

Synthesis, physico-chemical characterization and antibacterial studies of new Fe(III) and Cr(III) complexes with an ionic liquid-supported Schiff base ligand

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An ionic liquid-supported Schiff base 1-{2-(2-hydroxy-5-bromobenzylamine)ethyl}-3-ethylimidazolium tetrafluoroborate and its Fe(III) and Cr(III) complexes has been prepared and characterized by various analytical and spectroscopic methods such as elemental analysis, UV-visible, FTIR, ¹H NMR, mass spectra, TGA/DTG, molar conductance and magnetic susceptibility measurements. Based on these spectral studies octahedral geometry has been proposed for both complexes. Molar conductance of the complexes is showing their electrolytic nature. The Schiff base ligand and its complexes have tested for *in vitro* antibacterial activities against gram positive and gram negative bacteria to assess their inhibition potentials. Cr(III) complex has shown higher activity than the Fe(III) complex against the tested bacteria *S. aureus* and *E. coli*.

Keywords: Ionic liquid, Schiff base, Fe(III) complex, Cr(III) complex, Antibacterial Studies

Ionic liquids (ILs) are molten salts (melting point below 100 °C) composed of inorganic or organic anions paired with large, usually asymmetric organic cations. In reality, most ILs are liquid at room temperature and are defined as room temperature ionic liquids (RTILs). ILs possess unique physicochemical and solvation properties that can be tuned for specific applications and often produce interesting results when employed instead of traditional molecular solvents^{1,2}. In addition, most ILs pose several unique properties, such as negligible vapor pressure³, no miscibility with nonpolar solvents and high thermal and chemical stability⁴⁻⁶. In recent years, they have received considerable attention due to their wide electrochemical window such as high ionic conductivity⁷ and a broad temperature range of the liquid state. Moreover, the physical properties of ILs such as density, melting point, polarity, Lewis acidity, viscosity and enthalpy of vaporization can be tuned by changing the cation and anion pairing⁸. IL-based solvent system typically exhibits enhanced reaction kinetics resulting in the efficient use of time and energy¹. Due to these properties they are considered as a new generation of solvent for catalysis, ecofriendly reaction media for organic synthesis and a successful replacement for conventional media in chemical processes^{1,9}.

Recently, many workers have focused on the preparation of new ionic liquids with different functional groups in the cationic moiety, called functionalized ionic liquids (FILs) and their application in chemical research¹⁰⁻¹⁵. Such functionalization of the cations 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^{16,17}.

Schiff bases are termed as 'privileged ligands' as they are synthesized by the condensation of aldehydes and imines. They play a key role in coordination chemistry, particularly for having varied denticities, chelating capability¹⁸⁻²⁰ and functionalities²¹. Schiff bases are reported to exhibit different types of biological actions such as antibacterial, antifungal and herbicidal activities due to the presence of azomethine linkage (-CH=N). In case of ionic liquid-supported Schiff-bases, they are attached to imidazolium tags and containing hetero-atoms such as N, O, and S to coordinate with metal ions and having unusual configurations²²⁻²⁶. Transition metal complexes with Schiff base ligand exhibit variety of applications including biological, medicinal and analytical in addition to their roles in organic synthesis and catalysis. In our laboratory, we have been interested in developing new functionalized ionic liquids and

their transition metal complexes and finding out their antibacterial activities.^{25,26} The present study deals with the synthesis and physico-chemical characterizations of an ionic liquid-supported Schiff base ligand 1-{2-(2-hydroxy-5-bromobenzylamine)ethyl}-3-ethylimidazolium tetrafluoroborate and its Fe(III) and Cr(III) complexes. The synthesized compounds were characterized by various analytical and spectroscopic methods. The Schiff base and its complexes were screened for their *in vitro* antibacterial activity against gram negative bacterium *Escherichia coli* and gram positive bacterium *Staphylococcus aureus*.

