Transition metal complexes obtained from an ionic liquid-supported Schiff base: synthesis, physicochemical characterization and exploration of antimicrobial activities

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Abstract. An ionic liquid-supported Schiff base 1-{2-(2-hydroxy-5-chlorobenzylamine) ethyl}-3-methylimidazolium tetrafluoroborate and its Co(II), Ni(II), Cu(II), Mn(III), Fe(III) and Cr(III) complexes were synthesized and characterized by various analytical (elemental analysis, molar conductance and magnetic susceptibility measurements) and spectroscopic (PXRD, SEM, ESI-MS, UV-Visible, FT-IR, ¹H NMR and ¹³C-NMR) methods. Based on these spectral data and spectra, tetra coordinated and hexacoordinated geometries were assigned for the synthesized metal complexes. Molar conductance of the complexes showed their (1:2) electrolytic nature. The Schiff base ligand and its complexes were screened for *in vitro* antimicrobial activities against some naturally available gram positive and gram negative bacteria to assess their inhibition potentials. Maximum inhibition zone was produced by the Cu(II) complex (**5a**) in plates of *Klebsiella pneumoniae* while the minimum inhibition zone was produced by in plates of *Bacillus cereus*.

Keywords. Ionic liquid; Schiff base; transition metal complexes; antimicrobial studies.

1. Introduction

The search of environmentally benign nonaqueous solvents that could easily be recovered or recycled, and the use of efficient and selective catalyst are two primary aims for the development of the sustainable and green chemical process.¹ Ionic liquids (ILs), which are the new class of solvents, also termed as neoteric solvents, lead to a new green chemical revolution. Their unique array of physicochemical properties along with negligible vapor pressure makes ILs suitable for various applications.² These new solvents are also termed as room temperature ionic liquids (RTILs) or liquid organic salts. ILs are a class of substances that are entirely made of ions (cations and anions) and are liquid at a temperature lower than 100 °C. They have many attractive features, including low flammability, a wide liquid range, high ionic conductivity, high thermal and chemical stability, good dissolution power toward many

substrates and wide electrochemical windows.^{3,4} Owing to these attracting properties, ILs have been recognized as solvents or reagents for a variety of applications, including organic catalysis,^{5–10} inorganic synthesis,¹¹ biocatalysis,^{12–16} polymerization^{17,18} and engineering fluids.^{19,20} Again, due to their designable properties, ILs have recently been exploited as solvents or materials for a variety of pharmaceutical applications.^{21,22} Recently, chemists have focused much attention on the synthesis, characterization and application of new ionic liquids called functionalized ionic liquids (FILs). FILs are defined as ionic liquids in which functional group are covalently attached to the cation or anion (or both). Conceptually, the functionalized ion of a FILs may be regarded as possessing two elements. The first is a core that contains the ionic charge and behaves as the locus for the second element i.e., the substituent group.^{23–25} In most cases, the functional group is cation-tethered. The introduction of such functionality can imbue the

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salt with an ability to act as a reaction medium as well as a catalyst or reagent in some chemical reactions.^{26,27}

Schiff bases and its transition metal complexes have captured a crucial role in the progress of modern coordination chemistry. They are also being found as a key material in the growth of inorganic biochemistry, catalysis, optical materials, etc.²⁸ At present, transition metal complexes derived from multidentate unsymmetrical Schiff base ligands carrying both $-\text{NH}_2$ (amine) and $-\text{OH}$ (hydroxyl) groups have drawn much attention.²⁹ Schiff base complexes catalyze a wide number of heterogeneous and homogeneous reactions and their activity may be altered by varying metal ions, coordination sites and the ligand nature.³⁰ Schiff base ligands having N, S and O as donor atoms exhibit a wide range of biological applications and gained special interest due to the number of ways they can bond to the metal ions.³¹ In this research work, the synthesis, physico-chemical characterization and antimicrobial activities of new transition metal complexes derived from an ionic liquid-supported Schiff base, 1-{2-(2-hydroxy-5-chlorobenzylideneamino)ethyl}-3-methylimidazolium tetrafluoroborate have been discussed.

