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

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Abstract. Co(II), Ni(II) and Cu(II) complexes of an ionic liquid-supported Schiff base 1-{2-[(2-hydroxy-5-bromobenzylidene)amino]ethyl}-3-ethylimidazolium tetrafluoroborate were synthesized and characterized by various analytical and spectroscopic methods such as elemental analysis, UV-Visible, FT-IR, ¹H NMR, ESI MS, molar conductance and magnetic susceptibility measurements. Based on the spectral studies, tetra coordinated geometry was proposed for the complexes and molar conductance of the complexes revealed their electrolytic nature. The synthesized Schiff base and its complexes were evaluated for *in vitro* antibacterial activities against Gram positive and Gram negative bacteria. The complexes along with the Schiff base showed very significant biological activity against the tested bacteria.

Keywords. Ionic liquid-supported Schiff base; Co (II)complex; Ni (II)complex; Cu (II)complex; antibacterial activity.

1. Introduction

Ionic liquids (ILs) are organic salts which have low melting points below the boiling point of water and are stable in a 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 conductivity² and thermal stability.^{3–5} ILs are touted 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 a functional group as a part of cation or anion, has presently become a subject of interest.^{10–15} There is a 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 enhanced stability of metal salts.¹⁶ Metal-containing ILs are considered as promising new materials 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 a 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 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

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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} We reported in previous articles the synthesis, characterization and biological influence of Cu(II), Mn(II) and Co(II) complexes of analogous ionic liquid-supported Schiff bases.^{27,28} This paper reports on the synthesis of transition metal 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 demonstrated.

2. Experimental

2.1 Materials

All the reagents used 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-hydroxy benzaldehyde, 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 described in the literature.

2.2 Instrumentation

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 an FT-NMR (Bruker Avance-II 400 MHz) spectrometer using DMSO- d_6 and D_2O 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 was determined with the aid of AAS (Varian, SpectraAA 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 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. Molar conductances were measured at (298.15 ± 0.01) K with a Systronic conductivity meter, TDS-308. Magnetic susceptibilities were measured at room temperature using a magnetic susceptibility balance (Magway MSB Mk1, Sherwood Scientific Ltd). The melting point of the ligand and its complexes

were determined by the 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.

2.3 Synthesis of 1-(2-aminoethyl)-3-ethylimidazolium tetrafluoroborate, [2-aeem] BF_4 (**1**)

The amino functionalized ionic liquid [2-aeem] BF_4 was synthesized by following a literature procedure.²⁹ Yield: 79%; $\text{C}_7\text{H}_{14}\text{F}_4\text{N}_3\text{B}$: Anal. Found: C, 37.02; H, 6.12; N, 18.38% Calc.: C, 37.04; H, 6.22; N, 18.51%. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H}}$) 3447, 3086, 2896, 1626, 1452, (ν_{BF_4}) 1084. ESI-MS (m/z): Calc.: 140; Found: 140 ($[\text{M-BF}_4]^+$, $\text{M}=[\text{C}_7\text{H}_{14}\text{N}_3]^+$). ^1H NMR (400 MHz, D_2O , TMS): δ 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); ^{13}C NMR (400 MHz, D_2O , TMSO) δ : 135.95, 123, 122.50, 50.81, 45.54, 45.3, 14.57.

2.4 Synthesis of imidazolium ionic liquid-tagged Schiff base, LH (**2**)

The ionic liquid-tagged Schiff base (LH) was synthesized by a slight modification of a literature procedure.³⁰ A mixture of 5-bromo-2-hydroxy benzaldehyde (2.01 g, 10 mmol) and [2-aeem] BF_4 (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 EtOH. The precipitate was filtered, washed with cold ethanol and dried to afford the expected ligand as a light yellow solid.

