by using standard metal solutions procured from Sigma-Aldrich, Germany. ESI-MS spectra were obtained on a JMS-T100LC spectrometer. The purity of the synthesized products was confirmed by thin layer chromatography (TLC) Merck 60 F254 silica gel plates (layer thickness 0.25 mm) and the spots were visualized using UV-light. The UV-visible spectra were obtained from JascoV-530 double beam spectrophotometer using CH₃OH as solvent. Specific conductance was measured at (298.15 \pm 0.01) K with a Systronic conductivity TDS-308 metre. Magnetic susceptibility was measured with a Sherwood Scientific Ltd. magnetic susceptibility balance (Magway MSB Mk1) at ambient temperature. The melting point of synthesized compounds was determined by open capillary method. Antibacterial activity (*in vitro*) of the synthesized ligand and complexes were evaluated by well diffusion method against six bacterial strains (two Gram-positive and four Gram-negative). The bacterial strains were obtained from MTCC, Chandigarh, India.

2.1 Synthesis of 1-(2-aminoethyl)-3-ethylimidazolium tetrafluoroborate [2-aeim]BF₄ (1a)

The FIL was synthesized by following a literature procedure [25]. [2-aeim]BF₄ was obtained as yellow oil; (98 mg, 70%); ¹H NMR (400 MHz, D₂O, TMS): δ = ¹H NMR (400 MHz, D₂O): δ = 3.63 (m, 2H, NH₂—CH₂), 4.16 (s, 3H, CH₃), 4.49 (t, 1H, N—CH₂), 4.56 (t, 1H, N—CH₂), 7.40 (s, 1H, NCH), 7.50 (s, 1H, NCH), 8.61 (s, 2H, NH₂), 8.87 (s, 1H, N(H)CN); IR (KBr): ν = 3447, 3086, 2896, 1626, 1452, 1084. ESI-MS (*m/z*) calc for [C₇H₁₄N₃]⁺: 140, found: 140 [M-BF₄]⁺. Anal. calcd. for C₇H₁₄F₄N₃B: C 37.04, H 6.22, N 18.51, found: C 36.99, H 6.14, N 18.43.

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

5-nitro-2-hydroxybenzaldehyde (1.67 g, 10 mmol) and [2-aeim]BF₄ (2.27 g, 10 mmol) were taken in methanol and stirred at 25°C for 4 h. After completion of reaction, the product was diluted using ethanol. The precipitate was filtered, washed with cold EtOH and dried properly to collect the expected ligand as a yellowish brown solid; (282 mg, 75%). mp. 95–97°C. ¹H NMR: (400 MHz, DMSO-*d*₆, TMS): δ = 3.36 (q, 2H, N—CH₂), 3.60 (s, 3H, CH₃), 3.92 (t, 2H, N—CH₂), 4.60 (t, 2H, N—CH₂), 7.44 (s, 1H, NCH), 7.52 (s, 1H, NCH), 7.53 (s, 1H, N=CH), 7.61–7.59 (m, 3H, Ar-H), 8.65 (s, 1H, N(H)CN), 8.88 (s, 1H, OH). ¹³C NMR: (400 MHz, DMSO-*d*₆, TMS): δ = 159.76, 138.43, 134.08, 130.47, 130.31, 123.89, 119.80, 118.65, 110.65, 39.86, 39.65, 39.24, 39.03 and 38.82. IR (KBr): ν = 3448 (O—H), 3071, 1664 (C=N), 1343 (N—O), 1293 (C—O), 1095 (B—F). UV/vis (methanol, λ_{max}): 206, 234, 306 nm; ESI-MS (CH₃OH, *m/z*) [M-BF₄]⁺ calcd. for [C₁₄H₁₇N₄O₃]⁺: 289, found; 289. Anal. calcd. for C₁₄H₁₇N₄O₃BF₄ (376): C 44.71, H 4.56, N 14.90. found: C 44.64, H 4.49, N 14.83.

2.3 Synthesis of the metal complexes (3a, 4a and 5a)

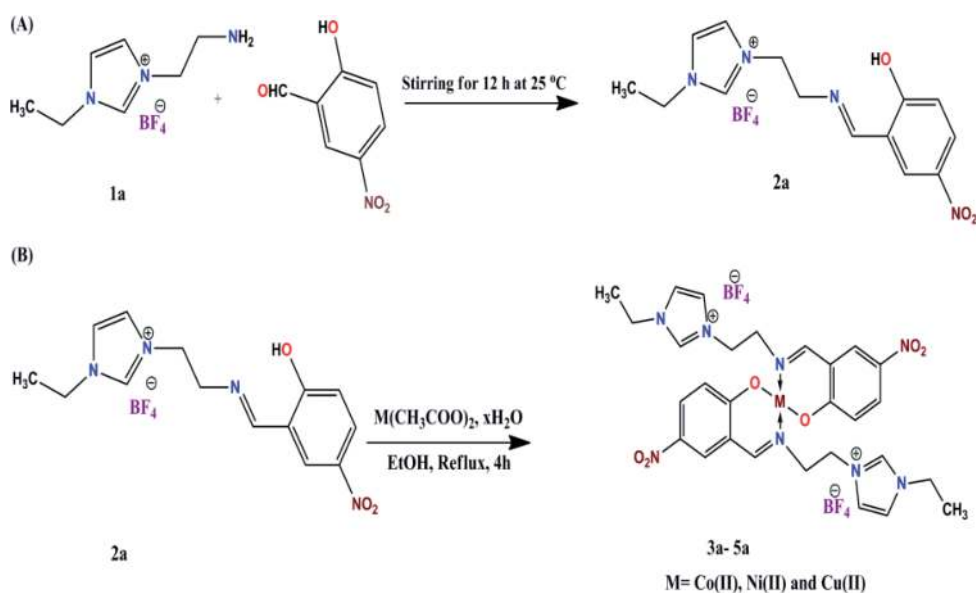
To an ethanolic solution of ligand, LH (2c) (0.376 g, 1 mmol) in round bottomed flask, metal acetate salt Co(II), Ni(II) and Cu(II), *viz.*, (0.5 mmol) dissolved in ethanol was added and the reaction mixture was refluxed for 12 h until the starting materials were completely consumed as monitored by TLC. 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 × 3). Finally it was dried in vacuum desiccators to obtain the solid product. The complexes were soluble in *N,N*-dimethylformamide, dimethylsulfoxide, acetonitrile, methanol and water. A schematic representation of the syntheses is given in **Figure 1**.

2.3.1 Co(II) complex (3a)

Brown solid; (0.54 g, 67%), decomposes at ~293°C. IR (KBr): ν = 3386 (O—H), 1648 (C=N), 1332 (N—O), 1177 (C—O), 1106 (B—F), 651 (M—O), 510 (M—N). UV/vis (methanol, λ_{max}/nm): 227, 246, 358. ESI-MS (CH₃OH, *m/z*) [M-2BF₄]⁺ calcd. for [C₂₈H₃₂CoN₈O₆]⁺: 635, found: 635; anal. calcd. for C₂₈H₃₆CoB₂F₈N₈O₈ (809): C 41.56, H 3.99, N 13.85, Co 7.28, found: C 41.36, H 3.71, N 13.55, Co 7.12.