2. Experimental

2.1 Materials and physical measurements

Analytical grade chemicals were used for synthesis without further purification. 1-methyl imidazole, 2-bromoethylamine hydrobromide, 5-chloro-2-hydroxybenzaldehyde and NaBF_4 (sodium tetrafluoroborate) were collected from Sigma Aldrich, Germany. Metal acetates $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, $[\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ and metal chlorides [anhydrous FeCl_3 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$] 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. FT-IR spectra were recorded by KBr pellets on a Perkin-Elmer Spectrum FT-IR spectrometer (RX-1). ^1H -NMR spectra were recorded on an 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 ($2\theta = 0-90^\circ$). SEM images were taken in JEOL-JSM-IT-100. Elemental micro-analysis (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. Mass 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 a solvent.

Specific conductance was measured at $(298.15 \pm 0.01) \text{ K}$ 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 the open capillary method. Antimicrobial activity (*in vitro*) of the synthesized ligand and complexes were evaluated by well diffusion method against two gram-positive (*Staphylococcus aureus* and *Bacillus cereus*) and two gram-negative (*Escherichia coli* and *Klebsiella pneumoniae*) bacteria.

2.2 Synthesis of [1-(2-aminoethyl)-3-methylimidazolium tetrafluoroborate, [2-aemim][BF_4]] (1a)

This amine functionalized ionic liquid was synthesized by slight modification of literature procedure.³² 1-methylimidazole (4.10 g, 0.05 mol), 2-bromoethylamine hydrobromide (10.25 g, 0.05 mol) and NaBF_4 (5.5 g, 0.05 mol) were used. The product was obtained as yellow oil. Yield: 71%; $\text{C}_6\text{H}_{12}\text{F}_4\text{N}_3\text{B}$: Anal. Found: C, 33.58; H, 5.42; N, 19.65%. Calc.: C, 33.84; H, 5.68; N, 19.73%. IR (KBr, cm^{-1}): ($\nu_{\text{N-H}}$) 3439, 2369, 2055, 1634 ($\text{C}=\text{N}$), 1297, (ν_{BF_4}) 1087. ESI-MS (m/z): Calc.: 126; Found: 126 ($[(\text{M}-\text{BF}_4)^+]$, $\text{M} = [\text{C}_6\text{H}_{12}\text{N}_3]^+$). ^1H NMR (400 MHz, D_2O , TMS): δ 3.22 (2H, t, $\text{NH}_2\text{-CH}_2$); 4.23 (3H, s, CH_3), 4.43 (1H, t, N-CH_2), 7.42 (1H, s, NCH), 7.49 (1H, s, NCH), 8.67 (2H, s, NH_2), 8.75 (1H, s, N(H)CN); ^{13}C NMR (400 MHz, D_2O , TMS): δ 137.07, 124.28, 122.33, 54.37, 39.58, 37.53.

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

5-chloro-2-hydroxybenzaldehyde (1.57 g, 10 mmol) and [2-aemim] BF_4 (2.13 g, 10 mmol) were taken in a round bottomed flask and methanol was used as solvent. The reaction mixture was stirred at room temperature for 12 h. After completion of reaction, ethanol was used to dilute the solid. The precipitate was filtered, washed with cold ethanol and dried properly to collect the Schiff base as a light yellow solid. Yield: 73%; M.p.: $93-95^\circ\text{C}$; $\text{C}_{13}\text{H}_{15}\text{N}_3\text{OClIBF}_4$: Anal. Found: C, 44.14; H, 4.09; N, 11.83(%). Calc.: C, 44.42; H, 4.30; N, 11.95%. IR (KBr, cm^{-1}): ($\nu_{\text{O-H}}$) 3448, 3071, ($\nu_{\text{CH}=\text{N}}$) 1665, ($\nu_{\text{C-O}}$) 1279, (ν_{BF_4}) 1106. UV-Vis (Methanol) $\lambda_{\text{max/nm}}$: 220, 250, 336. ESI-MS (m/z): Calc. 264; Found: 264 ($[(\text{M}-\text{BF}_4)^+]$, $\text{M} = [\text{C}_{13}\text{H}_{15}\text{ClN}_3\text{O}]^+$). ^1H NMR (400 MHz, D_2O , TMS): δ 2.49 (2H, t, N-CH_2), 3.51 (2H, t, N-CH_2), 4.28 (3H, s, CH_3), 6.97–6.90 (3H, m, Ar-H), 7.62 (1H, s, NCH), 7.63 (1H, s, NCH), 10.18 (1H, s, $\text{N}=\text{CH}$), 7.70 (1H, s, N(H)CN), 9.30 (1H, s, OH). ^{13}C NMR: ^1H NMR (400 MHz, D_2O , TMS): δ 165.81, 142.24, 139.44, 130.53, 124.32, 122.05, 110.01, 39.85, 39.64, 39.22, 39.01, 38.80 and 38.60.