2.4a **LH(2)**: M.p.: 98–100 °C; Yield: 65–70%; $\text{C}_{14}\text{H}_{17}\text{N}_3\text{OBBF}_4$ Anal. Found: C, 40.91; H, 4.11; N, 10.21%. Calc.: C, 41.01; H, 4.18; N, 10.25(%) IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H}}$) 3449, ($\nu_{\text{CH=N}}$) 1673, ($\nu_{\text{C-O}}$) 1276, (ν_{BF_4}) 1114. UV-Vis (Methanol) $\lambda_{\text{max}}/\text{nm}$: 218, 250, 336. ESI-MS (m/z): Calc. 323; Found: 323 ($[\text{M-BF}_4]^+$, $\text{M}=[\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}]^+$). ^1H NMR: (400 MHz, DMSO- d_6 , TMS): δ 3.32 (3H, s, CH_3), 3.82 (1H, t, N-CH_2), 3.99 (1H, t, N-CH_2), 4.52 (1H, t, N-CH_2), 6.91–6.85 (3H, m, Ar-H), 7.33 (1H, s, NCH), 7.42 (1H, s, NCH), 8.50 (1H, s, N=CH), 7.73 (1H, s, N(H)CN), 9.10 (1H, s, OH). ^{13}C NMR (400 MHz, DMSO- d_6 , TMSO): 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.

2.5 Synthesis of metal complexes (**3**, **4** and **5**)

To a solution of ligand, LH (0.410 g, 1 mmol), in EtOH (20 mL) solution of ethanolic metal acetate salt Co(II), Ni(II) and Cu(II), *viz.*, (0.5 mmol) was added and 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

Scheme 1. Synthesis of the ionic liquid-tagged Schiff base, 1-[(2-[(2-hydroxy-5-bromobenzylidene)amino]ethyl)-3-ethylimidazolium tetrafluoroborate] (2), and M(II) complexes (3, 4 and 5) from LH (2).

mixture was cooled to room temperature. The precipitate was collected by filtration, washed successively with cold ethanol (3×10 mL). 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 is shown in Scheme 1.

2.5a Co(II) complex (4): Brown solid; M.p.: 128–130 °C; $\text{C}_{28}\text{H}_{32}\text{CoBr}_2\text{F}_8\text{N}_6\text{O}_2$; Anal. Found: C, 38.16; H, 3.53; N, 9.32, Co, 6.42%. Calc.(%) for C, 38.35; H, 3.68; N, 9.58; Co, 6.72%. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H/H}_2\text{O}}$) 3442, ($\nu_{\text{CH=N}}$) 1629, ($\nu_{\text{C-O}}$) 1316, (ν_{BF_4}) 1019, (ν_{Br}) 713, ($\nu_{\text{M-O}}$) 633, ($\nu_{\text{M-N}}$) 523. UV-Vis (Methanol) $\lambda_{\text{max}}/\text{nm}$: 220, 338, 394. ESI-MS (m/z): Calc. 701: Found: 701 ($[\text{M-BF}_4]^+$, $\text{M} = [\text{C}_{28}\text{H}_{32}\text{CoBr}_2\text{N}_6\text{O}_2]^+$).

2.5b Ni(II) complex (5): Light green solid; M.p. 140–142 °C; $\text{C}_{28}\text{H}_{32}\text{NiBr}_2\text{F}_8\text{N}_6\text{O}_2$; Anal. Found: C, 38.11; H, 3.50; N, 9.37, Ni, 6.33%. Calc.: C, 38.36; H, 3.68; N, 9.58; Ni, 6.69%. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H/H}_2\text{O}}$) 3437, ($\nu_{\text{CH=N}}$) 1627, ($\nu_{\text{C-O}}$) 1314, (ν_{BF_4}) 1018, (ν_{Br}) 715, ($\nu_{\text{M-O}}$) 634, ($\nu_{\text{M-N}}$) 535. UV-Vis (Methanol) $\lambda_{\text{max}}/\text{nm}$: 219, 340, 400. ESI-MS (m/z): Calc. 700: Found: 702 ($[\text{M}+2]\text{-BF}_4$, $\text{M} = [\text{C}_{28}\text{H}_{32}\text{NiBr}_2\text{N}_6\text{O}_2]^+$).

