

## **CHAPTER VIII**

### **Synthesis, Physico-chemical characterization and potential biological applications of Transition metal complexes obtained from an ionic liquid-supported Schiff base ligand: 1-{2-(2-hydroxy-5-chloro-benzylideneamino)ethyl}-3-methylimidazolium tetrafluoroborate**

#### **8.1. 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 of the main aims for the development of sustainable and green chemical process [1]. Ionic liquids (ILs), which are the new class of solvents, also termed as neoteric solvents that leads to a new green chemical revolution. Their unique array of physical-chemical 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 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 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 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 of the cases the functional group is cation-tethered. The introduction of this type of functionality can

imbue the 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 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 activities 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 wide range of biological applications and are gained special interest due to the number of ways they can bonded to the metal ions [31]. In this chapter the synthesis, physico-chemical characterization and biological studies 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.

## 8.2. Experimental Section

### 8.2.1. Materials and Methods

Analytical grade chemicals were used for synthesis without further purification. 1-methyl imidazole, 2-bromoethylamine hydrobromide, 5-chloro-2-hydroxybenzaldehyde and  $\text{NaBF}_4$  (sodium tetrafluoroborate) were collected from Sigma Aldrich, Germany. Metal acetates and metal chlorides were used as obtained from SD Fine Chemicals, India.  $\text{CH}_3\text{OH}$ , petroleum ether,  $\text{CHCl}_3$ , DMF and DMSO were used after purification by standard methods described in the literature. The FIL, 1-(2-aminoethyl)-3-methylimidazolium tetrafluoroborate, [2-aemim] $\text{BF}_4$  (**1d**) was prepared by following a literature procedure [32]. The synthesis and structural characterization of the FILs (**1d**) have been described earlier in chapter II.

FT-IR spectra were recorded by KBr pellets on a Perkin-Elmer Spectrum FT-IR spectrometer (RX-1).  $^1\text{H-NMR}$  spectra were recorded on a FT-NMR (Bruker Avance-II 400 MHz) spectrometer by using  $\text{D}_2\text{O}$  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 ( $2\theta= 0\text{-}90^\circ$ ). SEM images were taken in JEOL-JSM-IT-100.

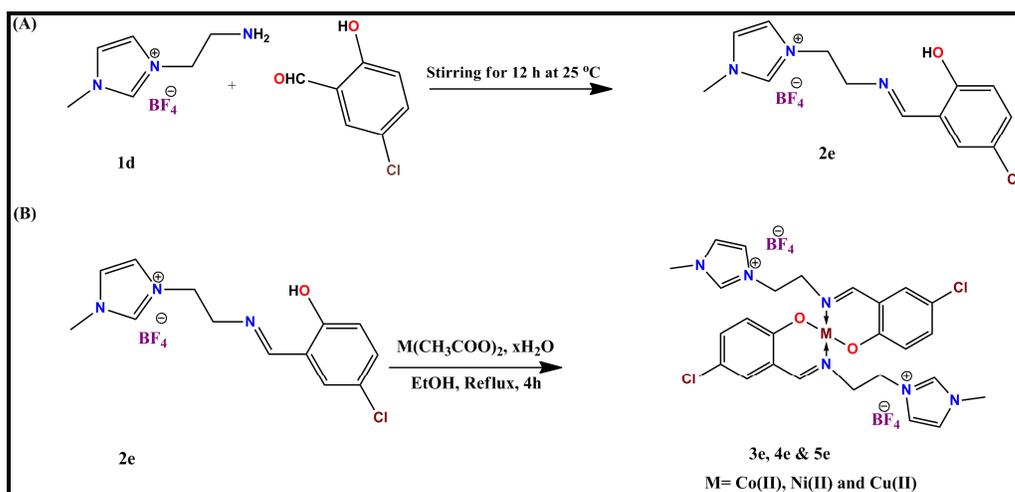
Elemental microanalysis (CHN analysis) was performed on Perkin–Elmer (Model 240C) analyzer. Metal content was obtained from AAS (Varian, SpectrAA 50B) by using standard metal solutions procured from Sigma-Aldrich, Germany. Mass spectra were obtained on a JMS-T100LC spectrometer. The purity of the synthesized 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 JascoV-530 double beam Spectrophotometer using CH<sub>3</sub>OH 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 well diffusion method against four bacterial strains (Two gram positive and two gram negative).

### 8.2.2. Synthesis of imidazolium ionic liquid-supported Schiff base, LH (2e)

5-chloro-2-hydroxybenzaldehyde (1.57 g, 10 mmol) and [2-aeim]BF<sub>4</sub> (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. 2.57 g (yield, 73 %). M. p. 93-95 °C. Anal. Calc. for C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>OCIBF<sub>4</sub> (351.54): C, 44.42; H, 4.30; N, 11.95. Found: C, 44.14; H, 4.09; N, 11.83 %. FT-IR (KBr, cm<sup>-1</sup>) 3448 (O-H), 3071, 1665 (C=N), 1279 (C-O), 1106 (B-F). <sup>1</sup>H NMR: (400 MHz, DMSO-*d*<sub>6</sub>): δ 2.49 (t, 2H, N-CH<sub>2</sub>), 3.51 (t, 2H, N-CH<sub>2</sub>), 4.28 (s, 3H, CH<sub>3</sub>), 6.97–6.90 (m, 3H, Ar-H), 7.62 (s, 1H, NCH), 7.63 (s, 1H, NCH), 10.18 (s, 1H, N=CH), 7.70 (s, 1H, N(H)CN), 9.30 (s, 1H, OH). <sup>13</sup>C NMR: (400 MHz, DMSO-*d*<sub>6</sub>): 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. UV-Vis (Methanol, λ<sub>max</sub>): 220, 250, 336 nm; ESI-MS (CH<sub>3</sub>OH, m/z): 264 ([M-BF<sub>4</sub>]<sup>+</sup>, M= [C<sub>13</sub>H<sub>15</sub>ClN<sub>3</sub>O]<sup>+</sup>).

### 8.2.3. Synthesis of the metal complexes (3e, 4e and 5e)

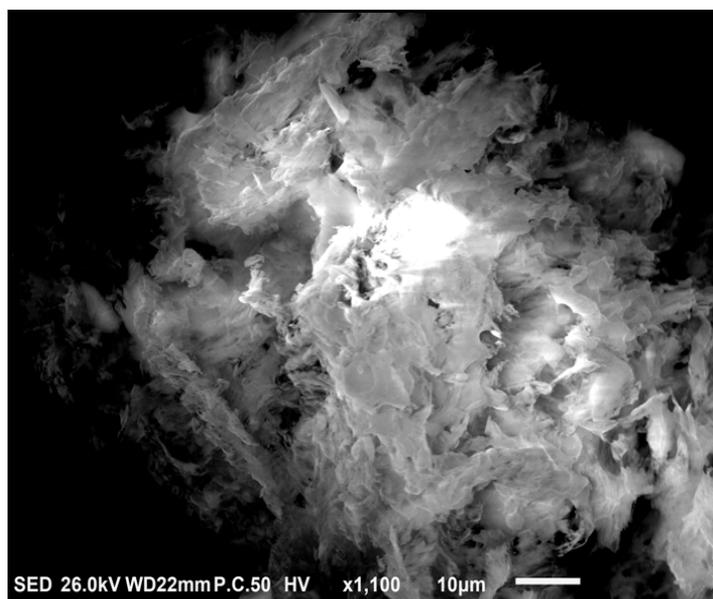
To a solution of ligand, (2e) (0.352 g, 1 mmol) in ethanol (20 mL), metal acetate salt Co(II), Ni(II) and Cu(II), viz., (0.5 mmol) dissolved in ethanol was added gradually in a round bottomed flask. The mixture was refluxed for 4 h until the starting materials were completely consumed as monitored by 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. The complexes are soluble in *N,N*-dimethylformamide, dimethylsulphoxide, acetonitrile, methanol and water. A schematic representation of the synthesis is shown in Scheme 8.1.