2.3.2 Ni(II) complex (4a)

Light green solid; (0.56 g, 69%), decomposes at ~293°C. IR (KBr): ν = 3396 (O—H), 1637 (C=N), 1330 (N—O), 1172 (C—O), 1102 (B—F), 646 (M—O), 526 (M—N).

**Figure 1.**

Synthesis of Ionic liquid supported Schiff base (2a) and its metal complexes 3a, 4a and 5a from 2a.

UV/vis (methanol, λ_{max} /nm): 220, 340, 400. ESI-MS (CH₃OH, m/z) [M-2BF₄]⁺ calcd. for [C₂₈H₃₂NiN₈O₆]⁺: 634, found: 634; anal. calcd. for C₂₈H₃₆NiB₂F₈N₈O₈ (809): C 41.57, H 3.99, N 13.85, Ni 7.26, found: C 41.22, H 3.63, N 13.46, Ni 7.11.

2.3.3 Cu(II) complex (5a)

Dark green solid; (0.57 g, 70%), decomposes at ~295°C. IR (KBr): $\nu = 3429$ (O—H), 1656 (C=N), 1334 (N—O), 1175 (C—O), 1103 (B—F), 633 (M—O), 471 (M—N). UV/vis (methanol, λ_{max} /nm): 226, 244, 354. ESI-MS (CH₃OH, m/z) [M-2BF₄]⁺ calcd. for [C₂₈H₃₂CuN₈O₆]⁺: 634, found: 634. Anal. calcd. for C₂₈H₃₆CuB₂F₈N₈O₈ (813.76): C 41.33, H 3.96, N 13.77, Cu 7.81, found: C 41.12, H 3.61, N 13.46, Cu 7.61.

2.4 Antibacterial assay

The synthesized ligand (2a) and complexes (3a, 4a and 5a) were screened against the Gram-negative bacteria (*E. coli*, *P. aeruginosa*, *P. vulgaris* and *E. aerogenes*) and Gram-positive bacteria (*S. aureus* and *B. cereus*) strains. The tests were performed using agar disc diffusion method [26]. The nutrient agar (Hi-Media Laboratories Limited, Mumbai, India) was put in an autoclave at 121°C and 1 atm for 15–20 min. The sterile nutrient medium was kept at 45–50°C and then 100 μ L of bacterial suspension containing 10⁸ colony-forming units (CFU)/mL was mixed with sterile liquid nutrient agar and poured into the sterile Petri dishes. All the stock solutions were made by dissolving the compounds in dimethylsulfoxide (DMSO). The concentrations of the tested compounds were 10, 20, 30, 40 and 50 μ g/mL. The tested microorganisms were grown on nutrient agar medium in Petri dishes. The samples were soaked in a filter paper disc of 1 mm thickness and 5 mm diameter. The discs were kept on Petri plates and incubated for 24 h at 37°C. The diameter of the inhibition zone (including disc diameter of 5 mm) was measured. Each experiment was carried out three times to minimize the error and the mean values were accepted.

3. Results and discussion

All the isolated compounds were stable at room temperature to be characterized by different analytical and spectroscopic methods. The complexes are soluble in *N,N*-dimethylformamide, dimethylsulfoxide, acetonitrile, methanol and water.

3.1 FT-IR spectral studies

The assignments of the IR bands of the synthesized Co(II), Ni(II) and Cu(II) complexes had been made by comparing with the bands of ligand (LH) to determine the coordination sites involved in chelation. FT-IR spectra of LH (**2a**) showed a strong broad band at 3448–3071 cm^{-1} ; which was due to the hydrogen bonded phenolic group (—OH) with H—C(=N) group in the ligand (OH...N=C) [27, 28]. The broad band appeared at 3386–3429 cm^{-1} for the metal complexes (**3a**, **4a** and **5a**) suggested the presence of the solvated water molecules (probably for the presence of —NO_2 group in the ligand and intrinsic property of the anion tetrafluoroborate) [29–31]. The band corresponding to the azomethine group (—C=N) of the ligand was found at 1664 cm^{-1} . This band gets shifted in the range 1637–1656 cm^{-1} because of coordination of N atom of azomethine linkage to the Co^{2+} , Ni^{2+} and Cu^{2+} ions respectively [32]. The band for phenolic C—O of free ligand was observed at 1293 cm^{-1} which moved to lower wave number 1172–1177 cm^{-1} for the complexes (**3a**, **4a** and **5a**) upon complexation. This fact established the bonding of ligand (**2a**) to the metal atoms through the N atom of azomethine and O atom of phenolic group [33]. The bands appeared in the region of 1102–1107 cm^{-1} for the metal complexes were assigned for B—F stretching frequency. FT-IR spectra of the LH (**2a**) and its complexes showed strong bands at 1330–1343 cm^{-1} which were assigned for the NO_2 group [34]. The spectra of the metal complexes exhibited bands at 633–651 and 471–526 cm^{-1} were attributed to M—O and M—N stretching vibrations, respectively [35]. IR spectra are given in **Figures 2–8**.

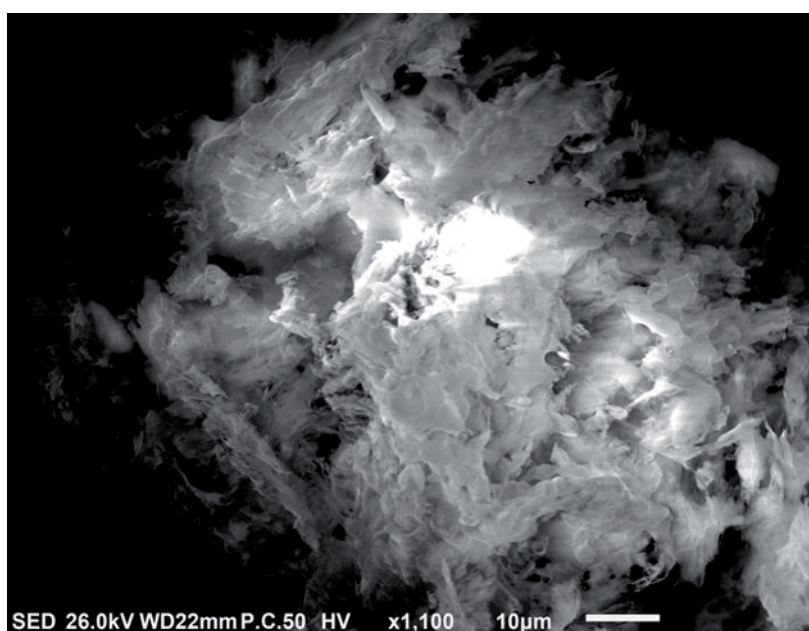


Figure 2.
SEM image of Co(II) complex (**3a**).