2.5c Cu(II) complex (6): Dark green solid; M.p. 147–149 °C; $\text{C}_{28}\text{H}_{32}\text{CuBr}_2\text{F}_8\text{N}_6\text{O}_2$; Anal. Found: C, 38.07; H, 3.49; N, 9.31, Cu, 6.99%. Calc.: C, 38.15; H, 3.66; N, 9.53; Cu, 7.21%. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H/H}_2\text{O}}$) 3448, ($\nu_{\text{CH=N}}$) 1625, ($\nu_{\text{C-O}}$) 1317, (ν_{BF_4}) 1014, (ν_{Br}) 717, ($\nu_{\text{M-O}}$) 648, ($\nu_{\text{M-N}}$) 559. UV-Vis (Methanol) $\lambda_{\text{max}}/\text{nm}$: 222, 342, 396. ESI-MS (m/z): Calc. 705: Found: 705 ($[\text{M-BF}_4]^+$, $\text{M} = [\text{C}_{28}\text{H}_{32}\text{CuBr}_2\text{N}_6\text{O}_2]^+$).

2.6 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^{31,32} by NCCLS (National Committee for Clinical Laboratory Standards, 1997, India). The nutrient agar (Hi-Media Laboratories Limited, Mumbai, India) was autoclaved at 121 °C and 1 atm for 15–20 min. 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 extract and placed on the nutrient agar media plates. The different concentrations were made by adding with DMSO. The plates were incubated for 24 h 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.

3. Results and Discussion

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

3.1 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. IR

Figure 1. IR spectrum of: (A) 1-{2-[(2-hydroxy-5-bromobenzylidene)amino]ethyl}-3-ethylimidazolium tetrafluoroborate (**2**); (B) Co(II) complex (**3**); (C) Ni(II) complex and (**4**) and (D) Cu(II) complex (**5**).

spectra of the ligand, LH (**2**) and its metal complexes (**3** to **5**) are given in Figure 1. Only the distinct and characteristic peaks have been discussed. IR spectra of the ligand exhibited a strong broad absorption band at 3450–3236 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).^{33,34} All the complexes showed broad diffuse band at 3437–3448 cm^{-1} which may be attributed to the presence of the coordinated/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.^{35–37} 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 1314–1317 cm^{-1} for all the complexes. This fact suggests the involvements of phenolic C–O in the coordination process.³⁸ This interpretation is further confirmed by the appearance of M–O band at 633–638 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 is shifted to the lower frequencies in the range 1625–1629 cm^{-1} in case of the metal complexes, indicating the participation of azomethine group (–C=N) in the coordination sphere.³⁹ This is further emphasized by the appearance of a new weak to medium intensity absorption band in the region 523–559 cm^{-1} that may be attributed to M–N stretching vibration for the metal complexes.⁴⁰ The bands in the range of 1014–1019 cm^{-1} for the spectra of metal complexes are assigned for B–F stretching frequency.

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. ESI-MS spectrum of the compound, [2-aeem]BF₄ showed a peak at 140 ([M–BF₄]⁺, which corresponds to M⁺, [M=C₇H₁₄N₃]⁺).⁴¹ The ligand (LH) exhibited a peak (*m/z*) at 323 [M–BF₄]⁺, which can be assigned to [M=C₁₄H₁₇N₃O]⁺.⁴² The Co(II) complex (**3**) displayed a peak (*m/z*) at 701.49 which corresponds to the [M–BF₄]⁺ ion. A peak (*m/z*) at 701.62 in the ESI-MS spectrum of Ni(II) complex (**4**) is assigned to the [M+H–BF₄]⁺ ion. In the ESI-MS spectrum, the Cu(II) complex (**5**) exhibited a peak (*m/z*) at 705.74 which is assigned to the [M–BF₄]⁺ ion.⁴³ (The ESI-MS spectra of the complexes and ligand are given in Figures S1 and S2 in Supplementary Information). 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.

