

New Co(II) and Cu(II) complexes derived from an imidazolium ionic liquid-based Schiff base: synthesis, physico chemical characterization and exploration of antibacterial activities

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Two new Co(II) and Cu(II) complexes from an imidazolium ionic liquid based Schiff base 1-{2-(2-hydroxy-5-nitrobenzylideneamino)ethyl}-3-ethylimidazolium tetrafluoroborate have been synthesized and characterized by different analytical and spectroscopic techniques such as elemental analysis (CHN analysis), UV-Visible, ¹H-NMR, FTIR, Mass-spectra, Powder X-ray diffraction analysis, magnetic susceptibility measurements and molar conductance data. From these analytical results, tetra coordinated 1:2 metal-ligand stoichiometry is suggested for the both complexes. The molar conductance data of the complexes reveal their electrolytic nature (1:2). The synthesized complexes along with the ligand have been screened for *in vitro* antibacterial applications against gram negative and gram positive bacteria to assess their inhibition potentials. The complexes are proved to be very effective against the tested organisms.

Keywords: Ionic liquid-based Schiff base, Co(II) complex, Cu(II) complex, Antibacterial study

Ionic liquids (ILs) may be defined as “ionic materials”, with low melting points (below 100 °C) generally based on inorganic or organic anions paired with large, usually asymmetric organic cations. 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 have negligible vapor pressure as well as high thermal stability³⁻⁶. 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 conductivity⁷ 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 pairing⁸. IL-based solvent system typically exhibits enhanced reaction kinetics resulting in the efficient use of time and energy¹. Owing to these properties, ILs are treated as a new generation 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 capability¹⁸⁻²⁰, functionalities and diverse range of biological, pharmacological and antitumor activities^{21,22}. Schiff-bases containing hetero-atom such as N, O and S are drawn special interest for their varied ways of coordination with various transition metal ions and having unusual configurations.²³⁻²⁴ The present study reports the syntheses and physico-chemical characterizations of an IL-based Schiff base, 1-{2-(2-hydroxy-5-nitrobenzylideneamino) ethyl}-3-ethylimidazolium tetrafluoroborate and its Co(II) and Cu(II) complexes. The Schiff base ligand and its complexes were screened for their *in vitro* antibacterial activities against gram negative bacteria *Escherichia coli*, *Pseudomonas Aeruginosa*, *Proteus vulgaris*, *Enterobactor aerogenes* and gram positive bacteria *Staphylococcus aureus* and *Bacillus cereus*. Both the complexes and the ligand were found most effective against the tested gram negative/positive bacteria.

Materials and Methods

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 sodium tetrafluoroborate (NaBF_4) were purchased from Sigma Aldrich, Germany. Metal acetates and other reagents were used as obtained from SD Fine Chemicals, India. CH_3OH , petroleum ether, CHCl_3 , DMF and DMSO were used after purification by standard methods described in the literature. FTIR spectra were recorded by KBr pellets on a Perkin-Elmer Spectrum FTIR spectrometer (RX-1). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a FT-NMR (Bruker Avance-II 400 MHz) spectrometer by using D_2O and $\text{DMSO-}d_6$ as solvents. Powder X-ray diffraction (XRD) data were obtained on INEL XRD Model Equinox 1000 using $\text{Cu K}\alpha$ 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 CH_3OH as solvent. Specific conductance was measured at (298.15 ± 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 disc diffusion method against six bacterial strains (two gram positive and four gram negative). The bacterial strains were obtained from MTCC, Chandigarh, India.

Synthesis of the imidazolium based ionic liquid, 1-(2-aminoethyl)-3-ethylimidazolium tetra fluoroborate [2-aeim] BF_4 (1)

The FIL was synthesized by following a literature procedure²⁵. [2-aeim] BF_4 was obtained as yellow oil (Fig. 1). Yield: 77 %; $\text{C}_7\text{H}_{14}\text{F}_4\text{N}_3\text{B}$: Anal.(%) Calc.: C, 37.04; H, 6.22; N, 18.51. Found (%): C, 36.99; H, 6.14; N, 18.43. IR (KBr, ν/cm^{-1}): ($\nu_{\text{N-H}}$) 3447, 3086, 2896, 1626, 1452; (ν_{BF_4}) 1084. ESI-MS (m/z) Calc.