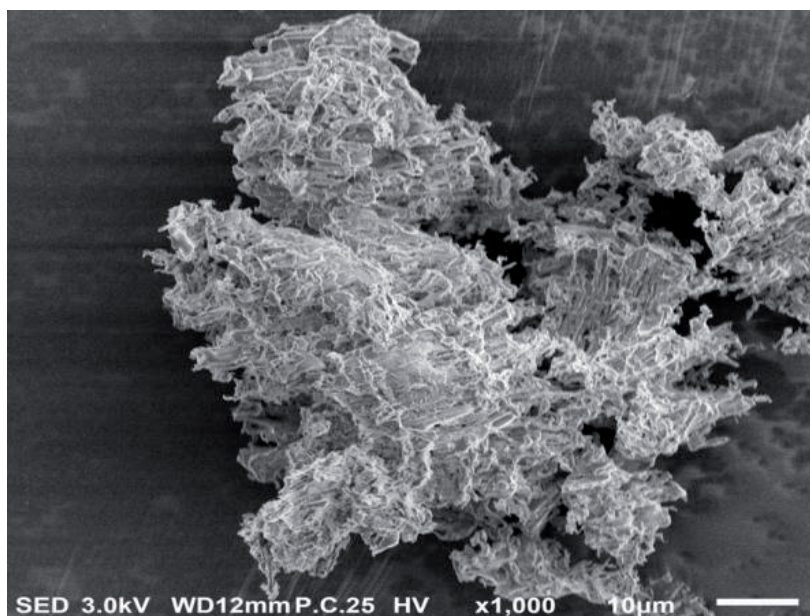


Figure 3.
SEM image of Ni(II) complex (4a).

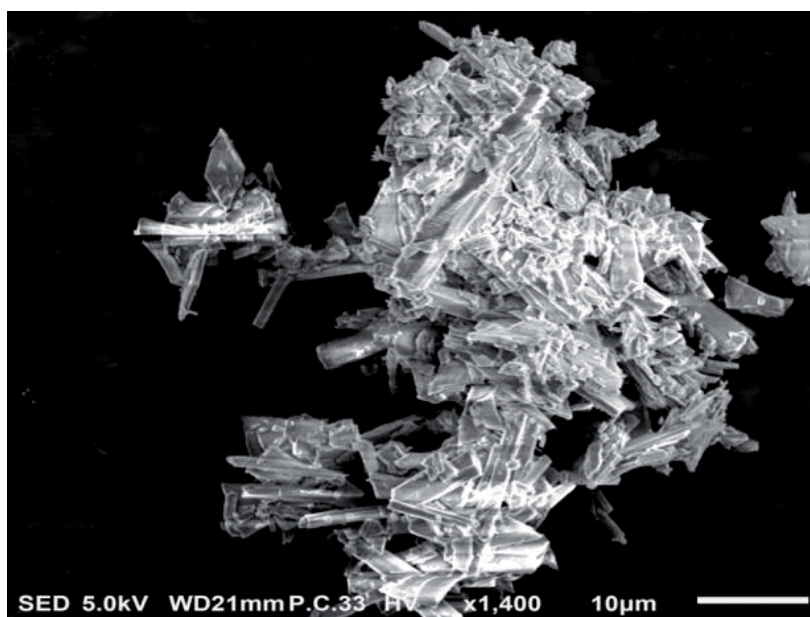


Figure 4.
SEM image of Cu(II) complex (5a).

3.2 ^1H NMR and ^{13}C NMR spectral studies

^1H NMR and ^{13}C NMR spectra of Schiff base were recorded in $\text{DMSO-}d_6$ (as shown in **Figures 9** and **10**). ^1H NMR spectra of the ligand showed singlet at 7.60 ppm which was assignable to proton of the azomethine linkage (—CH=N—) might be because of the effect of the *ortho*-hydroxyl group in the aromatic ring. A singlet at 8.88 ppm was assigned to hydroxyl proton (—OH). The downfield shift of the phenolic (—OH) proton was observed due to intramolecular (O—H...N) hydrogen bonding in the ligand [36]. ^{13}C NMR spectra of ligand exhibited peaks at δ 159.76 and 138.43 which were detected for the phenolic (C—O) and imino

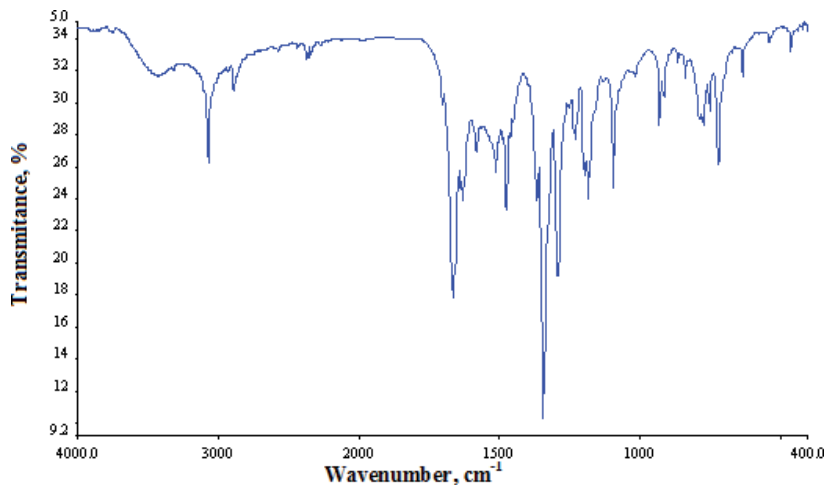


Figure 5.
FT-IR spectra of ligand (2a).

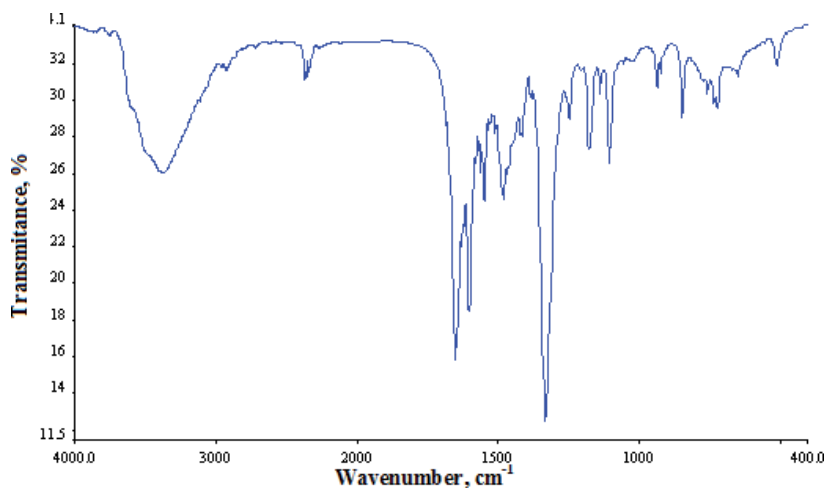


Figure 6.
FT-IR spectra of Co(II) complex (3a).