**Scheme 8.1.** Synthesis of the ionic liquid-supported Schiff base, 1-{2-(2-hydroxy-5-chlorobenzylideneamino)ethyl}-3-methylimidazolium tetrafluoroborate (2e), and its metal complexes (3e, 4e and 5e) from (2e).

#### 8.2.3.1. Co(II) complex (3e):

Brown solid; 0.53 g (yield, 70 %), decomposes at  $\sim$  253 °C. Anal. Calc. for C<sub>26</sub>H<sub>28</sub>CoCl<sub>2</sub>B<sub>2</sub>F<sub>8</sub>N<sub>6</sub>O<sub>2</sub> (760): C, 41.09; H, 3.71; N, 11.06, Co, 7.75. Found: C, 40.69; H, 3.41; N, 10.86, Co, 7.62 %. FT-IR (KBr, cm<sup>-1</sup>): 3438 (O-H), 1628 (C=N), 1316 (C-O), 1075 (B-F), 638 (M-O), 523(M-N). UV-Vis (Methanol,  $\lambda_{\text{max}}$ /nm): 220, 340, 401. ESI-MS (CH<sub>3</sub>OH, m/z): 585 ([M-2BF<sub>4</sub>]<sup>+</sup>, M= [(C<sub>26</sub>H<sub>28</sub>CoCl<sub>2</sub>N<sub>6</sub>O<sub>2</sub>)<sup>+</sup>]).



**Fig 8.1.** SEM image of Co(II) complex (**3e**)

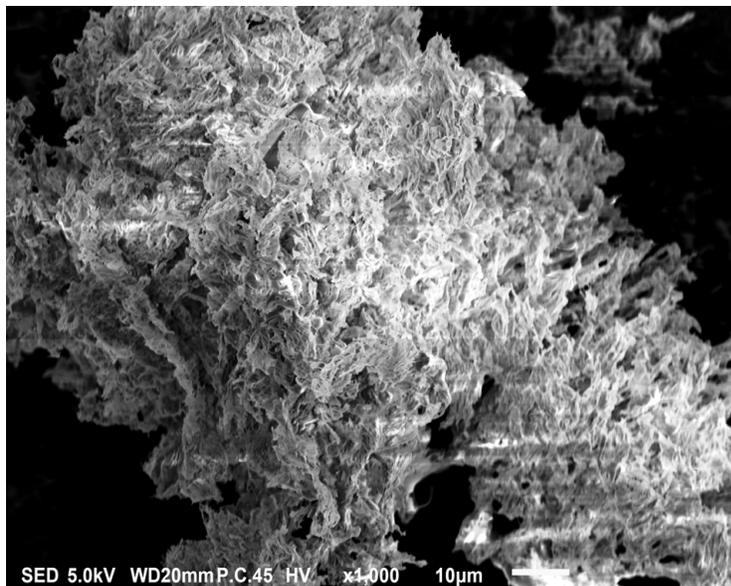
**8.2.3.2. Ni(II) complex (4e):** Light green solid; 0.52 g (yield, 69 %), decomposes at ~ 251 °C. Anal. Calc. for  $C_{26}H_{28}NiCl_2B_2F_8N_6O_2$  (759.75): C, 41.10; H, 3.71; N, 11.06; Ni, 7.26. Found: C, 41.02; H, 3.63; N, 10.46, Ni, 7.19 %. FT-IR (KBr,  $cm^{-1}$ ): 3453 (O-H), 1628 (C=N), 1322 (C-O), 1012 (B-F), 565 (M-O), 439 (M-N). UV-Vis (Methanol,  $\lambda_{max}/nm$ ): 220, 340, 400. ESI-MS ( $CH_3OH$ ,  $m/z$ ): 586 ( $[M+2H-2BF_4]^+$ ),  $M = [(C_{26}H_{28}NiCl_2N_6O_2)]^+$ .



**Fig 8.2.** SEM image of Ni(II) complex (**4e**)

**8.2.3.3. Cu(II) complex (5e):**

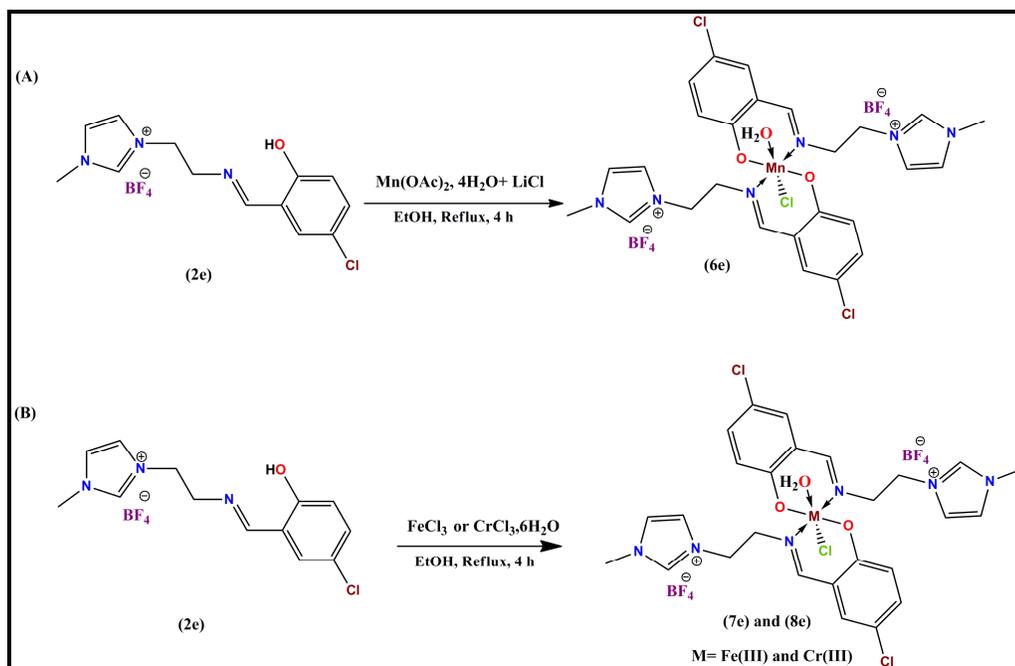
Dark green solid; 0.54 g (yield, 71 %), decomposes at ~ 265 °C. Anal. Calc. for  $C_{26}H_{28}CuCl_2B_2F_8N_6O_2$  (764.60): C, 40.84; H, 3.69; N, 10.99; Cu, 8.31. Found: C, 40.12; H, 3.51; N, 10.46, Cu, 8.11 %. FT-IR (KBr,  $cm^{-1}$ ): 3448 (O-H), 1624 (C=N), 1320 (C-O), 1012 (B-F), 651 (M-O), 565 (M-N). UV-Vis (Methanol,  $\lambda_{max}/nm$ ): 222, 242, 394. ESI-MS ( $CH_3OH$ ,  $m/z$ ): 588 ( $[M-H-2BF_4]^+$ ,  $M = [(C_{26}H_{28}CuCl_2N_6O_2)^+]$ ).



**Fig 8.3.** SEM image of Cu(II) complex (5e)

**8.2.4. Synthesis of the metal complexes (6e, 7e and 8e)**

The Schiff base (2e) (1.76 g, 5 mmol) was taken in round bottomed flask and dissolved in EtOH (20 mL).  $Mn(CH_3COO)_2 \cdot 4H_2O$  (0.61 g, 2.5 mmol) and LiCl (0.15 g, 2.5 mmol) for complex 6e and  $FeCl_3$  (0.405 g, 2.5 mmol) or  $CrCl_3 \cdot 6H_2O$  (0.66 g, 2.5 mmol) for the complex 7e and 8e respectively, also in the same solvent was added and the reaction mixture was refluxed for 4 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  $C_2H_5OH$  (10 mL  $\times$  3), dry ether (10 mL  $\times$  3) respectively and finally dried in desiccators to obtain the desired product. The complexes are soluble in *N,N*-dimethylformamide, dimethylsulphoxide, acetonitrile, methanol and water. A schematic representation of the syntheses is given in Scheme. 8.2.