140: Found: 140 ($[\text{M-BF}_4]^+$, $\text{M} = \text{C}_7\text{H}_{14}\text{N}_3$)⁺. $^1\text{H NMR}$ (400 MHz, D_2O , TMS): $\delta = 3.63$ (2H, m, $\text{NH}_2\text{-CH}_2$), 4.16 (3H, s, CH_3), 4.49 (1H, t, N-CH_2), 4.56 (1H, t, N-CH_2), 7.40 (1H, s, NCH), 7.50 (1H, s, NCH), 8.61 (2H, s, NH_2), 8.87 (1H, s, N(H)CN).

Synthesis of imidazolium ionic liquid-based Schiff base, LH (2)

5-nitro-2-hydroxybenzaldehyde (1.67 g, 10 mmol) and [2-aeim] BF_4 (2.27 g, 10 mmol) were taken in methanol and stirred at 25°C for 4 h²⁶. After completion of reaction, the product was diluted using ethanol (EtOH). The precipitate was filtered, washed with cold EtOH and dried properly to collect the expected ligand as a yellowish brown solid. The reaction was shown in Scheme 1.

LH (2): M.p: $95-97^\circ\text{C}$; Yield: 69 %; $\text{C}_{14}\text{H}_{17}\text{N}_4\text{O}_3\text{BF}_4$: Anal. (%) Calc.: C, 44.71; H, 4.56; N, 14.90. Found (%): C, 44.64; H, 4.49; N, 14.83. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H}}$) 3448, 3071; ($\nu_{\text{CH=N}}$) 1664; (ν_{NO_2}) 1343; ($\nu_{\text{C-O}}$) 1293; (ν_{BF_4}) 1095. UV-visible (Methanol), $\lambda_{\text{max}}/\text{nm}$: 206, 234, 306. ESI-MS (m/z) Calc. 289: Found: 289 ($[\text{M-BF}_4]^+$, $\text{M} = \text{C}_{14}\text{H}_{17}\text{N}_4\text{O}_3$)⁺. $^1\text{H NMR}$: (400 MHz, $\text{DMSO-}d_6$, TMS): δ 3.36 (2H, q, N-CH_2), 3.60 (3H, s, CH_3), 3.92 (2H, t, N-CH_2), 4.60 (2H, t, N-CH_2), 7.44 (1H, s, NCH), 7.52 (1H, s, NCH), 7.53 (1H, s, N=CH), 7.61-7.59 (3H, m, Ar-H), 8.65 (1H, s, N(H)CN), 8.88 (1H, s, OH). $^{13}\text{C NMR}$: (400 MHz, $\text{DMSO-}d_6$, 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, 38.82.

Synthesis of metal complexes (3, 4)

To a ethanolic solution of LH (2) (0.376 g, 1 mmol), a solution of metal(II) acetate of cobalt or copper (0.5 mmol) in warm EtOH was added drop wise and the corresponding mixture was stirred for 3-4 h (Scheme 2), until the starting ingredients were completely consumed as monitored by TLC. On completion of the reaction,