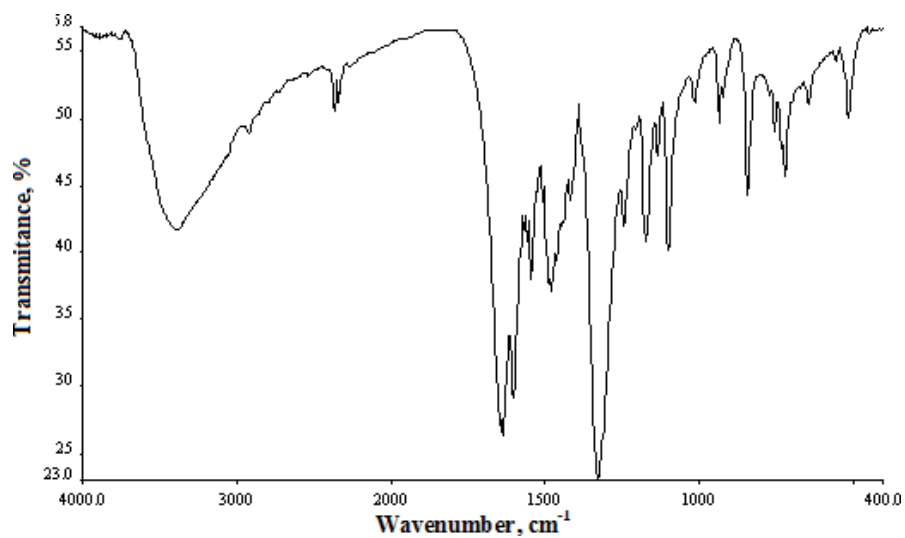


Figure 7.
FT-IR spectra of Ni(II) complex (4a).

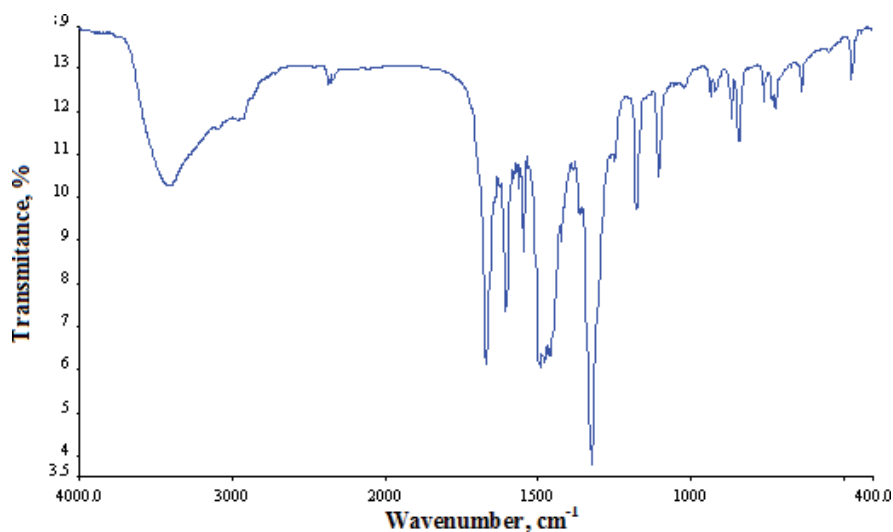


Figure 8.
FT-IR spectra of Cu(II) complex (5a).

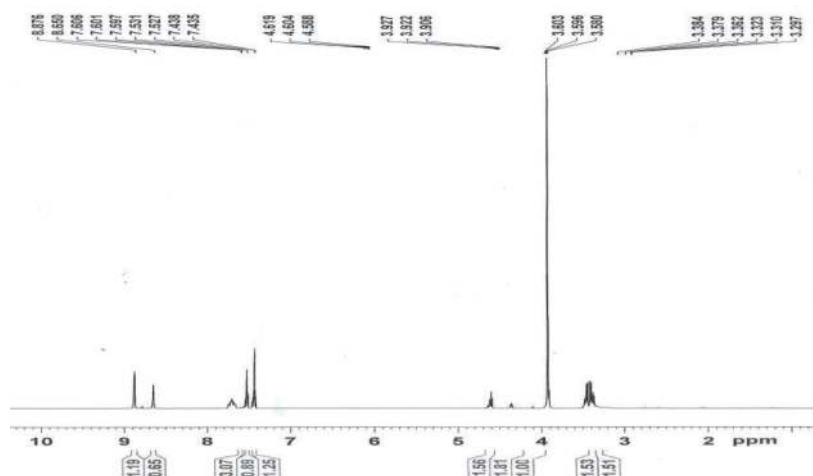


Figure 9.
 ^1H NMR spectra of LH (2a).

(—CH=N) carbon atoms (due to keto-imine tautomerism). The aromatic carbons showed peaks at δ 134.08, 130.47, 130.31, 123.89, 119.80 and 118.65.

3.3 PXRD analysis

The PXRD analysis of the synthesized compounds was carried out to find whether the particle nature of the samples was amorphous or crystalline. The PXRD spectrum of ligand (LH) exhibited sharp peaks because of their crystalline nature although the spectra of the two complexes did not show such peaks for their amorphous nature (as shown in **Figures 11–14**). The crystalline sizes were calculated using Debye Scherer's equation: $D = 0.9 \lambda / \beta \cos \theta$, where constant 0.9 is the shape factor, λ is the X-ray wavelength (1.5406 Å), β is the full width at half maximum (FWHM) and θ is the Bragg diffraction angle. The experimental average grain sizes of LH and its metal complexes were found to be 31.71 nm (**2a**), 7.76 nm (**3a**), 3.26 nm (**4a**) and 4.52 nm (**5a**).

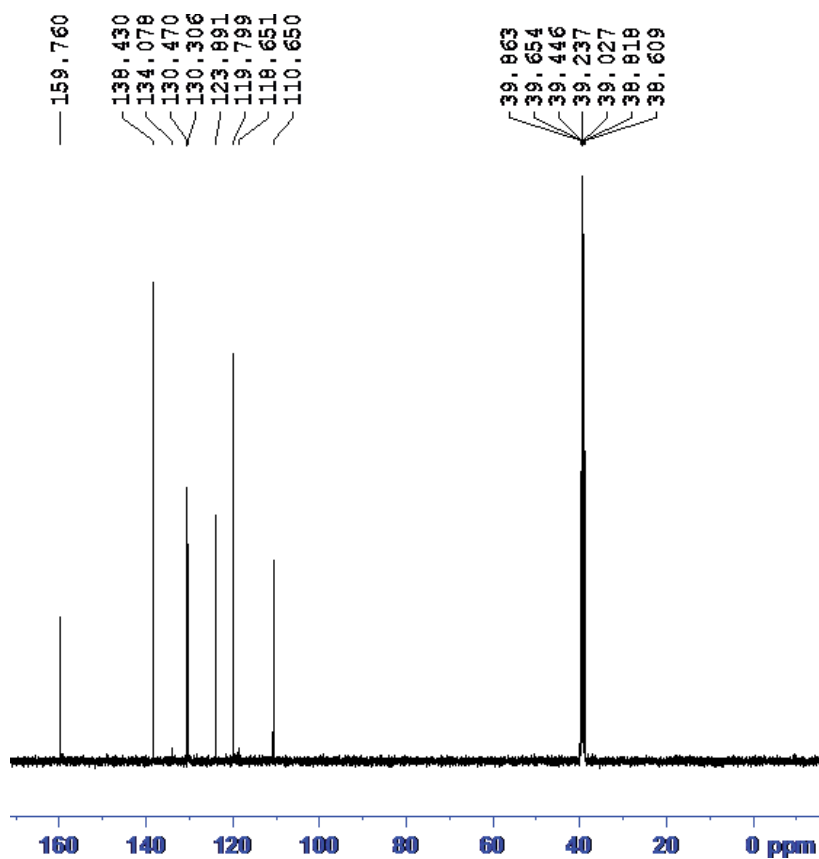


Figure 10.
 ^{13}C NMR spectra of LH (2a).