Materials and Methods

Materials and physical measurements

All the reagents used were of analytical grade and used without further purification. 1-ethyl imidazole, 2-bromoethylamine hydrobromide and sodium tetrafluoroborate were procured from Sigma Aldrich, Germany. 5-bromo-2-hydroxybenzaldehyde, anhydrous FeCl₃, CrCl₃.6H₂O and all other chemicals were used as received from SD Fine Chemicals, India. CH₃OH, petroleum ether, CHCl₃, 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 FTIR spectrometer (RX-1). ¹H-NMR spectra were recorded on a FTNMR (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 ($2\theta = 0-90^\circ$). SEM images were taken in JEOL-JSM-IT-100. 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. 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 Jasco V-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 meter. 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. Thermal analysis (TGA) was performed in a temperature range of 25–800 $^\circ$ C (heating rate 10 $^\circ$ C/min) by using Perkin-Elmer thermal analyzer in Al₂O₃ crucible under N₂ atmosphere. Antibacterial activities (*in vitro*) of the synthesized compounds were tested by well diffusion method against *Staphylococcus aureus* and *Escherichia coli* by using *Ampicillin* as the reference antibiotic.

Synthesis of the imidazolium ionic liquid, 1-(2-aminoethyl)-3-ethylimidazolium tetra-fluoroborate [2-aeim]BF₄(1)

The amino functionalized ionic liquid [2-aeim]BF₄ was synthesized by following a literature procedure²⁷. The chemical structure and photograph of the synthesized ionic liquid is shown in Fig. 1. The expected ionic liquid was obtained as yellow oil. Yield: 1.7 g, 79%; C₇H₁₄F₄N₃B: Anal. (%) Calcd.: C, 37.04; H, 6.22; N, 18.51. Found (%): C, 37.02; H, 6.12; N, 18.38 %. IR (KBr, $\nu_{\text{cm}^{-1}}$): ($\nu_{\text{N-H}}$) 3447, 3086, 2896; ($\nu_{\text{C=N}}$) 1626, 1452; (ν_{BF_4}) 1084. ESI-MS (m/z) Calc.: 140, Found 140 ([M-BF₄]⁺, M= [C₇H₁₄N₃]⁺). ¹H NMR (400 MHz, D₂O, TMS): δ 3.22 (2H, m, NH₂-CH₂), 4.16 (3H, s, CH₃), 4.49 (1H, t, N-CH₂), 4.56 (1H, t, N-CH₂), 7.40 (1H, s, NCH), 7.50 (1H, s, NCH), 8.61 (2H, s, NH₂), 8.87 (1H, s, N(H)CN). ¹³C-NMR (400 MHz, D₂O, TMS): δ 137.07, 124.28, 122.33, 54.37, 39.58, 37.53.

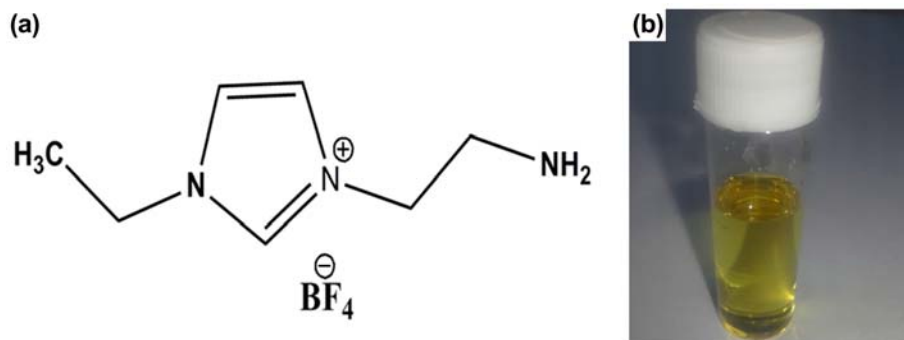


Fig. 1 — (a) Chemical structure and (b) Photograph of synthesized amino functionalized ionic liquid [2-aeim]BF₄.