**Scheme 8.2.** Synthesis of the M(III) complexes (**6e**, **7e** and **8e**) from (**2e**).

#### 8.2.4.1. Mn(III) complex (**6e**):

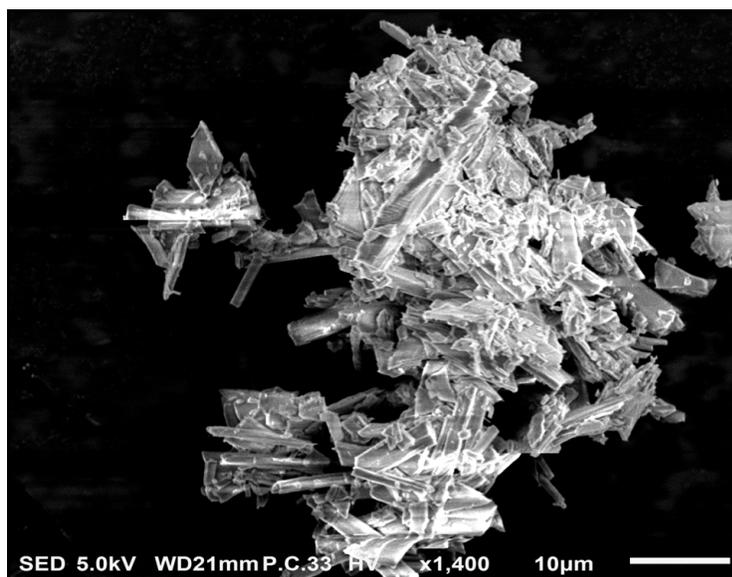
Light brown solid; 2.7 g (yield, 67%). decomposes at  $\sim 269$  °C. Anal. Calc. for  $\text{C}_{26}\text{H}_{30}\text{MnB}_2\text{Cl}_3\text{F}_8\text{N}_6\text{O}_3$  (809.46): C, 38.58; H, 3.74; N, 10.38, Cr, 6.79. Found: C, 38.35; H, 3.56; N, 10.12, Cr, 6.52 %. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3433 (O-H/ $\text{H}_2\text{O}$ ), 1649 (C=N), 1314 (C-O), 1019 (B-F), 651 (M-N), 528 (M-O). UV-Vis (Methanol)  $\lambda_{\text{max}}/\text{nm}$ : 216, 244, 340. ESI-MS: ( $\text{CH}_3\text{OH}$ ,  $m/z$ ) = 618 ( $[\text{M}+2\text{H}-2\text{BF}_4-\text{H}_2\text{O}]^+$ , M =  $[\text{C}_{26}\text{H}_{28}\text{MnCl}_3\text{N}_6\text{O}_2]^+$ ).



**Fig 8.4.** SEM image of Mn(III) complex (**6e**).

**8.2.4.2. Fe(III) complex (7e):**

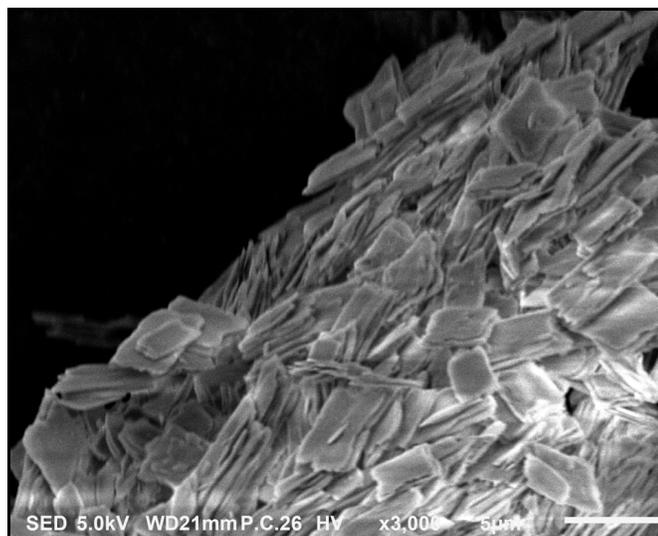
Grey solid, 2.8 g (yield, 69%), decomposes at  $\sim 270$  °C. Anal. Calcd. for  $C_{26}H_{30}FeB_2Cl_3F_8N_6O_3$  (810.37): C, 38.54; H, 3.73; N, 10.37; Fe, 6.89. Found: C, 38.12; H, 3.63; N, 10.09, Fe, 6.71 %. FT-IR (KBr,  $cm^{-1}$ ): 3430 (O-H/ $H_2O$ ), 1661 (C=N), 1276 (C-O), 1116 (B-F), 543 (M-N), 453 (M-O). UV-Vis (Methanol)  $\lambda_{max}/nm$ : 215, 243, 343. ESI-MS: ( $CH_3OH$ ,  $m/z$ ) = 618 ( $[M-H-2BF_4-H_2O]^+$ ,  $M=[C_{26}H_{28}FeCl_3N_6O_2]^+$ ).



**Fig 8.5.** SEM image of Fe(III) complex (7e)

**8.2.4.3. Cr(III) complex (8e):**

Light green solid; 2.6 g (yield, 65%). decomposes at  $\sim 267$  °C. Anal. Calc. for  $C_{26}H_{30}CrB_2Cl_3F_8N_6O_3$  (806.52): C, 38.72; H, 3.75; N, 10.42, Cr, 6.45. Found: C, 38.42; H, 3.61; N, 10.10, Cr, 6.22 %. FT-IR (KBr,  $cm^{-1}$ ): 3431 (O-H/ $H_2O$ ), 1660 (C=N), 1276 (C-O), 1116 (B-F), 543 (M-N), 452 (M-O). UV-Vis (Methanol)  $\lambda_{max}/nm$ : 220, 338, 394. ESI-MS: ( $CH_3OH$ ,  $m/z$ ) = 613 ( $[M-2BF_4-H_2O]^+$ ,  $M=[C_{26}H_{28}CrCl_3N_6O_2]^+$ ).



**Fig 8.6.** SEM image of Cr(III) complex (8e).

#### **8.4.5. 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 samples. 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 minutes. The media was cooled down to room temperature and poured in sterile petri plates at sterile condition of Laminar air flow cabinet. 100µl of bacterial strains were added separately to each petriplates 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.

#### **8.3. Results and Discussion**

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

### 8.3.1. FT-IR spectral studies

In order to justify the coordination sites, the FT-IR spectra of Schiff base (**2e**) and all the complexes (**3e-8e**) were studied carefully. FT-IR spectra of LH (**2e**) showed a strong band at 3448-3071  $\text{cm}^{-1}$ ; which was due to the hydrogen bonded phenolic group (-OH) with H-C(=N) group in the ligand (OH...N=C) [34, 35]. The broad band appeared at 3453-3430  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ . This band gets shifted in the range 1661-1624  $\text{cm}^{-1}$  because of coordination of N atom of azomethine linkage to the metal ions [39]. The band for phenolic C-O of free ligand was observed at 1279  $\text{cm}^{-1}$  which was moved to the wave number 1322-1276  $\text{cm}^{-1}$  for the complexes after complexation. This fact suggested the bonding of ligand (**2e**) to the metal atoms through the N atom of azomethine and O atom of phenolic group [40]. The bands appeared in the region of 1116-1012  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ , which was beyond the experimental IR range [42, 43]. FT-IR spectra of the Schiff base and its metal complexes are shown in Figs 8.7, Fig 8.8-8.13.