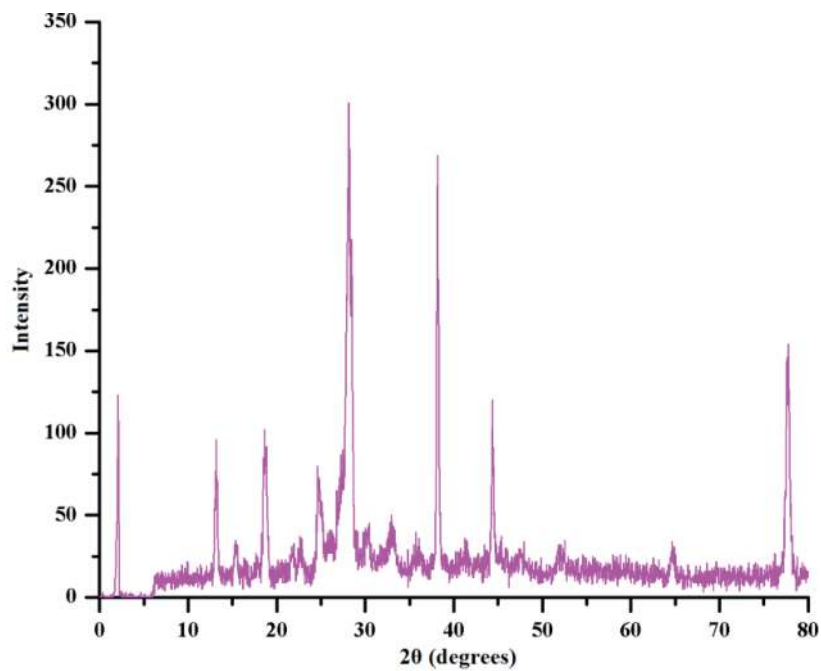


Figure 11.
PXRD spectra of LH (2a).

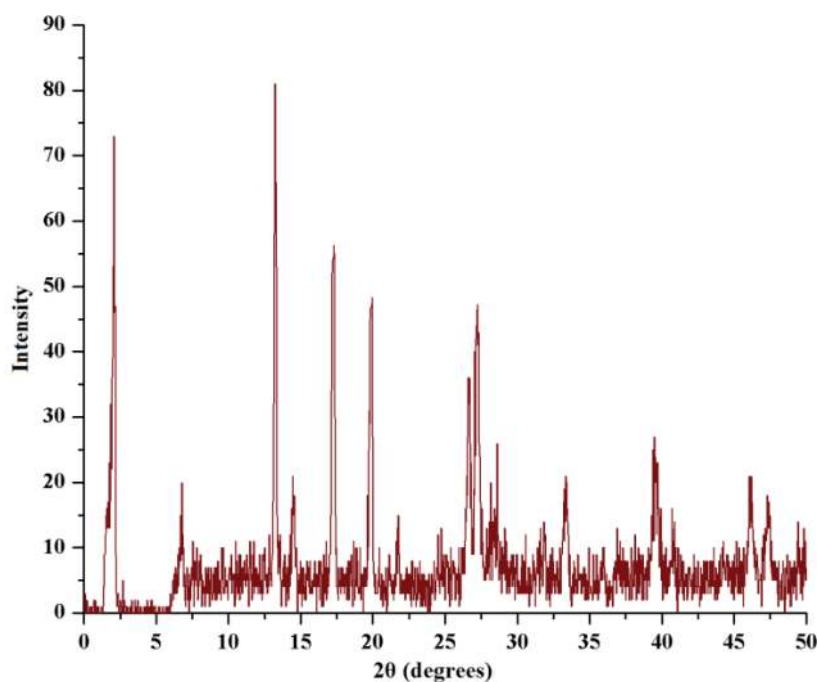


Figure 12.
PXRD spectra of Co(II) complex (3a).

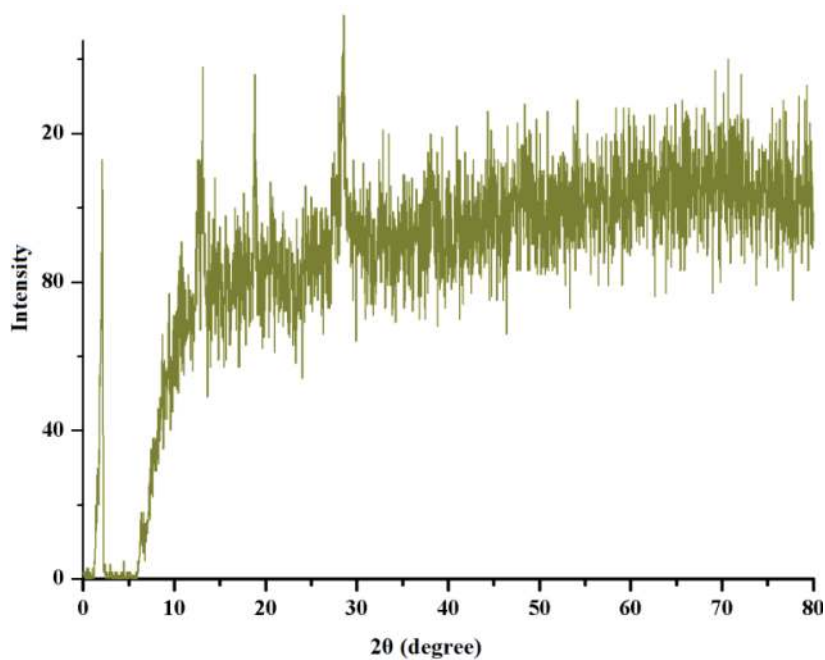


Figure 13.
PXRD spectra of Ni(II) complex (4a).

3.4 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. Mass-spectra of the LH (2a) had a molecular ion peaks at m/z 289, that corresponds to $[M-BF_4]^+$, $[M = C_{14}H_{17}N_4O_2]^+$. The metal complexes (3a, 4a and 5a) exhibited molecular ion peaks (m/z) at 635 ($M = [C_{28}H_{32}CoN_8O_6]^+$), at 634 ($M = [C_{28}H_{32}NiN_8O_6]^+$) and at 639 ($M = [C_{28}H_{32}CuN_8O_6]^+$) which confirmed

their stoichiometry as Co(L)_2 , Ni(L)_2 and Cu(L)_2 respectively. 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.

3.5 Electronic spectra and magnetic moment

The UV-visible spectra of the Schiff base and its metal complexes (as depicted in **Figure 15**) were recorded at room temperature using methanol as solvent.