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

The Schiff base (LH) was synthesized by a slight modification of a literature procedure²⁸. 5-bromo-2-hydroxybenzaldehyde (2.01 g, 10 mmol) and [2-aeim]BF₄ (2.27 g, 10 mmol) in methanol was stirred at room temperature for 4 h. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with ethanol. The precipitate was filtered, washed with cold ethanol and dried to afford the expected ligand as a light yellow solid. Yield: 1.2 g (69%); m. p.: 98–100 °C; C₁₄H₁₇N₃OBBrF₄: Anal.(%) Calcd.: C, 41.01; H, 4.18; N, 10.25%. Found (%): C, 40.81; H, 4.09; N, 10.20. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H}}$) 3449, 3230, 2923, 2866, ($\nu_{\text{CH=N}}$) 1675, ($\nu_{\text{C-O}}$) 1274, (ν_{BF_4}) 1114. ESI-MS (m/z): Calc. 323; Found: 322 ([M-H-BF₄]⁺, M= [C₁₃H₁₅BrN₃O]⁺). ¹H NMR: (400 MHz, DMSO-*d*₆, TMS): δ 2.49 (3H, s, CH₃), 3.82 (2H, q, N-CH₂), 3.99 (2H, t, N-CH₂), 4.52 (2H, t, N-CH₂), 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). ¹³C NMR (400 MHz, DMSO-*d*₆, TMS): 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 and 35.90.

Synthesis of the metal complexes (3, 4)

Ethanol solution of FeCl₃ (0.405 g, 2.5 mmol) or CrCl₃.6H₂O, (0.66 g, 2.5 mmol) was added to a solution of ligand LH (2.05 g, 5 mmol), in ethanol (20 mL) 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 mixture

was cooled to room temperature. The precipitate was collected by filtration, washed with cold C₂H₅OH (3×10 mL), dry ether (3×10 mL) respectively and finally dried in desiccators to obtain the solid product. The complexes are soluble in *N,N*-dimethylformamide, dimethylsulphoxide, acetonitrile, methanol and water. A schematic representation of the syntheses is shown in Scheme 1.

Fe(III) complex (**3**): Brown solid, Yield: 0.75 g; 65%; Decomposes at ~270 °C. C₂₈H₃₄FeBr₂ClF₈N₆O₃: Anal.(%) Calc.: C, 36.27; H, 3.70; N, 9.06; Fe, 6.02. Found (%): C, 36.12; H, 3.63; N, 9.01, Fe, 6.01. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H/H}_2\text{O}}$) 3422, 2933, 2863; ($\nu_{\text{CH=N}}$) 1671; ($\nu_{\text{C-O}}$) 1279; (ν_{BF_4}) 1116; ($\nu_{\text{M-O}}$) 535; ($\nu_{\text{M-N}}$) 449. ESI-MS (m/z): Calc.: 733; Found: 733; ([M-2BF₄-H₂O]⁺), M= [(C₂₈H₃₂FeClBr₂N₆O₂)⁺].

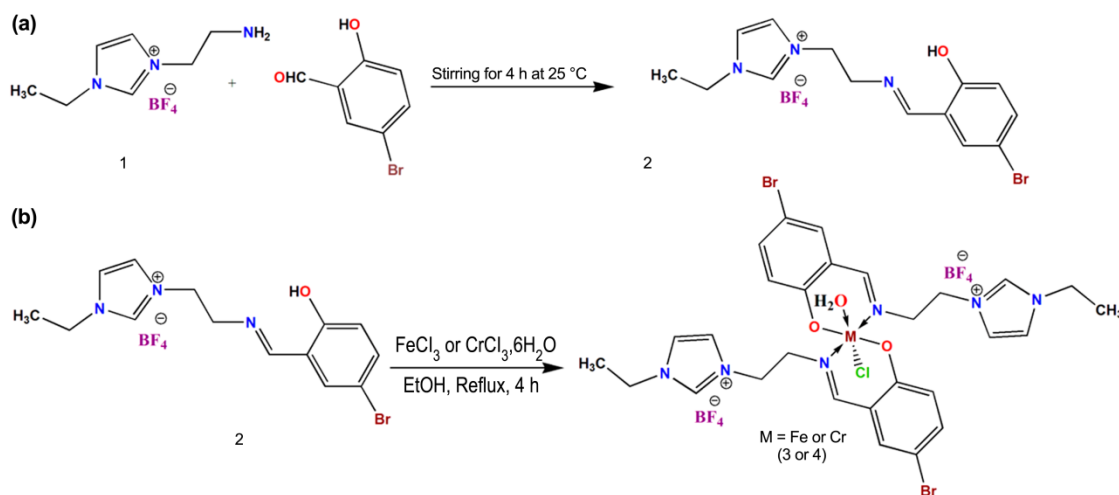
Cr(III) complex (**4**): Yellowish green solid, Yield: 0.77 g; 71%; Decomposes at ~270 °C. C₂₈H₃₄CrBr₂ClF₈N₆O₃: Anal. (%) Calc.: C, 36.42; H, 3.71; N, 9.10, Cr, 5.63. Found (%): C, 36.35; H, 3.56; N, 9.02, Cr, 5.62. IR (KBr, ν/cm^{-1}): ($\nu_{\text{O-H/H}_2\text{O}}$) 3438, 2926, 2867; ($\nu_{\text{CH=N}}$) 1670; ($\nu_{\text{C-O}}$) 1278; (ν_{BF_4}) 1112; ($\nu_{\text{M-O}}$) 538; ($\nu_{\text{M-N}}$) 446. ESI-MS (m/z): Calc.: 730; Found: 730; ([M-2BF₄-H₂O]⁺), M= [(C₂₈H₃₂CrClBr₂N₆O₂)⁺].