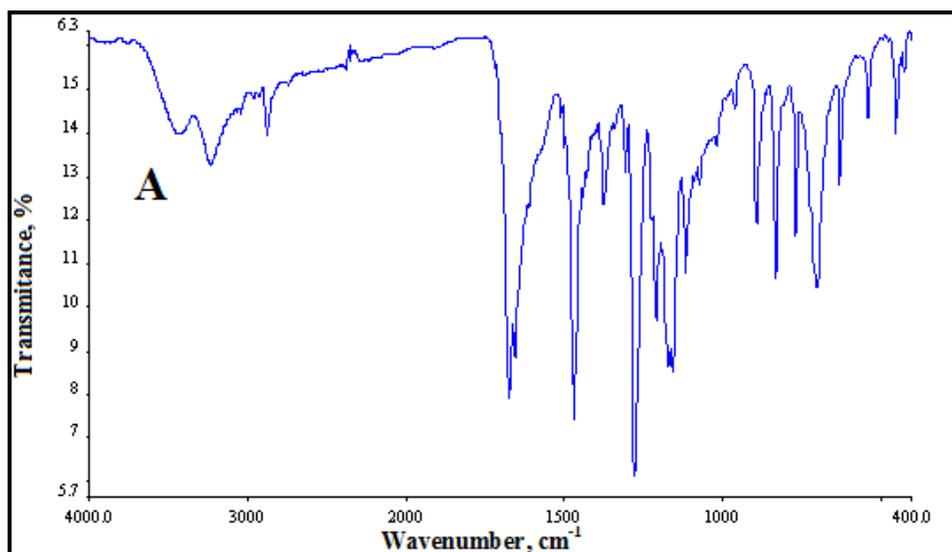


Fig 8.7. FT-IR spectra of ligand (**2e**).

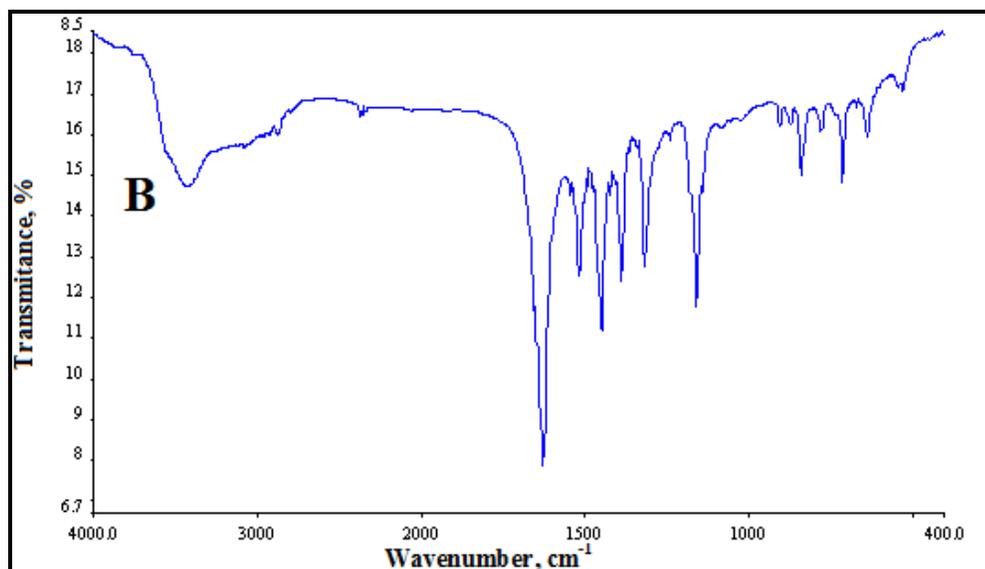


Fig 8.8. FT-IR spectra of Co(II) complex (3e).

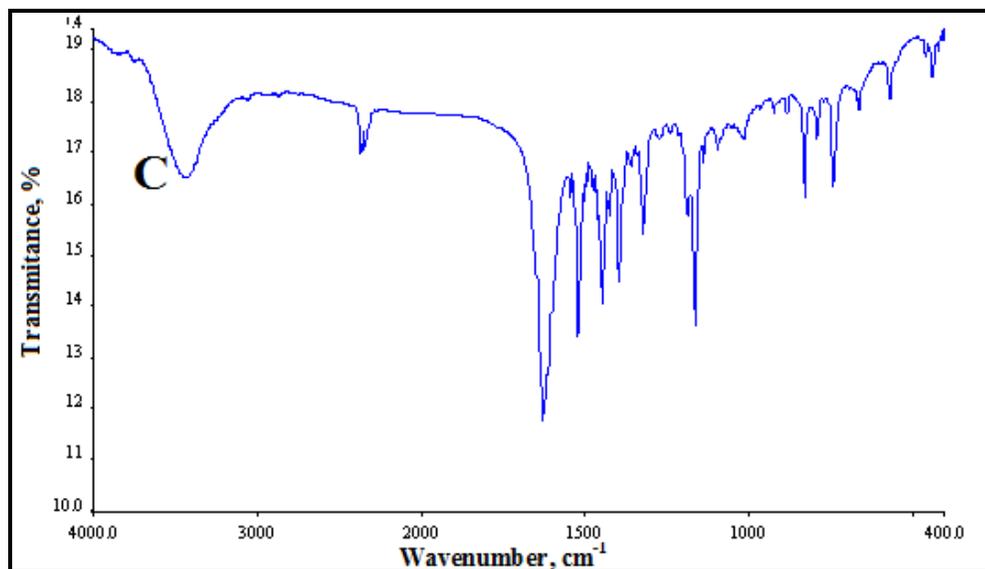


Fig 8.9. FT-IR spectra of Ni(II) complex (4e).

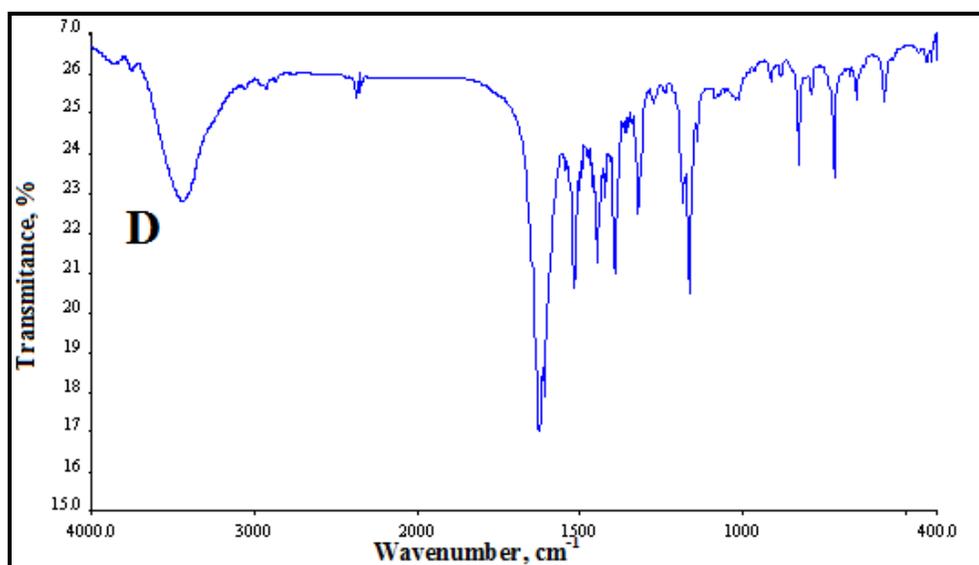


Fig 8.10. FT-IR spectra of Cu(II) complex (5e).

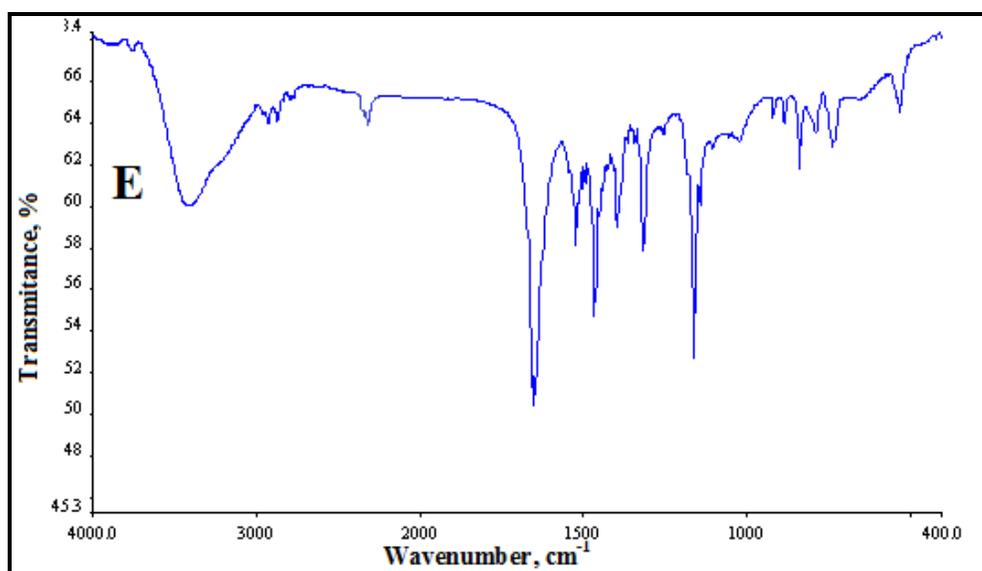


Fig 8.11. FT-IR spectra of Mn(III) complex (6e).