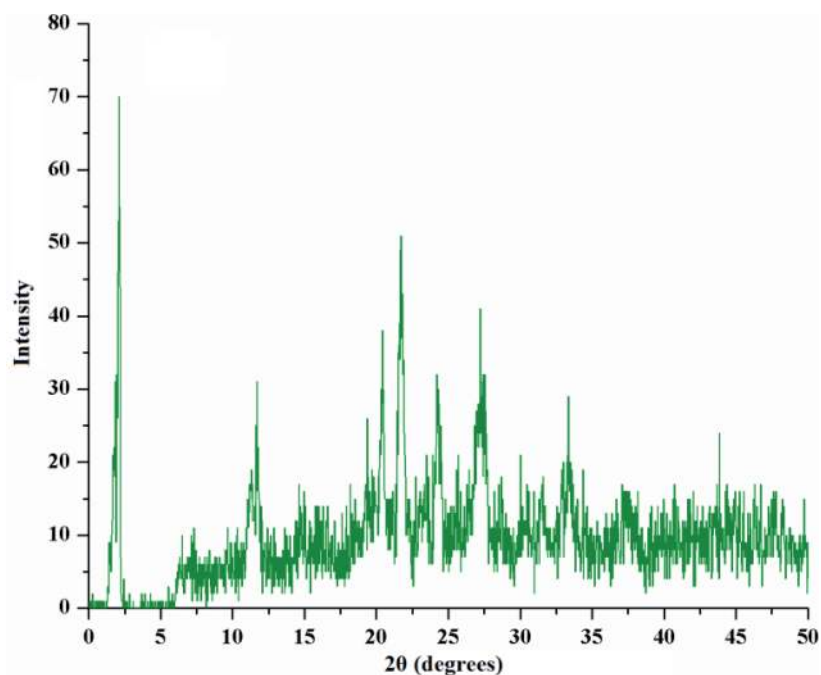


Figure 14.
PXRD spectra of Cu(II) complex (**5a**).

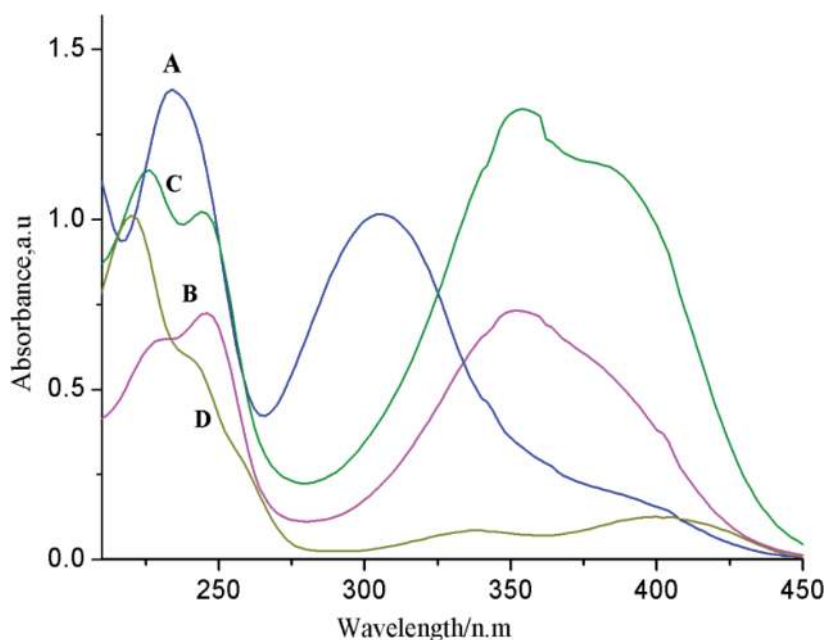


Figure 15.
UV-visible spectra in methanol (concentration of the solutions 1×10^{-4} M): (A) LH (**2a**); (B) Co(II) complex (**3a**); (C) Ni(II) complex (**4a**) and (D) Cu(II) complex (**5a**).

The LH (**2a**) exhibited three absorption bands at 306, 234 and 206 nm due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and transitions involved with the imidazolium moiety, respectively [37, 38]. For the complexes, the bands that appeared below 350 nm were ligand centered transitions ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$). The Co(II) complex (**3a**) displayed a band at 354 nm which could be attributed to the combination of ${}^2B_{1g} \rightarrow {}^1A_{1g}$ and ${}^1B_{1g} \rightarrow {}^2E_g$ transitions and supporting square planar geometry [39, 40]. The complex (**3a**) showed magnetic moment of 2.30 B.M. due to one unpaired electron. The Ni(II) complex (**4a**) was diamagnetic and the band appeared at around 400 nm due to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition is consistent with low spin square planar environment [41]. UV-visible spectra of Cu(II) complex (**5a**) exhibited $d \rightarrow \pi^*$ metal-ligand charge transfer transition (MLCT) at the region 358 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 geometry. The experimental magnetic moment value for **5a** was 1.84 B.M. consistent with the presence of an unpaired electron [42, 43].

3.6 Molar conductance

The molar conductance (Λ_m) of the metal complexes was determined by applying the relation $\Lambda_m = 1000 \times \kappa/c$, where κ and c stands for the specific conductance and molar concentration of metal complexes respectively. The complexes (1×10^{-3} M) were dissolved in DMF and their specific conductance was measured at (298.15 ± 0.01) K. The molar conductance data was observed as 123, 128 and $131 \text{ S cm}^{-1} \text{ mol}^{-1}$ for the metal complexes **3a**, **4a** and **5a** respectively indicating their 1:2 electrolytic natures.

3.7 Antimicrobial activity

Antibacterial study of LH (**2a**) and its complexes was carried out *in vitro* against the Gram-negative/positive bacterial strains, and the results are displayed in **Tables 1** and **2**

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	—	6	7	8	12	7	9	10	10	12	—	—	6	8	12
Co(II) complex	—	—	6	7	8	6	7	7	9	10	—	6	6	8	10
Ni(II) complex	6	7	8	9	9	—	—	7	8	10	—	—	6	8	10
Cu(II) complex	8	9	14	15	18	6	8	10	17	17	—	—	—	—	7

Table 1. Antibacterial activity data of Schiff base (**2a**) and its metal complexes (**3a**, **4a** and **5a**) against *E. coli*, *S. aureus* and *B. cereus* with their minimum zone of inhibition and MIC ($\mu\text{g/mL}$) mm values.

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	—	6	9	15	16	—	6	9	10	14	—	6	8	10	13
Co(II) complex	—	7	9	10	13	—	—	—	6	7	8	10	13	15	17
Ni(II) complex	—	—	6	7	9	—	—	6	7	8	8	10	12	12	16
Cu(II) complex	—	6	12	12	14	—	7	7	8	16	—	—	6	7	10

Table 2. Antibacterial activity data of Schiff base (**2a**) and its metal complexes (**3a**, **4a** and **5a**) against *P. aeruginosa*, *P. vulgaris* and *E. aerogenes* with their minimum zone of inhibition and MIC ($\mu\text{g/mL}$) mm values.