3.3 ¹H and ¹³C-NMR spectral studies

¹H-NMR and ¹³C-NMR spectra of ligand were recorded in DMSO-*d*₆ (Figures S3 and S4 in Supplementary Information). ¹H-NMR of the ligand showed singlet at 8.50 ppm is assignable to proton of the azomethine group (–CH=N–) presumably due to the effect of the *ortho*-hydroxyl group in the aromatic ring. A singlet at 9.10 ppm can tentatively be attributed to hydroxyl proton. The Schiff base displayed downfield shift of the –OH proton is due to intermolecular (O–H...N) hydrogen bond.⁴⁴ ¹³C-NMR spectra of ligand exhibited peaks at δ 137.31 and 135.59 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 123.76, 123.09, 122.41, 122.25 and 119.53. (¹H-NMR and ¹³C-NMR spectra are given in Figures S3 and Figure S4, Supplementary Information).

3.4 Molar conductance measurements

The molar conductance of the complexes (Λ_m) were measured by using the relation $\Lambda_m = 1000 \times \kappa / c$, 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 and their molar conductivities were measured at (298.15 ± 0.01) K. The conductance values were in the range of 134, 131 and 130 S cm^{−1} mol^{−1}, respectively, for the metal complexes (**3** to **5**), indicating their 1:2 (M:L) electrolytic behaviour.

3.5 Electronic absorption spectral and magnetic moment studies

UV-Visible spectra of the ligand and the metal complexes (Figure 2) were recorded at ambient temperature using methanol as solvent. The electronic spectrum of free Schiff base 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.^{45,46} 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 (**3**) displayed a band at 394 nm which could be assigned to the combination of ²B_{1g} → ¹A_{1g} and ¹B_{1g} → ²E_g transitions and supporting square planar geometry.^{47,48} The complex (**3**) shows the magnetic moment of 2.30 BM due to one unpaired electron. The Ni(II) complex (**4**) was diamagnetic and the

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

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

band around 400 nm due to $^1A_{1g} \rightarrow ^1B_{1g}$ transition is consistent with low spin square planar geometry.⁴⁹ The UV-visible spectra of Cu(II) complex (**5**) showing $d \rightarrow \pi^*$ 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.^{50,51} The observed magnetic moment for Cu(II) complex (**5**) was 1.82 B.M. consistent with the presence of a single unpaired electron.⁵²

3.6 Antibacterial activities

Minimum inhibitory concentration was measured by Broth Micron 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 into each of these tubes. A similar nutrient broth tube without sample was also inoculated and used as a control. The tubes were kept at 37°C for 24 h. 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 have shown promising result against all the bacterial strains (Table S1 in Supplementary Information). From the inhibitory values, it is clear that the Schiff based ligand is most effective against five organisms (MIC 10 µg/mL) except *E. aerogenes*. Co(II) complex (**3**) is most effective against *P. vulgaris* and *E. aerogenes*. Ni(II) complex (**4**) is observed very active against *E. coli*, *S. aureus*, *P. aeruginosa* and *E. aerogenes* (MIC 10 µg/mL). It is seen that Cu(II) complex (**5**) is most effective among the others samples due to their MIC value of 20 µg/mL against *E. coli*, *S. aureus*, *B. cereus* and 30 µg/mL against *P. aeruginosa* and *P. vulgaris*. The results are shown in Figure 3.

4. Conclusions

In this research, the preparation and physico-chemical characterization of new Co(II), Ni(II) and Cu(II) complexes bearing an ionic liquid-supported Schiff base 1-{2-[(2-hydroxy-5-bromobenzylidene)amino]ethyl}-3-ethylimidazolium tetrafluoroborate as ligand, 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 coordinates to the central metal ion through the azomethine nitrogen and phenolic oxygen atoms, yielding square planar complexes. The synthesized complexes showed reasonable antibacterial activity against the tested bacteria. Cu(II) complex (**5**)

showed most effective activity effective activity than the other samples.

Supplementary Information (SI)

Experimental biological assays data, ESI-MS and NMR spectral data for the ligand and complexes are given as Supplementary Information, available at www.ias.ac.in/chemsci.

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