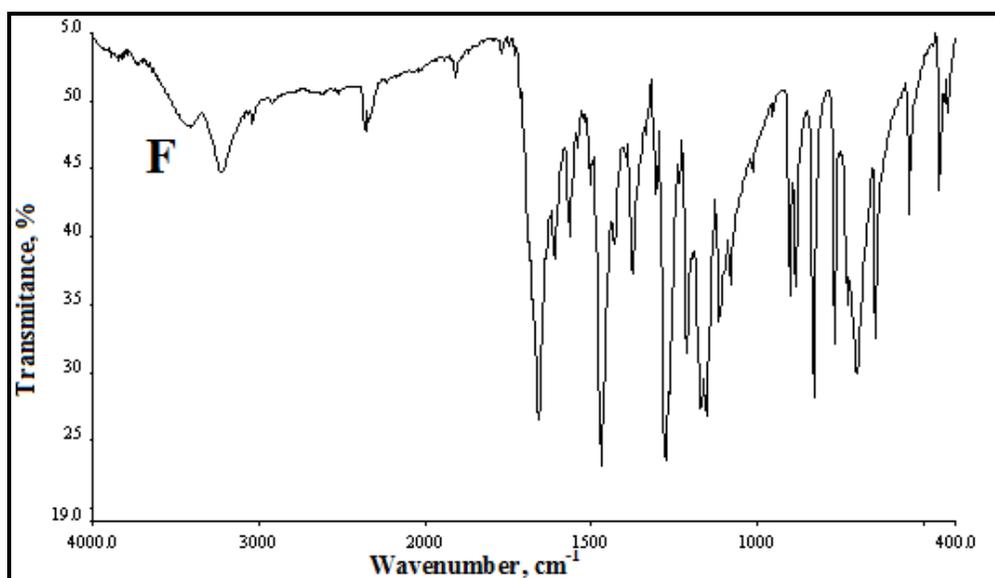


Fig 8.12. FT-IR spectra of Fe(III) complex (7e).

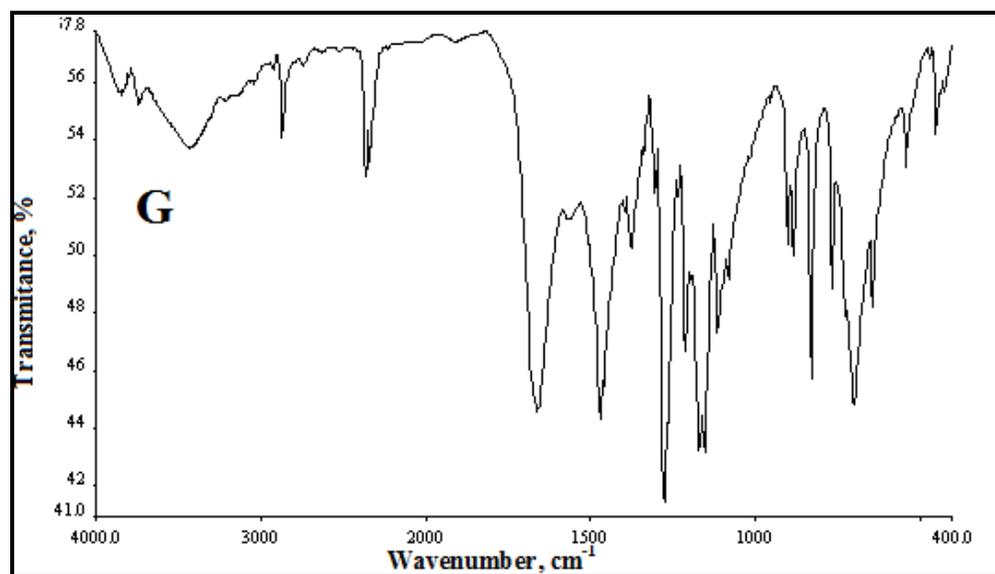
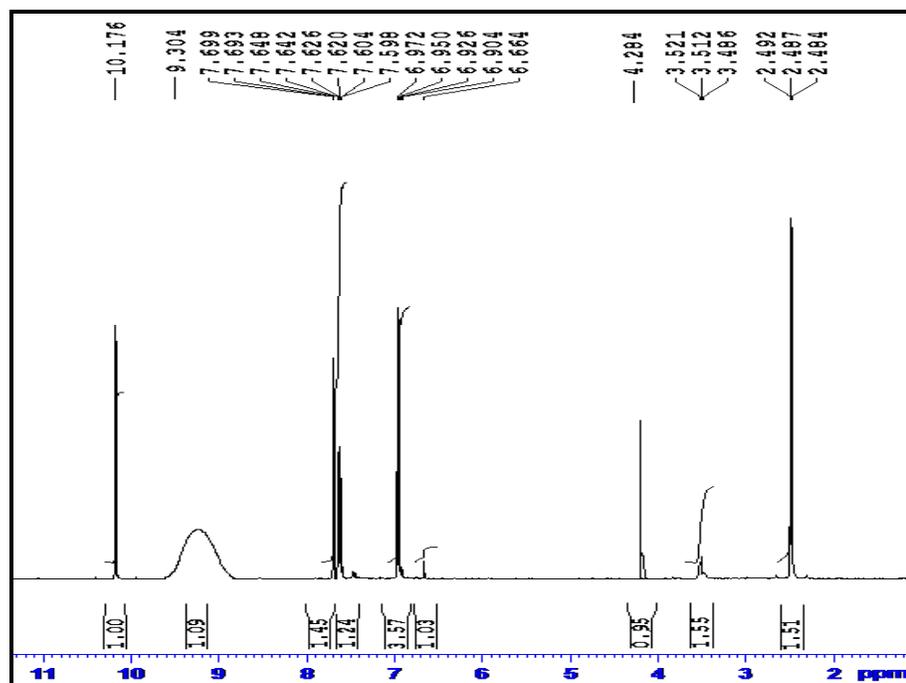
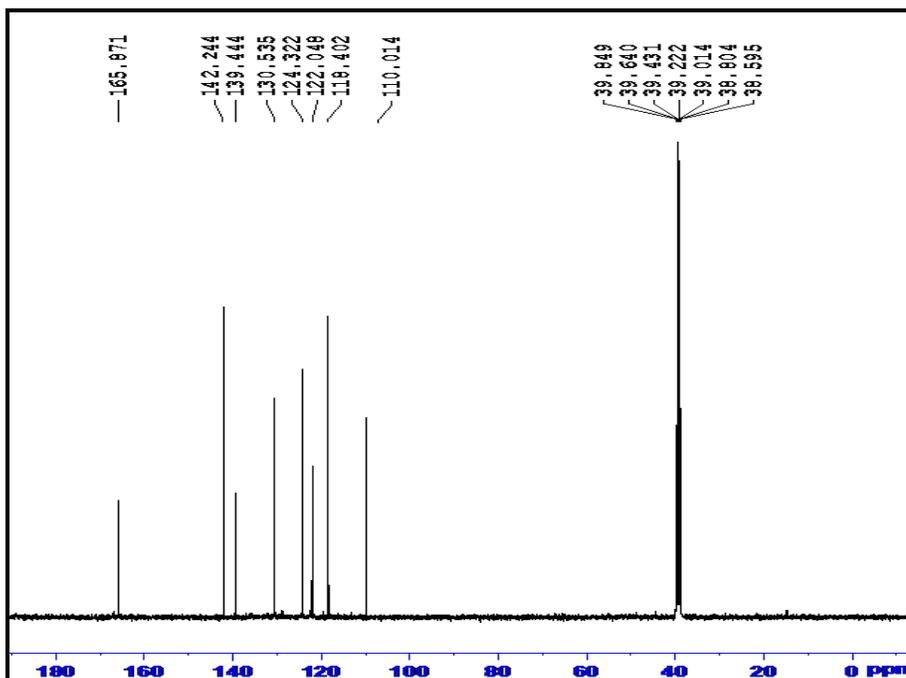


Fig 8.13. FT-IR spectra of Cr(III) complex (8e).