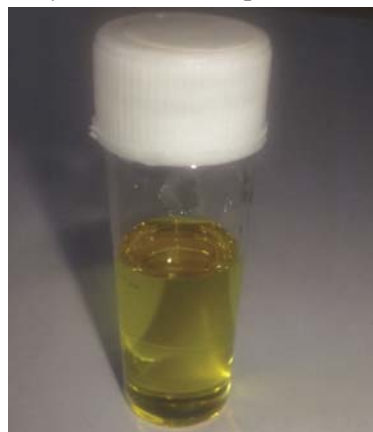
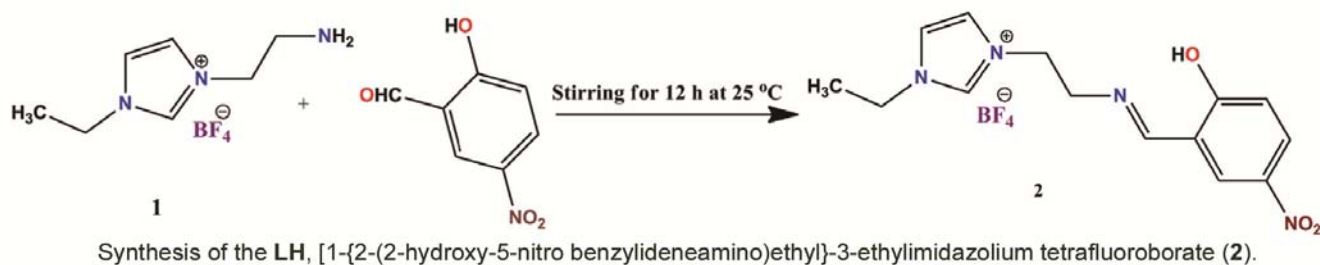
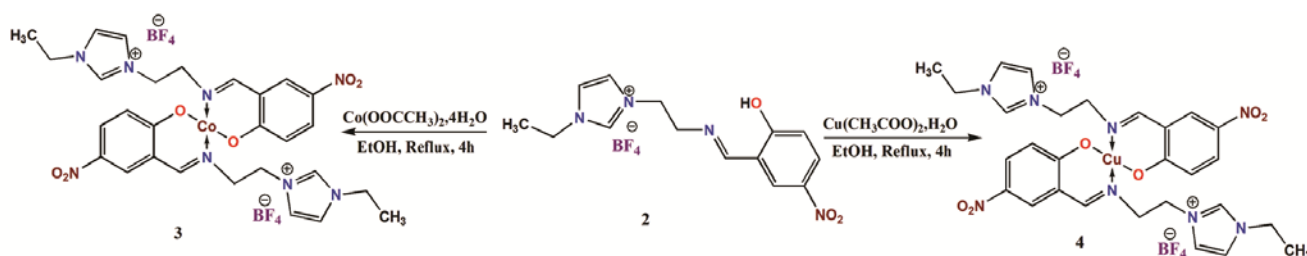


Fig. 1 — Yellow oil [2-aeim] BF_4 .



Scheme 1



Scheme 2

solvents were evaporated. The reaction mixture was cooled to room temperature. The product was obtained by filtration, washed with cold EtOH (10 mL × 3) followed by dry ether (10 mL × 3) and finally dried in vacuum to obtain the solid product. The complexes are soluble in methanol, acetonitrile, *N,N*-dimethylformamide (DMF), dimethylsulphoxide (DMSO) and sparingly soluble in water.

Co(II) complex (3) [Di(1-{2-(2-hydroxy-5-nitrobenzylideneamino)ethyl}-3-ethylimidazolium)Co(II) tetrafluoroborate: Brown solid; Yield 67 %; Decomposes at ~233 °C; C₂₈H₃₆CoB₂F₈N₈O₈; Anal. (%) Calc.: 41.56; H, 3.99; N, 13.85, Co, 7.28. Found (%): C, 41.36; H, 3.71; N, 13.55, Co, 7.12. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H/H}_2\text{O}}$) 3386; ($\nu_{\text{CH=N}}$) 1648; (ν_{NO_2}) 1332; ($\nu_{\text{C-O}}$) 1177; (ν_{BF_4}) 1106; ($\nu_{\text{M-O}}$) 651; ($\nu_{\text{M-N}}$) 510. UV-visible (Methanol) $\lambda_{\text{max}}/\text{nm}$: 227, 246, 358. ESI-MS (*m/z*) Calc. 635: Found: 634.45 ([M-BF₄]⁺, M= C₂₈H₃₂CoN₈O₆)⁺.

Cu(II) complex (4) [Di(1-{2-(2-hydroxy-5-nitrobenzylideneamino)ethyl}-3-ethylimidazolium)Cu(II) tetrafluoroborate: Dark green solid; Yield 71 %, Decomposes at ~246 °C; C₂₈H₃₆CuB₂F₈N₈O₈; Anal. (%) Calc.: 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. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H/H}_2\text{O}}$) 3429; ($\nu_{\text{CH=N}}$) 1656; (ν_{NO_2}) 1334; ($\nu_{\text{C-O}}$) 1175; (ν_{BF_4}) 1103; ($\nu_{\text{M-O}}$) 633; ($\nu_{\text{M-N}}$) 471. UV-visible (Methanol) $\lambda_{\text{max}}/\text{nm}$: 226, 244, 354. ESI-MS (*m/z*) Calc. 639: Found: 639 ([M-BF₄]⁺, M= C₂₈H₃₂CuN₈O₆)⁺.