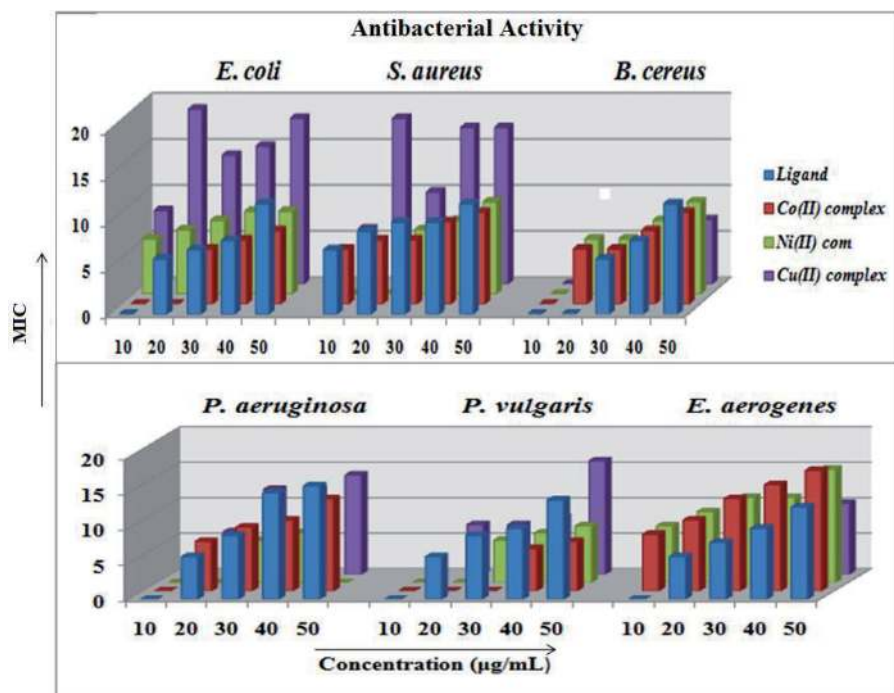


Figure 16.
 Inhibition zones for the LH (2a), Co(II) complex (3a), Ni(II) complex (4a) and Cu(II) complex (5a).

and also in **Figure 16**. Minimum inhibitory concentration (MIC) was measured by broth micro dilution susceptibility method. No inhibition zone was found for the solvent control (DMSO) for each bacterial suspension. A serial dilution of sample extracts was made in nutrient broth medium. Then 1 mL of standard (0.5 Mc Farland) bacterial suspension was inoculated into each of these tubes. A similar nutrient broth tube without sample extract was also inoculated and used as control. The samples under investigation have shown promising results against the tested bacterial strains. The LH (2a) was most effective against *S. aureus* only. The Co(II) complex (3a) showed most effectiveness against *S. aureus*, *E. aerogenes*. The Ni(II) complex (4a) showed higher activity against *E. aerogenes*. Although in other cases it showed moderate activity. It was found that Cu(II) complex (5a) was most effective against the tested bacteria. The observation suggested that the chelation could facilitate the capability of the complexes to penetrate bacterial cell membrane [44]. Such a chelation could enhance the lipophilic property of the corresponding metal ions that favors permeation towards the lipid layer of cell membrane. The activity of both the complexes and ligand enhanced as the concentration was increased which were due to the growth of degree of inhibition.

4. Conclusion

Herein this chapter, new Co(II), Ni(II) and Cu(II) complexes of an ionic liquid-supported Schiff base, 1-{2-(2-hydroxy-5-nitrobenzylideneamino)ethyl}-3-ethylimidazolium tetrafluoroborate were synthesized and characterized by different spectral and analytical techniques. The Schiff base ligand played as a potential bidentate ligand coordinating through the N-atom of azomethine and O-atom of phenolic group to the metal ions and thus formed 1:2 (M:L) complexes. Spectral and magnetic susceptibility data revealed that the ligand was arranged in square planer geometry around the central metal ions. The antibacterial study of the synthesized compounds was performed and metal complexes have exhibited promising activity against the tested bacteria.

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Nomenclature

[2-aeim][BF ₄] (1a)	1-(2-aminoethyl)-3-ethylimidazolium tetrafluoroborate
Ionic liquid-supported Schiff base, LH (2a)	1-{2-(2-hydroxy-5-nitrobenzylidene) ethyl}-3-ethylimidazolium tetrafluoroborate
Co(II) complex (3a)	[Di(1-{2-(2-hydroxy-5-nitrobenzylidene amino) ethyl}-3-ethylimidazolium) Co(II)] tetrafluoroborate
Ni(II) complex (4a)	[Di(1-{2-(2-hydroxy-5-nitrobenzylidene amino) ethyl}-3-ethylimidazolium) Ni(II)] tetrafluoroborate
Cu(II) complex (5a)	[Di(1-{2-(2-hydroxy-5-nitrobenzylidene amino) ethyl}-3-ethylimidazolium) Cu(II)] tetrafluoroborate

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References

- [1] Welton T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chemical Reviews*. 1999;**99**:2071-2083
- [2] Chiappe C, Pieraccini D. Kinetic study of the addition of trihalides to unsaturated compounds in ionic liquids. Evidence of a remarkable solvent effect in the reaction of ICl_2^- . *The Journal of Organic Chemistry*. 2004;**69**:6059-6064
- [3] Earle MJ, Esperanc JMSS, Gilea MA, Lopes JNC, Rebelo LPN, Magee J, et al. The distillation and volatility of ionic liquids. *Nature*. 2006;**439**:831-834
- [4] Rogers RD, Seddon KR. Ionic liquids—Solvents of the future? *Science*. 2003;**302**:792-793
- [5] Sheldon R. Green solvents for sustainable organic synthesis: State of the art. *Green Chemistry*. 2005;**7**:267-278
- [6] Wasserscheid P, Keim W. Ionic liquids—New “solutions” for transition metal catalysis. *Angewandte Chemie, International Edition*. 2000;**39**:3772-3789
- [7] Sakaebe H, Matsumoto H. *N*-methyl-*N*-propylpiperidinium bis(trifluoromethane sulfonyl)imide (PP13-TFSI)—Novel electrolyte base for Li battery. *Electrochemistry Communications*. 2003;**5**:594-598
- [8] Freire MG, Santos LMNBF, Fernandes AM, Coutinho JAP, Marrucho IM. An overview of the mutual solubilities of water-imidazolium-based ionic liquids systems. *Fluid Phase Equilibria*. 2007;**261**:449-454
- [9] Sheldon R. Catalytic reactions in ionic liquids. *Chemical Communications*. 2001;**23**:2399-2407
- [10] Yi F, Peng Y, Song G. Microwave-assisted liquid-phase synthesis of methyl 6-amino-5-cyano-4-aryl-2-methyl-4H-pyran-3-carboxylate using functional ionic liquid as soluble support. *Tetrahedron Letters*. 2005;**46**:3931-3933
- [11] Bates ED, Mayton RD, Ntai I, Davis JH. CO_2 capture by a task-specific ionic liquid. *Journal of the American Chemical Society*. 2002;**124**:926-927
- [12] Cole AC, Jensen JL, Ntai I, Tran KLT. Novel Brønsted acidic ionic liquids and their use as dual solvent-catalysts. *Journal of the American Chemical Society*. 2002;**124**:5962-5963
- [13] Li J, Peng Y, Song G. Mannich reaction catalyzed by carboxyl-functionalized ionic liquid in aqueous media. *Catalysis Letters*. 2005;**102**:159-162
- [14] Davis JH Jr, Forrester KJT, Merrigan J. Novel organic ionic liquids (OILs) incorporating cations derived from the antifungal drug miconazole. *Tetrahedron Letters*. 1998;**49**:8955-8958
- [15] Jodry JJ, Mikami JK. New chiral imidazolium ionic liquids: 3D-network of hydrogen bonding. *Tetrahedron Letters*. 2004;**45**:4429-4431
- [16] Fei Z, Geldbach TJ, Zhao D, Dyson PJ. From dysfunction to bis-function: On the design and applications of functionalised ionic liquids. *European Journal of Chemistry*. 2006;**12**:2122-2130
- [17] Lee S. Functionalized imidazolium salts for task-specific ionic liquids and their applications. *Chemical Communications*. 2006;**14**:1049-1063
- [18] Hadjikakou SK, Hadjiliadis N. Antiproliferative and anti-tumor activity of organotin compounds. *Coordination Chemistry Reviews*. 2009;**253**:235-249