### 8.3.2. $^1\text{H}$ and $^{13}\text{C}$ -NMR spectral studies

The  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of ligand (Shown in Fig 8.14 and Fig 8.15.) were recorded in  $\text{DMSO-}d_6$ . The  $^1\text{H}$ -NMR spectrum of ligand (2e) showed singlet at  $\delta$  10.18 ppm corresponds to proton of the azomethine linkage (-CH=N-) apparently because of the effect of the *ortho*-hydroxyl group in the aromatic ring. A singlet at  $\delta$  9.30 ppm was assigned to hydroxyl proton (-OH). The downfield shift of

Fig 8.14.  $^1\text{H-NMR}$  spectra of LH(2e).Fig 8.15.  $^{13}\text{C-NMR}$  spectra of LH(2e).

the phenolic ( $-\text{OH}$ ) proton was observed due to intramolecular ( $\text{O-H}\cdots\text{N}$ ) hydrogen bonding in the ligand [44].  $^{13}\text{C-NMR}$  spectra of ligand exhibited peaks at  $\delta$  165.81 and 142.24 probably due to the phenolic ( $\text{C-O}$ ) and imino ( $-\text{CH}=\text{N}$ ) carbon atoms (due

to Keto-imine tautomerism). The chemical shifts due to the aromatic carbons appeared at  $\delta$  139.44-110.01 ppm.

### 8.3.3. 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 (**2e**) 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 (Figs 8.16-8.22). 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,  $\lambda$  is the X-ray wavelength (1.5406 Å),  $\beta$  is the full width at half maximum (FWHM) and  $\theta$  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 (**2e**), 3.96 nm (**3e**), 2.56 nm (**4e**), 3.82 nm (**5e**), 3.32 nm (**6e**), 8.91nm (**7e**) and 11.94 nm (**8e**).

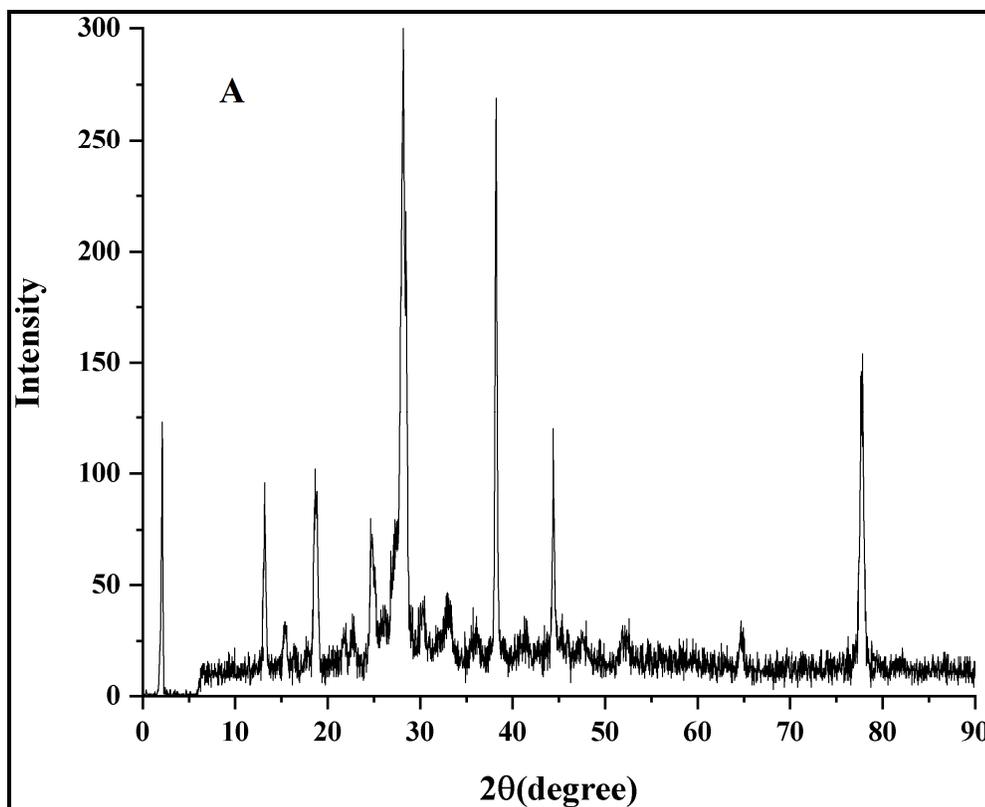


Fig 8.16. PXRD spectra of LH (**2e**).

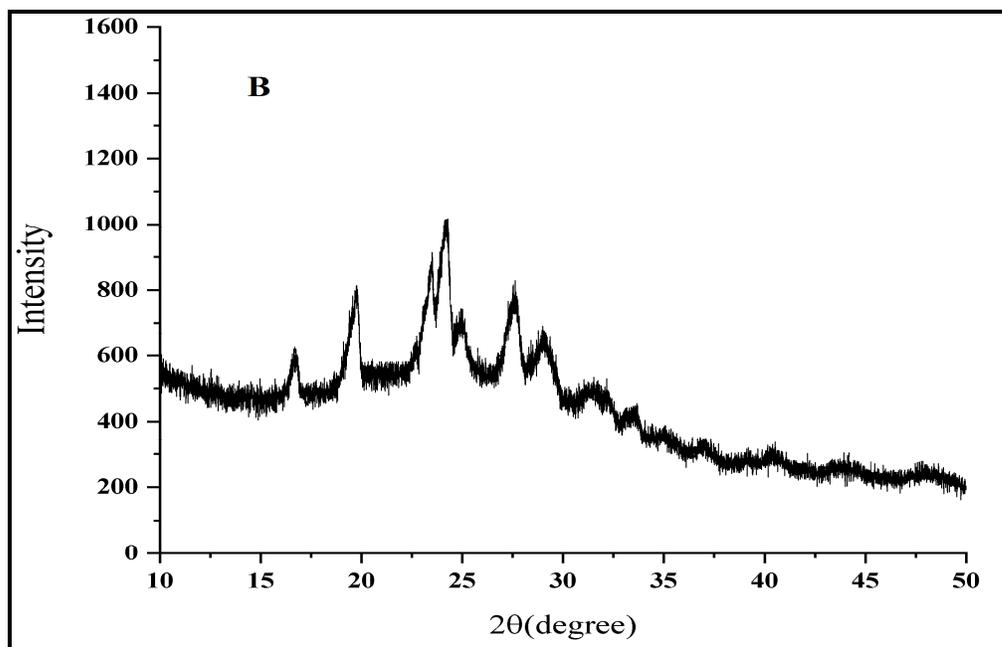


Fig 8.17. PXRD spectra of Co(II) complex (3e).