Antibacterial activity

The synthesized ligand (2) and complexes (3 and 4) 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 method²⁷. 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 μL 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 DMSO. The concentrations of the tested compounds were 10, 20, 30, 40 and 50 $\mu\text{g}/\text{mL}$. The tested microorganisms were grown on nutrient agar medium in Petri dishes. The samples were soaked in a filter paper disk 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.

Results and Discussion

FTIR spectroscopy

FTIR spectra of LH (2) showed a strong broad band at 3448–3071 cm^{-1} ; which corresponds to the

H-bonded phenolic group (-OH) with H-C(=N) group in the ligand (OH...N=C)^{28,29}. The broad band appeared at 3386–3429 cm⁻¹ for the metal complexes (**3** and **4**) suggests the presence of the solvated water molecules (probably due to the intrinsic property of the anion tetrafluoroborate)³⁰⁻³². The band corresponding to the azomethine group (-C=N) of the ligand was found at 1664 cm⁻¹. This band gets shifted to the range 1648–1656 cm⁻¹ because of coordination of N atom of azomethine linkage to the Co²⁺ and Cu²⁺ ions³³. The band for phenolic C-O of the ligand was detected at 1293 cm⁻¹ which moved to lower wave number 1177–1175 cm⁻¹ for the complexes (**3** and **4**) upon complexation. This fact suggests the bonding of ligand (LH) to the Co²⁺ and Cu²⁺ ions through the N atom of azomethine and O atom of phenolic group³⁴. The bands appeared in the region of 1106–1103 cm⁻¹ for the complexes **3** and **4** were assigned for B-F stretching frequency. FTIR spectra of the LH (**2**) and its complexes show strong bands at 1332–1343 cm⁻¹ assigned to the NO₂ group³⁵. The spectra of the metal complexes (**3** and **4**), exhibited bands at 651–633 and 510–471 cm⁻¹ were attributed to M-O and M-N stretching vibrations, respectively³⁶. FT-IR spectra of the LH (**2**) and metal complexes (**3**) and (**4**) are given in Supplementary Data, Fig. S1.

¹H-NMR and ¹³C-NMR spectra

¹H-NMR spectra of LH (**2**) was recorded in DMSO-*d*₆. The spectrum of ligand showed singlet at 7.60 ppm assignable to proton of the azomethine linkage (-CH=N-) presumably due to the effect of the *ortho*-hydroxyl group in the aromatic ring. A singlet at 8.88 ppm is 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 ligand³⁷. ¹³C-NMR spectra of ligand exhibited peaks at δ 159.76 and 138.43 presumably due to the phenolic (C-O) and imino (-CH=N) carbon atoms (due to keto-imine tautomerism). The chemical shifts of the aromatic carbons appeared at δ 134.08, 130.47, 130.31, 123.89, 119.80 and 118.65. ¹H-NMR and ¹³C-NMR spectra of LH (**2**) are given in Supplementary Data, Figs S2 and S3.

X-ray powder diffraction analysis

The PXRD analysis of the synthesized compounds was carried out to observe the amorphous or crystalline nature of the samples. The PXRD spectrum of ligand (LH) exhibited sharp peaks because of their crystalline nature although the spectra

of the two complexes didn't show such peaks for their amorphous nature (Fig. 2). The crystalline sizes were calculated using Debye Scherer's equation:

$$D = 0.9 \lambda / \beta \cos \theta \quad \dots(1)$$

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 were found to be 31.71, 7.76 and 4.52 nm for LH (**2**), complex **3** and complex **4**, respectively.