Results and Discussion

All the isolated compounds were found to be air stable and were characterized by different analytical and spectroscopic methods.

IR spectral studies

The IR spectra of the complexes are compared with the ligand (LH) in order to determine the coordination



Synthesis of the ionic liquid-supported Schiff base, [1-{2-(2-hydroxy-5-bromo benzylideneamino)ethyl}-3-ethylimidazolium tetrafluoroborate (2), and its M(III) complexes (3 and 4) from LH (2).

Scheme 1

sites involved in chelation. IR spectra of the ligand showed a strong broad band around $3449\text{--}3230\text{ cm}^{-1}$, this band was assigned to the hydrogen bonded -OH of the phenolic group with H-C(=N) group of the ligand (OH...N=C)^{29,30}. The broad band at $3422\text{--}3438\text{ cm}^{-1}$ in the spectra of Fe(III) and Cr(III) complexes suggested the presence of coordinated water molecule. However, these bands appear stronger as compared to that of the ligand due to the moisture content of the ligand subject to the intrinsic nature of the anion tetrafluoroborate³¹⁻³³. In the ligand a band corresponding to the azomethine group (-C=N) was found at 1675 cm^{-1} . On complexation, this band gets shifted to lower wave number range $1671\text{--}1670\text{ cm}^{-1}$. This indicated the involvement of N-atom of azomethine (-C=N) group in the complex formation³⁴. The phenolic C-O of free ligand was observed at 1274 cm^{-1} . Upon complexation, this band was shifted to higher wave number $1279\text{--}1278\text{ cm}^{-1}$ for the complexes (**3** and **4**). This fact suggests the coordination of ligand to metal atom by the azomethine nitrogen and phenolic oxygen atom³⁵. The bands in the range of $1116\text{--}1112\text{ cm}^{-1}$ for the spectra of metal complexes were assigned for B-F stretching frequency. In the spectra of the complexes, bands observed at $535\text{--}538$ and $449\text{--}446\text{ cm}^{-1}$ were attributed to M-N and M-O stretching vibrations, respectively. The band due to M-Cl, expected to appear at around $320\text{--}250\text{ cm}^{-1}$, which was beyond the experimental IR range^{36,37}. (FTIR spectra of the ligand and its metal complexes are given in Fig. (2-4).

¹H and ¹³C-NMR spectral studies

¹H-NMR and ¹³C-NMR spectra of ligand (LH) were recorded in DMSO-*d*₆. ¹H-NMR of the ligand showed a singlet at δ 8.50 ppm 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 δ 9.10 ppm is attributed to hydroxyl proton. The LH (**2**) downfield shift of the -OH proton was due to intramolecular (O-H...N) hydrogen bonding³⁸. ¹³C-NMR spectra of LH (**2**) 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 of LH (**2**) are given in Supplementary Data, Figs S1 and S2.