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

To a solution of ligand, (2a) (0.352 g, 1 mmol) in ethanol (20 mL), metal acetate salt Co(II), Ni(II) and Cu(II), viz.,

Scheme 1. Synthesis of the metal complexes **3a**, **4a** and **5a** from Schiff base (**2a**).

(0.5 mmol) dissolved in ethanol was added gradually in a round-bottomed flask. The mixture was refluxed for 4 h until the starting materials were completely consumed as monitored by TLC. After that, solvents were evaporated and the reaction mixture was cooled to room temperature. The solid was collected by filtration, washed successively with cold ethanol (10 mL $\times$ 3). Finally, it was dried in vacuum desiccators to obtain the desired product. A schematic representation of the synthesis is shown in Scheme 1.

2.4a Co(II) complex (3a): Brown solid; Yield: 70%; Decomposes at $\sim 253^\circ\text{C}$. $\text{C}_{26}\text{H}_{28}\text{CoCl}_2\text{B}_2\text{F}_8\text{N}_6\text{O}_2$: Anal. Found: C, 40.69; H, 3.41; N, 10.86, Co, 7.62%. Calc.: 41.09; H, 3.71; N, 11.06, Co, 7.75%. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H}}$) 3438, ($\nu_{\text{CH=N}}$) 1628, ($\nu_{\text{C-O}}$) 1316, (ν_{BF_4}) 1075, ($\nu_{\text{M-O}}$) 638, ($\nu_{\text{M-N}}$) 523. UV-Vis (Methanol) $\lambda_{\text{max/nm}}$: 220, 340, 401. ESI-MS (m/z): Calc.: 585; Found: 585; $[\text{M}-2\text{BF}_4]^+$, $\text{M}=[(\text{C}_{26}\text{H}_{28}\text{CoCl}_2\text{N}_6\text{O}_2)^+]$.

2.4b Ni(II) complex (4a): Light green solid; Yield: 69%; Decomposes at $\sim 251^\circ\text{C}$. $\text{C}_{26}\text{H}_{28}\text{NiCl}_2\text{B}_2\text{F}_8\text{N}_6\text{O}_2$: Anal. Found: C, 41.02; H, 3.63; N, 10.46, Ni, 7.19%. Calc.: C, 41.10; H, 3.71; N, 11.06; Ni, 7.26%. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H}}$) 3453, ($\nu_{\text{CH=N}}$) 1628, ($\nu_{\text{C-O}}$) 1322, (ν_{BF_4}) 1012, ($\nu_{\text{M-O}}$) 565, ($\nu_{\text{M-N}}$) 439. UV-Vis (Methanol) $\lambda_{\text{max/nm}}$: 220, 340, 400. ESI-MS (m/z): Calc.: 584; Found: 586; $[\text{M}+2\text{H}-2\text{BF}_4]^+$, $\text{M}=[(\text{C}_{26}\text{H}_{28}\text{NiCl}_2\text{N}_6\text{O}_2)^+]$.

2.4c Cu(II) complex (5a): Dark green solid; Yield: 71%; Decomposes at $\sim 265^\circ\text{C}$. $\text{C}_{26}\text{H}_{28}\text{CuCl}_2\text{B}_2\text{F}_8\text{N}_6\text{O}_2$: Anal. Found: C, 40.12; H, 3.51; N, 10.46, Cu, 8.11%. Calc.: C, 40.84; H, 3.69; N, 10.99; Cu, 8.31%. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H}}$) 3448, ($\nu_{\text{CH=N}}$) 1624, ($\nu_{\text{C-O}}$) 1320, (ν_{BF_4}) 1012, ($\nu_{\text{M-O}}$) 651, ($\nu_{\text{M-N}}$) 565. UV-Vis (Methanol) $\lambda_{\text{max/nm}}$: 222, 242, 394. ESI-MS (m/z): Calc.: 589; Found: 588 $[\text{M}-\text{H}-2\text{BF}_4]^+$, $\text{M}=[(\text{C}_{26}\text{H}_{28}\text{CuCl}_2\text{N}_6\text{O}_2)^+]$.