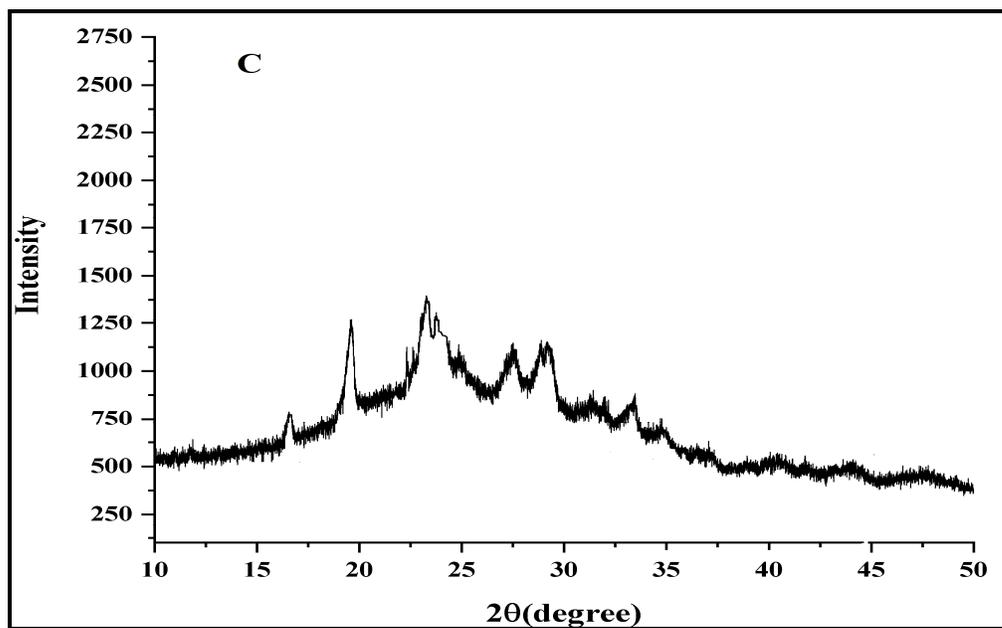


Fig 8.18. PXRD spectra of Ni(II) complex (4e).

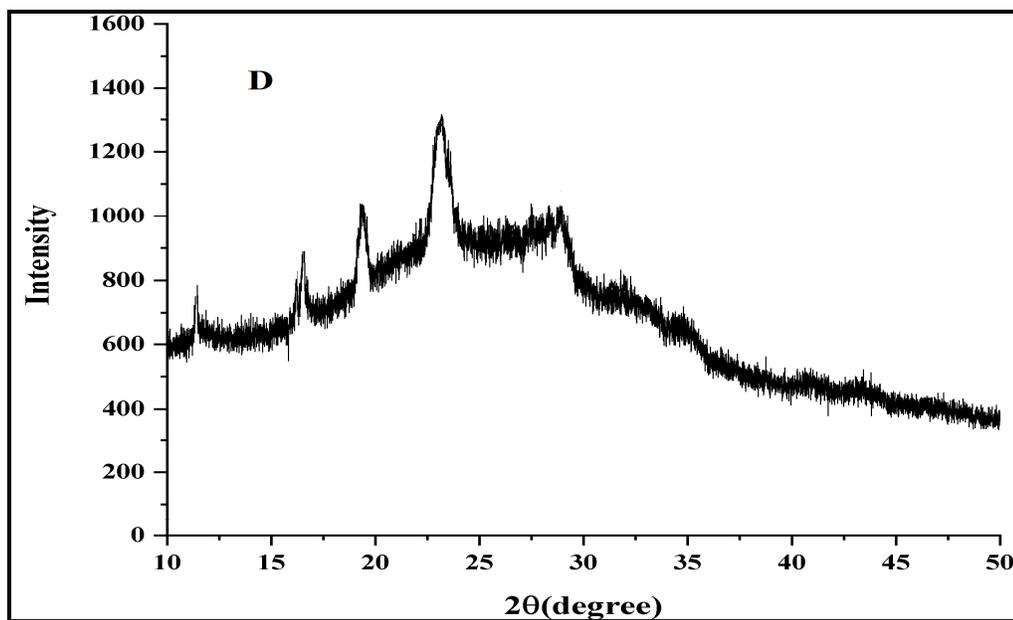


Fig. 8.19. PXRD spectra of Cu(II) complex (5e).

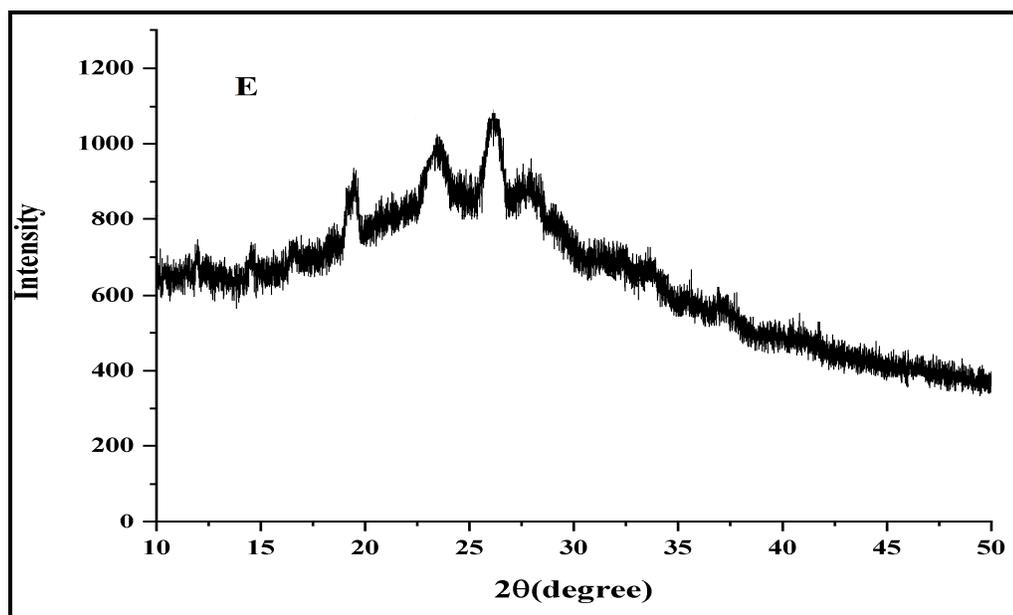


Fig 8.20. PXRD spectra of Mn(III) complex (6e).

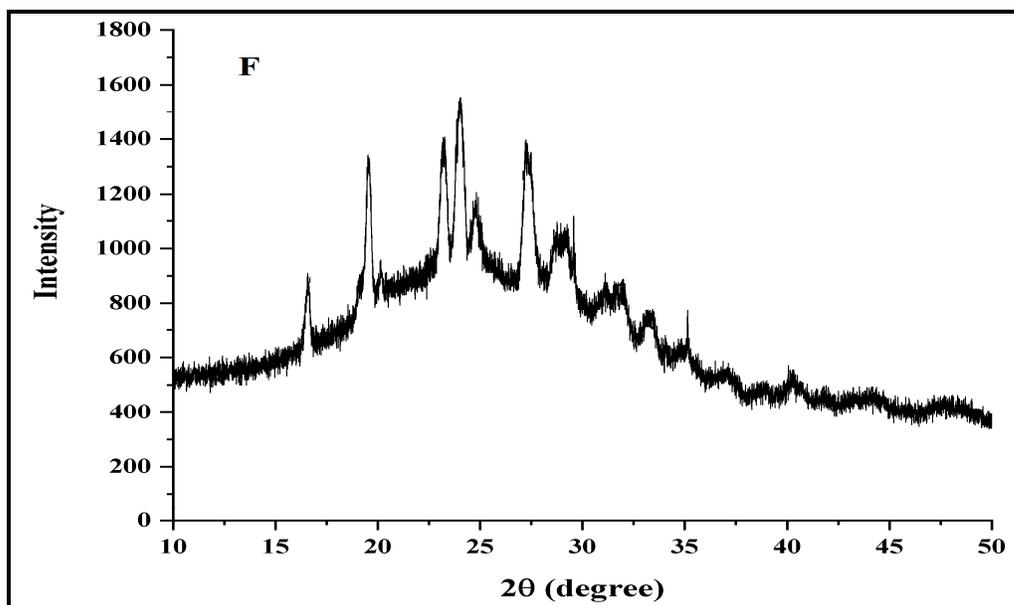


Fig 8.21. PXRD spectra of Fe(III) complex (7e).