Powder X-ray diffraction (PXRD) analysis

The PXRD analysis of the Schiff base and its metal complexes (**3** and **4**) were performed to confirm

whether the particle nature of the compounds was amorphous or crystalline. The PXRD spectrum of ligand (**2**) showed sharp peaks owing to their crystalline nature although the spectra of the complexes didn't show such peaks due to their amorphous nature (Supplementary Data, Fig. S3-S5). The crystalline sizes were calculated applying Debye Scherer's equation:

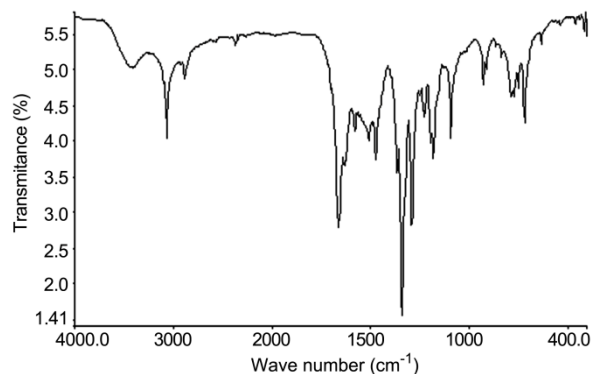


Fig. 2 — IR-spectra of LH(2).

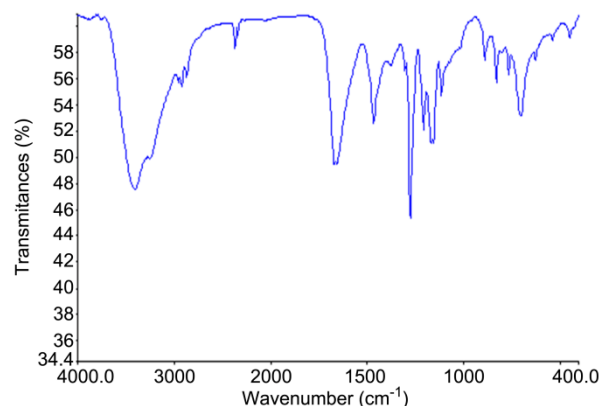


Fig. 3 — IR-spectra of Fe(III)complex (**3**).

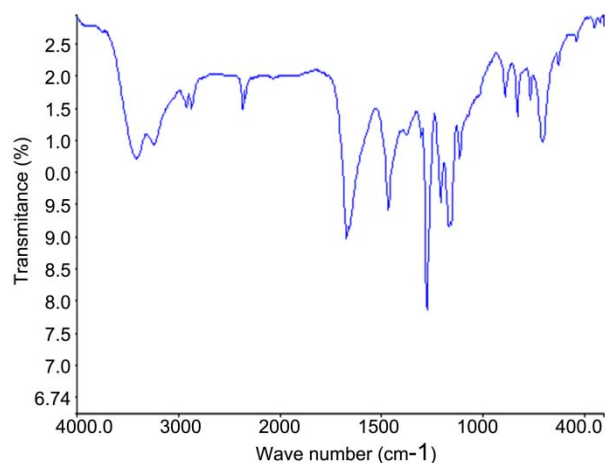


Fig. 4 — IR-spectra of Cr(III)complex (**4**).

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

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 of sizes was found to be 32.05 nm for the ligand, 11.96 nm for complex (3) and 12.56 nm for complex (4).

Mass spectral studies

ESI-MS spectrum of the ligand (LH) displayed a peak (m/z) at 322 that corresponds to $[M-H-BF_4]^+$ ion, $[M = C_{14}H_{17}N_3OBr]^+$. The mass spectra of the Fe(III) complex (3) showed peaks (m/z) at 733 and Cr(III) complex (4) displayed peaks (m/z) at 730 which was assigned for the $[M-2BF_4-H_2O]^+$ ion, $M = [C_{28}H_{32}FeBr_2ClN_6O_2]^+$ for complex (3) and $M = [C_{28}H_{32}CrBr_2ClN_6O_2]^+$ for complex (4), 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. (The ESI-MS spectra of the ligand and complexes are shown in Supplementary Data, Fig. S6-S8).