2.5 Synthesis of the metal complexes (6a, 7a and 8a)

The Schiff base (**2a**) (1.76 g, 5 mmol) was taken in a round-bottomed flask and dissolved in EtOH (20 mL). $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.61 g, 2.5 mmol) and LiCl (0.15 g, 2.5 mmol) for complex **6a** and FeCl_3 (0.405 g, 2.5 mmol) or $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (0.66 g, 2.5 mmol) for the complex **7a** and **8a** respectively, was also added in the same solvent and the reaction mixture was refluxed for 4–6 h. The reaction was monitored by TLC. On completion of the reaction, solvents were evaporated and cooled to room temperature. The solid was collected by filtration, washed with cold $\text{C}_2\text{H}_5\text{OH}$ (10 mL $\times$ 3), dry ether (10 mL $\times$ 3) respectively and finally dried in desiccators to obtain the desired product. A schematic representation of the syntheses is given in Scheme 2.

2.5a Mn(III) complex (6a): Light brown solid; Yield: 67%; Decomposes at $\sim 269^\circ\text{C}$. $\text{C}_{26}\text{H}_{30}\text{MnB}_2\text{Cl}_3\text{F}_8\text{N}_6\text{O}_3$: Anal. Found: C, 38.35; H, 3.56; N, 10.12, Mn, 6.52%. Calcd. for (%): C, 38.58; H, 3.74; N, 10.38, Mn, 6.79%. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H/H}_2\text{O}}$) 3433, ($\nu_{\text{CH=N}}$) 1649, ($\nu_{\text{C-O}}$) 1314, (ν_{BF_4}) 1019, ($\nu_{\text{M-O}}$) 651, ($\nu_{\text{M-N}}$) 528. UV-Vis (Methanol) $\lambda_{\text{max/nm}}$: 216, 244, 340. ESI-MS: (m/z): Calc. 616; Found: 618 $[\text{M}+2\text{H}-2\text{BF}_4-\text{H}_2\text{O}]^+$, $\text{M}=[\text{C}_{26}\text{H}_{28}\text{MnCl}_3\text{N}_6\text{O}_2]^+$.

2.5b Fe(III) complex (7a): Grey solid; Yield: 69%; Decomposes at $\sim 270^\circ\text{C}$. $\text{C}_{26}\text{H}_{30}\text{FeB}_2\text{Cl}_3\text{F}_8\text{N}_6\text{O}_3$: Anal. Found: C, 38.12; H, 3.63; N, 10.09, Fe, 6.71%. Calc.: C, 38.54; H, 3.73; N, 10.37; Fe, 6.89%. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H/H}_2\text{O}}$) 3430, ($\nu_{\text{CH=N}}$) 1661, ($\nu_{\text{C-O}}$) 1276 (ν_{BF_4}) 1116, ($\nu_{\text{M-O}}$) 543, ($\nu_{\text{M-N}}$) 453. UV-Vis (Methanol) $\lambda_{\text{max/nm}}$: 215, 243, 343. ESI-MS: (m/z): Calc.: 617; Found: 618 $[\text{M}-\text{H}-2\text{BF}_4-\text{H}_2\text{O}]^+$, $\text{M}=[\text{C}_{26}\text{H}_{28}\text{FeCl}_3\text{N}_6\text{O}_2]^+$.

2.5c Cr(III) complex (8a): Light green solid; Yield: 65%; Decomposes at $\sim 267^\circ\text{C}$. $\text{C}_{26}\text{H}_{30}\text{CrB}_2\text{Cl}_3\text{F}_8\text{N}_6\text{O}_3$:

Scheme 2. Synthesis of metal complexes **6a**, **7a** and **8a** from **2a**.