Mass-spectra

Mass-spectra of the LH (**2**) shows a molecular ion peaks at *m/z* 289, that corresponds to [M-BF₄]⁺,

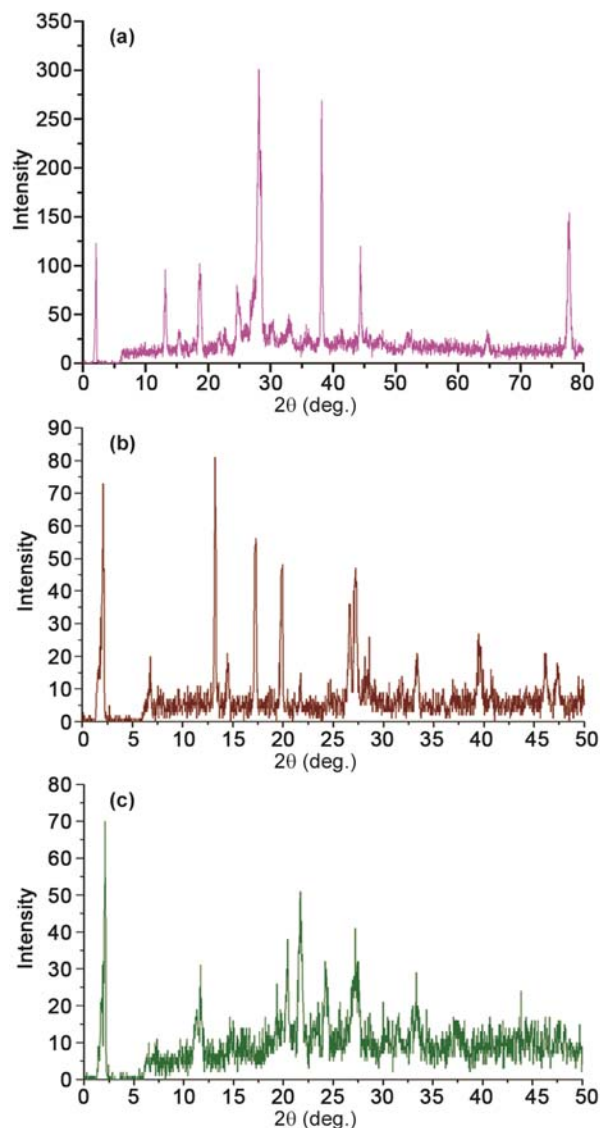


Fig. 2 — PXRD patterns of (a) LH (**2**), (b) Co(II) complex(**3**) and (c) Cu(II) complex(**4**).

[M= C₁₄H₁₇N₄O₂]⁺. The metal complexes (**3**, **4**) exhibited molecular ion peaks (*m/z*) at 635 (M= [C₂₈H₃₂CoN₈O₆]⁺) and at 639 (M= [C₂₈H₃₂CuN₈O₆]⁺) which confirmed their stoichiometry as Co(L)₂ and Cu(L)₂ (Shown in Supplementary Data, Figs S4 and S5). Thus the ESI-MS spectra along with CHN analysis data suggest the formation of Co(II) and Cu(II) metal complexes with 1:2 (M:L) stoichiometry.

Electronic absorption spectra and magnetic susceptibility

UV-visible spectra of the LH (**2**) and the metal complexes (**3**, **4**) (as depicted in Fig. 3) were recorded in methanol at ambient temperature. The electronic spectrum of LH (**2**) showed three absorption bands at 306, 234 and 206 nm due to *n*→*π*^{*}, *π*→*π*^{*} and transitions involved with the imidazolium moiety, respectively^{38,39}. The bands that appeared below 350 nm in the spectra of the metal complexes (**3**, **4**), were assigned as ligand centred transitions (*n*→*π*^{*} and *π*→*π*^{*}). The Co(II) complex (**3**) displayed a band at 354 nm which could be attributed to the combination of ²B_{1g}→¹A_{1g} and ¹B_{1g}→²E_g transitions and supporting square planar geometry^{40,41}. The experimental magnetic moment value 2.14 B.M. was found for the complex (**3**) because of an unpaired electron. The UV-visible spectra of Cu(II) complex (**4**) showing d→*π*^{*} metal-ligand charge transfer transition (MLCT) in the region 358 nm had been attributed to the combination of ²B_{1g}→²E_g and ²B_{1g}→²B_{2g} transitions in a distorted square planar environment^{42,43}. The magnetic moment for Cu(II) complex (**4**) was found 1.84 B.M. consistent with the presence of a single unpaired electron⁴⁴.