Electronic absorption spectral and magnetic moment studies

UV-visible spectra of the ligand and the metal complexes were recorded in methanol at ambient temperature. The electronic spectrum of free Schiff base showed three absorption bands at 318, 255 and 215 nm due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and transitions involved with the imidazolium moiety, respectively^{39,40}. In case of Fe(III) complex (3), with d^5 configuration showed bands at 387, 226 and 205 nm. The weak band at 387 nm was 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 have very weak and spin forbidden d-d transition which does not appear in the spectra due to the low intensity of the d-d transition. The observed magnetic moment of 5.56 B.M. for the complex (3) (theoretical value for Fe(III), $t_{2g}^3 e_g^2$ system is $\sqrt{35} = 5.92$) suggests high spin configuration of the metal ion in the Fe(III) complex (3) with five unpaired electrons⁴¹. UV-visible spectrum of the Cr(III) complex (4) exhibited three bands at 400, 340, 220 nm. These bands could be assigned 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) ion⁴²⁻⁴³. Again the complex (4) showed magnetic moment of 3.93 B.M. corresponding to three unpaired electrons (theoretical value for Cr(III), t_{2g}^3 system is $\sqrt{15} = 3.88$). The UV-visible spectra are given in Fig. 5.

Molar Conductance measurements

The molar conductance of the complexes (Λ_m) were determined by using the relation:

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

Where c and κ stands for the molar concentration of the metal complexes and specific conductance, respectively. The complexes (10^{-3} M) were dissolved in *N,N*-dimethylformamide (DMF) and their specific conductivities were measured at (298.15 ± 0.01) K. The molar conductance values were 128 and 133 S $cm^{-1} mol^{-1}$ for Fe(III) complex (3) and Cr(III) complex (4), respectively, indicating their 1:2 electrolytic behaviour.

Thermal analysis

Thermal behaviour of the complexes was studied by TGA (Fig. 6) over a temperature range of 25–800 °C in Al_2O_3 crucible under N_2 atmosphere.

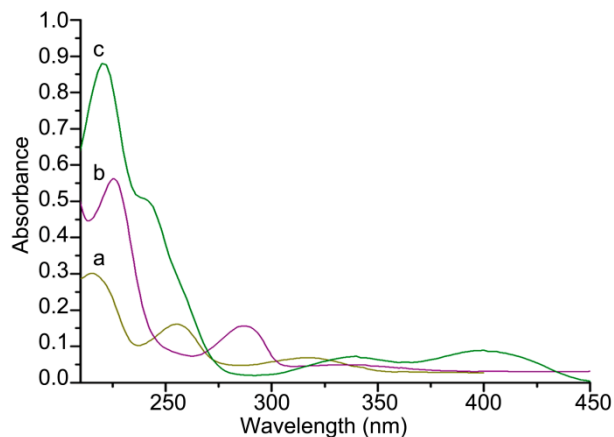


Fig. 5 — UV-visible spectra of: (a) LH (2), (b) Fe(III) complex (3) and (c) Cr(III) complex (4).

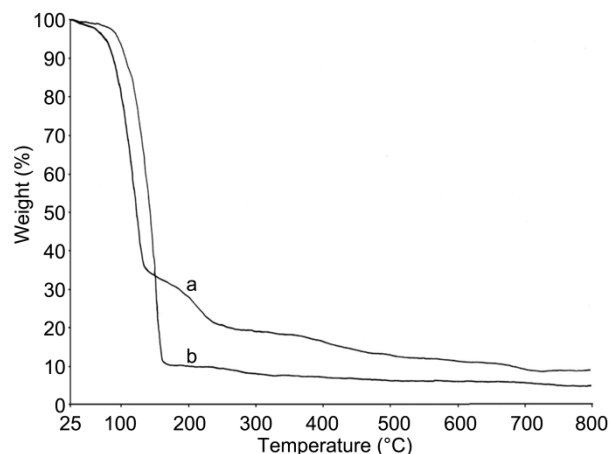


Fig. 6 — Thermogravimetric analysis of (a) Fe(III) complex (3) and (b) Cr(III) complex (4).

The temperature was programmed to increase linearly at 10 °C/min. TGA thermograms of the Fe(III) and Cr(III) complexes showed a first step decomposition around 110 °C with 10–18 % weight loss including the loss of coordinated water molecules and the anion parts of the complexes. At the temperature range 110–160 °C and 160–300 °C the major mass losses occurred due to the decomposition of the organic fragments of the complexes with the formation of different intermediates. These intermediates further decomposed at the temperature range of 300–750 °C followed by elimination of remaining organic parts. The decomposition was completed approximately at 800 °C leading to the formation of the stable metal oxides.³¹ The oxides formed were 8.61 % and 5.63 % for Fe(III) complex (3) and Cr(III) complex (4), respectively. These quantities of respective oxides are as per the stoichiometry of the complexes obtained from elemental analysis.