Anal. Found: C, 38.42; H, 3.61; N, 10.10, Cr, 6.22%. Calc.: C, 38.72; H, 3.75; N, 10.42, Cr, 6.45%. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H/H}_2\text{O}}$) 3431, ($\nu_{\text{CH=N}}$) 1660, ($\nu_{\text{C-O}}$) 1276, (ν_{BF_4}) 1116, ($\nu_{\text{M-O}}$) 543, ($\nu_{\text{M-N}}$) 452. UV-Vis (Methanol) $\lambda_{\text{max/nm}}$: 220, 338, 394. ESI-MS: (m/z): Calc.: 613; Found: 613 [$[\text{M}-2\text{BF}_4-\text{H}_2\text{O}]^+$, $\text{M}=[\text{C}_{26}\text{H}_{28}\text{CrCl}_3\text{N}_6\text{O}_2]^+$].

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, dimethylsulphoxide, acetonitrile, methanol and water.

2.6 Antimicrobial activity

Broth culture of overnight grown four bacterial strains of which two were gram-positive (*Staphylococcus aureus* and *Bacillus cereus*) and the other two-gram negative (*Escherichia coli* and *Klebsiella pneumoniae*) were used for the present study to assess the antimicrobial activities of synthesized compounds. Mueller-Hinton agar media (Himedia) was used for susceptibility tests. 38.0 g of MH media was added in 1000 mL of double distilled water and heated to dissolve completely. The media was sterilized by autoclaving at 20 lbs pressure at 121 °C for 20 min. The media was cooled down to room temperature and poured in sterile Petri plates at the sterile condition of laminar air flow cabinet. 100 μL of bacterial strains were added separately to each Petri plates containing media and agitated for mixing. 20 mg powdered samples were dissolved in 1000 μL of dimethyl sulfoxide (DMSO). Paper disc diffusion method was applied.³³ Circular paper disc were cut from Whatman 42 filter papers and were dipped in the sample solutions for one hour. The paper discs dipped in sample solutions were placed on the media containing bacterial culture and incubated overnight at 37 °C.

3.1 FT-IR spectral studies

In order to justify the coordination sites, the FT-IR spectra of the Schiff base (**2a**) and all the complexes (**3a–8a**) were studied carefully. FT-IR spectra of LH (**2a**) showed a strong band at 3448–3071 cm^{-1} ; which was due to the hydrogen bonded phenolic group (-OH) with H-C(=N) group in the ligand ($\text{OH}\dots\text{N}=\text{C}$).^{34,35} The broad band that appeared at 3453–3430 cm^{-1} for the metal complexes suggested the presence of the solvated (probably for the intrinsic property of the anion tetrafluoroborate) or coordinated water molecules.^{36–38} The band due to the azomethine group (-C=N) of the ligand was found at 1665 cm^{-1} . This band gets shifted in the range 1661–1624 cm^{-1} because of coordination of N atom of azomethine linkage to the metal ions.³⁹ The band for phenolic C-O of the free ligand was observed at 1279 cm^{-1} which were moved to the wave number 1322–1276 cm^{-1} for the complexes after complexation. This fact suggested the bonding of ligand (**2a**) to the metal atoms through the N atom of azomethine and O

atom of the phenolic group.⁴⁰ The bands appeared in the region of 1116–1012 cm^{-1} for the ligand and metal complexes were assigned for B-F stretching frequency. The spectra of the metal complexes exhibited bands at 651–543 and 565–439 cm^{-1} were attributed to M-O and M-N stretching vibrations, respectively.⁴¹ The band due to M-Cl, expected to appear at around 320–250 cm^{-1} , which was beyond the experimental IR range.^{42,43} (FT-IR spectra of the ligand and its metal complexes are given as Figure S1–S7 in Supplementary Information).

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

The ^1H -NMR and ^{13}C -NMR spectra of ligand were recorded in DMSO- d_6 . The ^1H -NMR spectrum of ligand (**2a**) showed singlet at δ 10.18 ppm corresponds to the proton of the azomethine linkage ($-\text{CH}=\text{N}-$) apparently because of the effect of the *ortho*-hydroxyl group in the aromatic ring. A singlet at δ 9.30 ppm was assigned to hydroxyl proton ($-\text{OH}$). The downfield shift of the phenolic ($-\text{OH}$) proton was observed due to intramolecular ($\text{O}-\text{H}\cdots\text{N}$) hydrogen bonding in the ligand.⁴⁴ ^{13}C -NMR spectra of ligand exhibited peaks at δ 165.81 and 142.24 probably due to the phenolic (C-O) and imino ($-\text{CH}=\text{N}$) carbon atoms (due to Keto-imine tautomerism). The chemical shifts due to the aromatic carbons appeared at δ 139.44–110.01 ppm. ^1H -NMR and ^{13}C -NMR spectra of LH (**2a**) are given as Figure S8 and S9 in Supplementary Information).