Molar conductance measurements

The molar conductance (*A_m*) of the ligand and metal complexes (**3**, **4**) were measured by applying the relation:

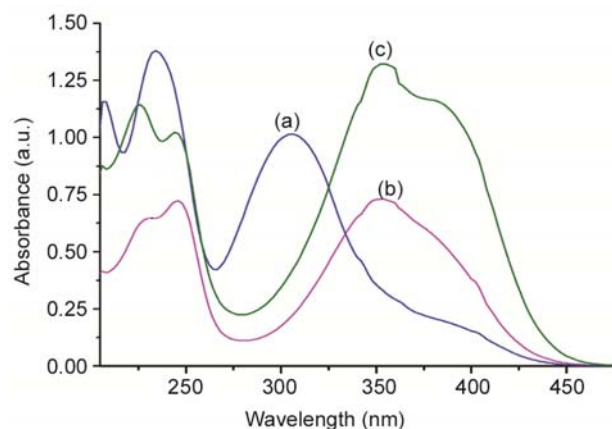


Fig. 3 — UV-visible spectra of: (a) the LH (**2**), (b) Co(II) complex (**3**) and (c) Cu(II) complex (**4**).

$$A_m = 1000 \times \kappa/c \quad \dots(2)$$

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 were measured at (298.15 ± 0.01) K. The molar conductance data was observed in the range of $123\text{--}131 \text{ S cm}^{-1} \text{ mol}^{-1}$ for the metal complexes **3** and **4** indicating their 1:2 electrolytic natures although the value $167 \text{ S cm}^{-1} \text{ mol}^{-1}$ was obtained for the free ligand⁴⁵.

Antibacterial activity

Antibacterial study of LH (**2**) and its complexes (**3**, **4**) was carried out *in vitro* against the gram negative/positive bacterial strains and the results were displayed in Fig. 4 and in Supplementary Data, Table S1. Minimum inhibitory concentration (MIC) was measured for all the samples. No inhibition zone was found for the solvent control (DMSO) for each bacterial suspension. The samples under investigation have shown promising results against the tested bacterial strains. The LH (**2**) was most effective against *S. aureus* only. The Co(II) complex (**3**) showed most effectiveness against *S. aureus*, *E. aerogenes* and Cu(II) complex (**4**) was found most effective against *E. coli* and *S. aureus*. The observation suggested that the chelation could facilitate the capability of the complexes to penetrate bacterial cell membrane⁴⁶. Such a chelation could enhance the lipophilic property of the corresponding metal ions that favours permeation towards the lipid

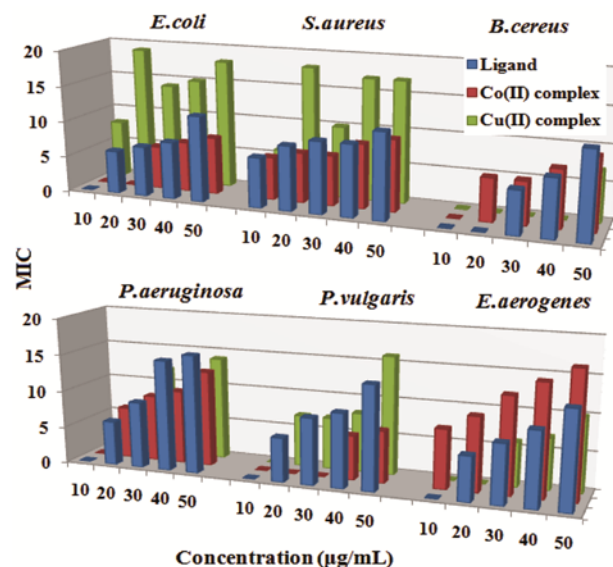


Fig. 4 — MIC for LH (**2**), Co(II) complex (**3**) and Cu(II) complex (**4**) against the gram positive/negative bacteria.

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.

Conclusions

In the present investigation, new Co(II) and Cu(II) complexes of an ionic liquid-based 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 both the complexes had square planar geometry. The antibacterial study of the synthesized compounds was performed and metal complexes showed more promising activity against the tested bacteria.

Supplementary Data

FTIR, ESI-MS spectra, ¹H NMR, ¹³C NMR spectra and experimental biological assays data of the Schiff base and metal complexes are attached as electronic supplementary data. Supplementary Data associated with this article are available in the electronic form at: [http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A\(03\)311-316_SupplData.pdf](http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(03)311-316_SupplData.pdf).

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