- [19] Garoufis A, Hadjikakou SK, Hadjiliadis N. Palladium coordination compounds as anti-viral, anti-fungal, anti-microbial and anti-tumor agents. *Coordination Chemistry Reviews*. 2009;**253**:1384-1397
- [20] Liu CM, Xiong RG, You XZ, Liu YJ, Cheung KK. Crystal structure and some properties of a novel potent Cu₂Zn₂SOD model Schiff base copper(II) complex. *Polyhedron*. 1996;**15**:4565-4571
- [21] Atkins AJ, Black D, Blake AJ, Marin-Bocerra A, Parsons S, Ruiz-Ramirez L, et al. Schiff-base compartmental macrocyclic complexes. *Chemical Communications*. 1996;**4**:457-464
- [22] Goku A, Tumer M, Demirelli H, Wheatley RA. Cd(II) and Cu(II) complexes of polydentate Schiff base ligands: Synthesis, characterization, properties and biological activity. *Inorganica Chimica Acta*. 2005;**358**:1785-1797
- [23] Mohindru A, Fisher JM, Rabinovitz M. Bathocuproine sulphonate: A tissue culture-compatible indicator of copper-mediated toxicity. *Nature*. 1983;**303**:64-65
- [24] Palet PR, Thaker BT, Zele S. Preparation and characterisation of some lanthanide complexes involving a heterocyclic beta-diketone. *Indian Journal of Chemistry Section A*. 1999;**38**:563-567
- [25] Song G, Cai Y, Peng Y. Amino-functionalized ionic liquid as a nucleophilic scavenger in solution phase combinatorial synthesis. *Journal of Combinatorial Chemistry*. 2005;**7**:561-566
- [26] Ahmed I, Beg AJ. Antimicrobial and phytochemical studies on 45 Indian medicinal plants against multi-drug resistant human pathogens. *Journal of Ethnopharmacology*. 2001;**74**:113-123
- [27] Yıldız M, Kılıc Z, Hökelek T. Intramolecular hydrogen bonding and tautomerism in Schiff bases, structure of 1,8-di[N-2-oxyphenyl-salicylidene]-3,6-dioxaoctane. *Journal of Molecular Structure*. 1998;**441**:1-10
- [28] Yeap G-Y, Ha S-T, Ishizawa N, Suda K, Boey P-L, Mahmood WAK. Synthesis, crystal structure and spectroscopic study of para substituted 2-hydroxy-3-methoxybenzalideneanilines. *Journal of Molecular Structure*. 2003;**658**:87-99
- [29] Abdel-Latif SA, Hassib HB, Issa YM. Studies on some salicylaldehyde Schiff base derivatives and their complexes with Cr(III), Mn(II), Fe(III), Ni(II) and Cu(II). *Spectrochimica Acta Part A*. 2007;**67**:950-957
- [30] Wang J, Pei Y, Zhao Y, Hu Z. Recovery of amino acids by imidazolium based ionic liquids from aqueous media. *Green Chemistry*. 2005;**7**:196-202
- [31] Han D, Row KH. Recent application of ionic liquids in separation technology. *Molecules*. 2010;**15**:2405-2426
- [32] Kohawole GA, Patel KS. The stereochemistry of oxovanadium(IV) complexes derived from salicylaldehyde and polymethylenediamines. *Journal of the Chemical Society Dalton Transactions*. 1981;**6**:1241-1245
- [33] Mahmoud MA, Zaitone SA, Ammar AM, Sallam SA. Synthesis, structure and antidiabetic activity of chromium(III) complexes of metformin Schiff-bases. *Journal of Molecular Structure*. 2016;**1108**:60-70
- [34] Ulusoy N, Gürsoy A, Ötük G. Synthesis and antimicrobial activity of some 1,2,4-triazole-3-mercaptoacetic acid derivatives. II *Farmaco*. 2001;**56**:947
- [35] Adams DM. Metal-Ligand and Related Vibrations: A Critical Survey of the Infrared and Raman Spectra

of Metallic and Organometallic Compounds. England: Edward Arnold (Publishers) Ltd London; 1967

[43] Lever ABP. Inorganic Electronic Spectroscopy. 2nd ed. Amsterdam: Elsevier; 1984

[36] Li B, Li YQ, Zheng WJ, Zhou MY. Synthesis of ionic liquid supported Schiff base. ARKIVOC. 2009;**11**:165-171

[44] Tweedy BG. Plant extracts with metal ions as potential antimicrobial agents. Phytopathology. 1964;**55**:910-915

[37] Peral F, Gallego E. Self-association of imidazole and its methyl derivatives in aqueous solution. A study by ultraviolet spectroscopy. Journal of Molecular Structure. 1997;**415**:187-196

[38] Shakir M, Nasam OSM, Mohamed AK, Varkey SP. Transition metal complexes of 13-14-membered tetraazamacrocycles: Synthesis and characterization. Polyhedron. 1996;**15**:1283-1287

[39] Chem LS, Cummings SC. Synthesis and characterization of cobalt(II) and some nickel(II) complexes with N,N'-ethylenebis(p-X-benzoylacetone iminato) and N,N'-ethylenebis(p-X-benzoylmonothioacetone iminato) ligands. Inorganic Chemistry. 1978;**17**:2358-2361

[40] Silverstein RM. Spectrometric Identification of Organic Compounds. 7th ed. United States of America: John Wiley & Sons; 2005

[41] Natarajan C, Tharmaraj P, Murugesan R. In situ synthesis and spectroscopic studies of copper(II) and nickel(II) complexes of 1-hydroxy-2-naphthylstyrylketoneimines. Journal of Coordination Chemistry. 1992;**26**:205-213

[42] Dehghanpour S, Bouslimani N, Welter R, Mojahed F. Synthesis, spectral characterization, properties and structures of copper(I) complexes containing novel bidentate iminopyridine ligands. Polyhedron. 2007;**26**:154-162