3.3 Powder X-ray diffraction analysis

The PXRD analysis of the synthesized ligand and metal complexes was carried out to confirm whether the particle nature of the samples was amorphous or crystalline. The PXRD spectrum of ligand (**2a**) displayed sharp peaks because of their crystalline nature although the spectra of the metal complexes didn't show such peaks due to their amorphous nature. 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 the Schiff base and its metal complexes were found to be 31.05 nm (**2a**), 3.96 nm (**3a**), 2.56 nm (**4a**), 3.82 nm (**5a**), 3.32 nm (**6a**), 8.91 nm (**7a**) and 11.94 nm (**8a**). PXRD pattern of the ligand and its metal complexes are shown in Figures 1, 2, 3, 4, 5, 6, 7.

3.4 Mass spectral studies

To clarify the structure of the synthesized compounds at the molecular level, electrospray ionization (ESI)

Figure 1. PXRD spectra of LH (**2a**).

Figure 2. PXRD spectra of Co(II) complex (**3a**).

Figure 3. PXRD spectra of Ni(II) complex (**4a**).

mass spectrometry was recorded using methanol as solvent. Mass-spectra of the LH (**2a**) had a molecular ion peaks at m/z 264, that corresponds to $[\text{M}-\text{BF}_4]^+$, ($\text{M}=[\text{C}_{13}\text{H}_{15}\text{ClN}_3\text{O}]^+$) ion. The Co(II) complex (**3a**) exhibited molecular ion peaks (m/z) at 585, which was assigned to $[\text{M}-2\text{BF}_4]^+$ ($\text{M}=[\text{C}_{26}\text{H}_{28}\text{CoCl}_2\text{N}_6\text{O}_2]^+$). The molecular ion peaks appeared at 586

Figure 4. PXRD spectra of Cu(II) complex (**5a**).

Figure 5. PXRD spectra of Mn(III) complex (**6a**).

Figure 6. PXRD spectra of Fe(III) complex (**7a**).

$([M+2H-2BF_4]^+, M=[(C_{26}H_{28}NiCl_2N_6O_2)^+])$ and at 588 $([M-H-2BF_4]^+, M=[(C_{26}H_{28}CuCl_2N_6O_2)^+])$ were assigned for Ni(II) complex (**4a**) and Cu(II) complex (**5a**) respectively. The mass spectra of the Mn(III) complex (**6a**) shown a molecular ion peak at 616 which was due to $[M+2H-2BF_4-H_2O]^+$ ion where $M=[C_{26}H_{28}MnCl_3N_6O_2]^+$. The Fe(III) complex (**7a**) and Cr(III) complex (**8a**) displayed peaks at 618 for $[M-H-2BF_4-H_2O]^+$, $M=[C_{26}H_{28}FeCl_3N_6O_2]^+$ ion and 613 for $[M-2BF_4-H_2O]^+$, $M=[C_{26}H_{28}CrCl_3N_6O_2]^+$ ion. The mass spectra of the ligand and complexes were

Figure 7. PXRD spectra of Cr(III) complex (**8a**).

Figure 8. UV-Visible spectra of the Schiff base (**2a**) and its metal complexes (**3a–8a**)

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 Figures S10–S16 in Supplementary Information).

3.5 Electronic absorption spectral and magnetic moment studies

The UV-Visible spectra of the Schiff base and its metal complexes (Figure 8) were recorded at ambient temperature using methanol as solvent. The LH (**2a**) exhibited three absorption bands at 336, 250 and 220 nm due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and transitions involved with the imidazolium moiety, respectively.^{45,46} For the complexes (**3a**, **4a** and **5a**), the bands that appeared below 350 nm were ligand centred transitions ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$). The Co(II) complex (**3a**) showed a shoulder at 398 nm which was attributed to the combination of

Figure 9. MIC of the Cu(II) complex against the tested organisms *Klebsiella pneumonia* and *Bacillus cereus*.