Antibacterial studies

Antibacterial activity of the synthesized compounds was studied in vitro against the gram negative (*Escherichia coli*) and gram positive (*Staphylococcus aureus*) bacterial strains by agar disc diffusion method^{44,45} by NCCLS (National Committee for Clinical Laboratory Standards, 1997) and inoculated with 0.5 McFarland standard. 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 10⁸ colony-forming units (CFU)/mL were mixed with sterile liquid nutrient agar and poured into the sterile Petri dishes. Upon solidification of the medium, filter disc (5 mm diameter) was individually soaked with different concentration (10, 20, 30, 40, 50 µg/mL) of each compound and placed on the solidified nutrient agar media plates. The different concentrations were made by 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. Minimum inhibitory concentration 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 compound was made in nutrient broth medium. Then 1 mL of standard (0.5 McFarland) bacterial suspension was inoculated into each of these tubes. A similar nutrient broth tube without sample compound was also inoculated and

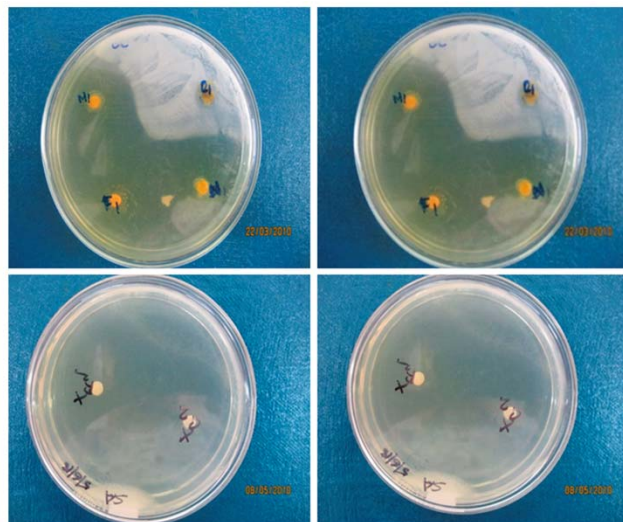


Fig. 7 — MIC for Fe(III) complex (3) (left panel) and Cr(III) complex (4) (right panel) against *S. aureus*.

used as control. The ligand was highly active against the *E. coli* (gram negative) and *S. aureus* (gram positive) bacteria for the concentrations⁴⁶ 20, 30, 40 and 50 µg/mL. In case of metal complexes, the data showed that the Cr(III) complex was more active than the Fe(III) complex^{47,48}. The antibacterial assays is shown in Fig. 7 and data is given in Supplementary Data, Table S1. Their biological activities of the Cr(III) complex was higher that of the *Ampicillin* antibiotic.

Conclusions

Here in this study an ionic liquid-supported Schiff base 1-{2-(2-hydroxy-5-bromobenzylamine)ethyl}-3-ethylimidazolium tetrafluoroborate and its Fe(III) and Cr(III) complexes were synthesized and characterized by different spectral and analytical techniques. These data suggest distorted octahedral geometry for both the metal complexes. The Schiff base acts as a bidentate ligand coordinating through the azomethine nitrogen and phenolic oxygen atom to the metal ions and thus formed 1:2 (M:L) complexes with Fe(III) and Cr(III) ions. The synthesized complexes along with the ligands were tested for their *in vitro* antibacterial activities. A detectable antibacterial activity was observed in case of the Schiff base ligand and Cr(III) complex against the tested bacteria *Escherichia coli* and *Staphylococcus aureus*.

Supplementary Data

¹HNMR, ¹³CNMR spectra, ESI-MS spectra, PXRD images and Experimental biological assays data of the Schiff base and metal complexes are attached as supplementary information. Supplementary Data

associated with this article are available in the electronic form at: [http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A\(02\)155-161_SupplData.pdf](http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(02)155-161_SupplData.pdf).

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