${}^2B_{1g} \rightarrow {}^1A_{1g}$ and ${}^1B_{1g} \rightarrow {}^2E_g$ transitions and supporting square planar geometry.^{47,48} The complex (**3a**) showed a magnetic moment of 2.32 B.M. due to an unpaired electron. The Ni(II) complex (**4a**) was diamagnetic and the band observed at around 400 nm due to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition was consistent with low spin square planar geometry.⁴⁹ UV-visible spectra of Cu(II) complex (**5a**) displayed $d \rightarrow \pi^*$ metal-ligand charge transfer transition (MLCT) at the region 395 nm was assigned for a combination of ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions in a distorted square planar geometry.^{50,51} The experimental magnetic moment value for **5a** was 1.82 B.M. consistent with the presence of an unpaired electron.⁵² In the UV-Visible spectra of Mn(III) complex (**6a**) three bands at 339, 243 and 216 nm were observed. Due to its d^4 electronic structure; the electronic transition was assigned to ${}^5T_{2g} \rightarrow {}^5E_g$ which proposed that the metal centre was effectively coordinated by ligand in an octahedral environment.^{53,54} The observed magnetic moment was found 4.84 B.M. for Mn(III) complex (**6a**). The Fe(III) complex (**7a**), (d^5 configuration) showed

bands at 343, 245 and 215 nm. The band at 343 nm, assigned to the spin and parity forbidden ${}^6A_{1g} \rightarrow T_{2g}$ transition of Fe(III) ion in an octahedral field. The high spin octahedral Fe(III) complexes used to show very weak and spin forbidden d-d transition which didn't appear in the spectra due to the low intensity of the d-d transition. The observed magnetic moment of 5.62 B.M. for **7a** suggested high spin configuration of the metal ion with five unpaired electrons.⁵⁵ UV-visible spectrum of the Cr(III) complex (**8a**) exhibited three bands at 394, 338, 220 nm. These bands could be attributed to ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively suggesting octahedral geometry around the Cr(III) ion.^{52,56} Again the complex **8a** showed the magnetic moment of 3.93 B.M. corresponding to three unpaired electrons.

3.6 Antimicrobial activities

Antimicrobial susceptibility tests were conducted to assess the efficacy of synthesized compounds. The

seven synthesized compounds showed variable results (Figure 9 and Table S1 in Supplementary Information). All the compounds except **6a** showed positive responses. The samples showed almost similar results for gram-positive and negative bacterial samples. Maximum inhibition zone was produced by the Cu(II) complex (**5a**) in plates of *Klebsiella pneumoniae* while the minimum inhibition zone was produced by *Bacillus cereus*. *Staphylococcus aureus* showed maximum susceptibility for all the samples in comparison to the other bacterial cultures. So, it was concluded that the ligand (**2a**) along with its metal complexes (**3a**, **4a**, **5a**, **6a**, **7a** and **8a**) inhibited the growth of pathogenic bacteria like *Staphylococcus aureus*, *Bacillus cereus*, *Escherichia coli* and *Klebsiella pneumoniae*.

4. Conclusions

In this research work, new transition complexes of an ionic liquid-based Schiff base, 1-{2-(2-hydroxy-5-chlorobenzylideneamino)ethyl}-3-methylimidazolium tetrafluoroborate were synthesized and characterized by different spectral and analytical techniques. The Schiff base ligand acts as a potential bidentate ligand coordinating through the N-atom of azomethine and O-atom of the phenolic group to the metal ions and thus formed 1:2 (M:L) complexes. Spectral and analytical data suggested that the ligand was arranged in square planar geometry in case of Co(II), Ni(II) and Cu(II) complexes although in case of Mn(III), Fe(III) and Cr(III) complexes it was oriented in octahedral geometry around the central metal ions. The antimicrobial studies of the synthesized compounds were performed and the ligand along with the metal complexes has exhibited promising activity against the tested bacteria.

Supplementary Information (SI)

FT-IR, ¹H NMR, ¹³C NMR spectra, ESI-MS spectra, SEM images and experimental biological assays data of the Schiff base and metal complexes are attached as supplementary information. Supplementary information is available at www.ias.ac.in/chemsci.

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