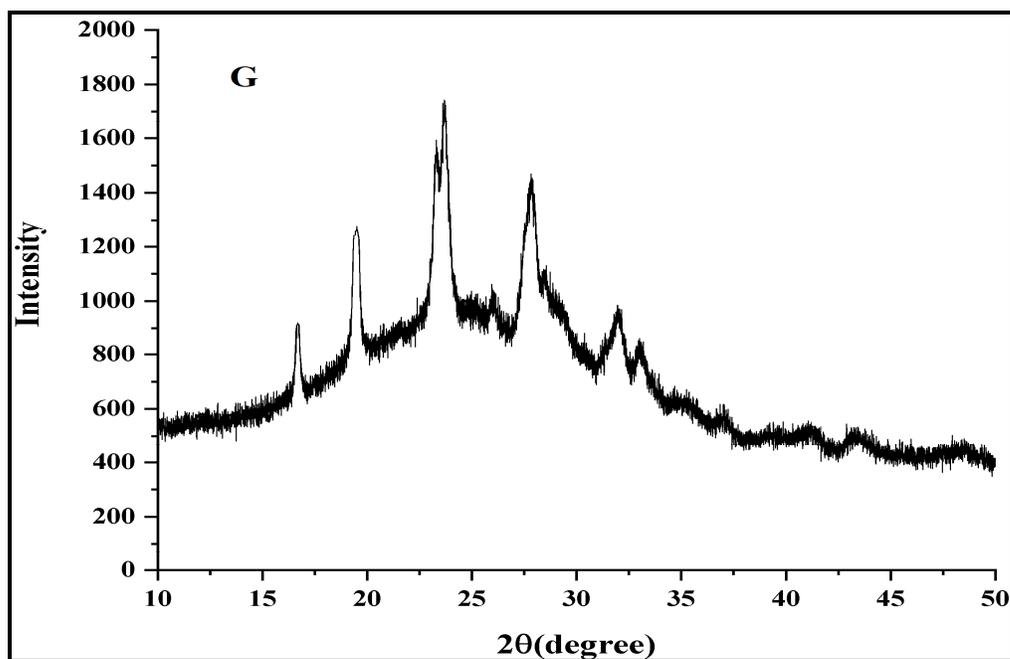


Fig 8.22. PXRD spectra of Cr(III) complex (8e).

#### 8.3.4. Mass spectral studies

To clarify the structure of the synthesized compounds at the molecular level, electrospray ionization (ESI) mass spectrometry was recorded using methanol as solvent. Mass-spectra of the LH (2e) had a molecular ion peaks at  $m/z$  264, that

corresponds to  $[M-BF_4]^+$ , ( $M = [C_{13}H_{15}ClN_3O]^+$ ) ion. The Co(II) complex (**3e**) exhibited molecular ion peaks ( $m/z$ ) at 585, which was assigned to  $[M-2BF_4]^+$  ( $M = [(C_{26}H_{28}CoCl_2N_6O_2)]^+$ ) ion. The molecular ion peaks appeared at 586 ( $[M+2H-2BF_4]^+$ ,  $M = [(C_{26}H_{28}NiCl_2N_6O_2)]^+$ ) and at 588 ( $[M-H-2BF_4]^+$ ,  $M = [(C_{26}H_{28}CuCl_2N_6O_2)]^+$ ) were assigned for Ni(II) complex (**4e**) and Cu(II) complex (**5e**) respectively. The mass spectra of the Mn(III) complex (**6e**) 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 (**7e**) and Cr(III) complex (**8e**) 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 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 Figs 8.23-8.29.

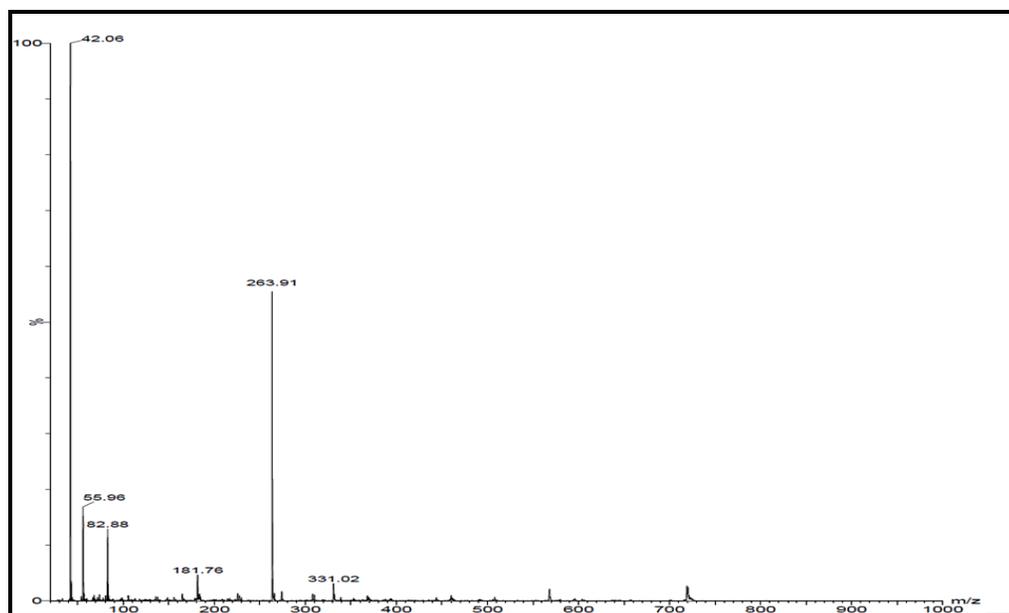


Fig 8.23. ESI-MS spectrum of LH (**2e**).

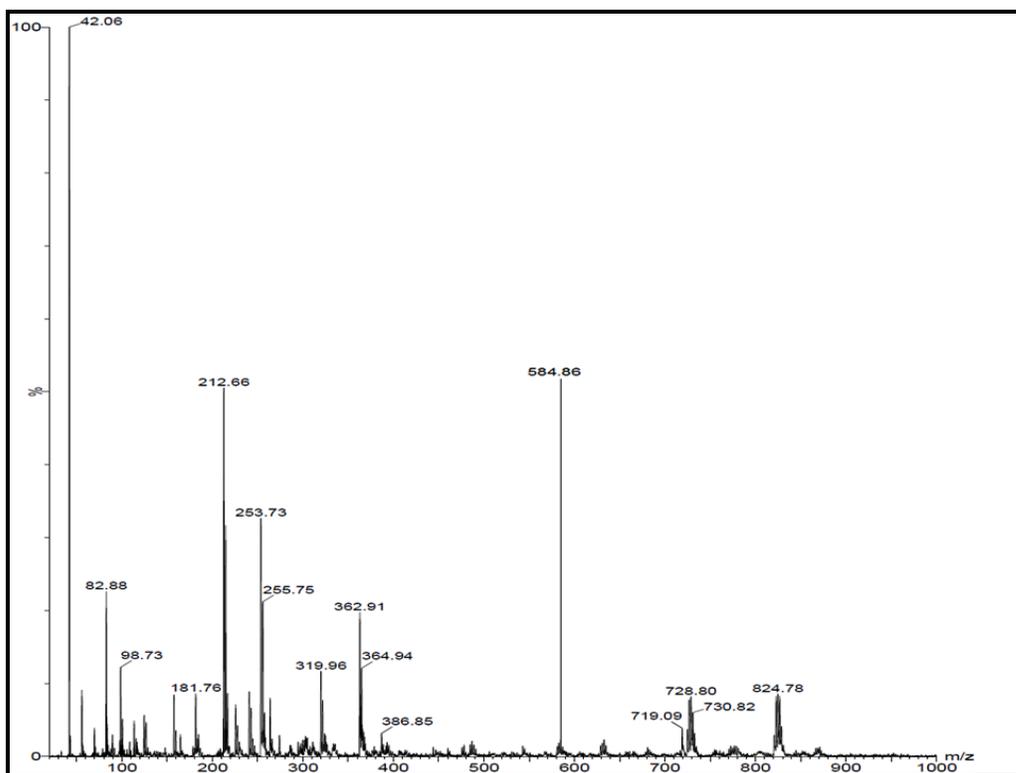


Fig 8.24. ESI-MS spectrum of Co(II) complex (3e).

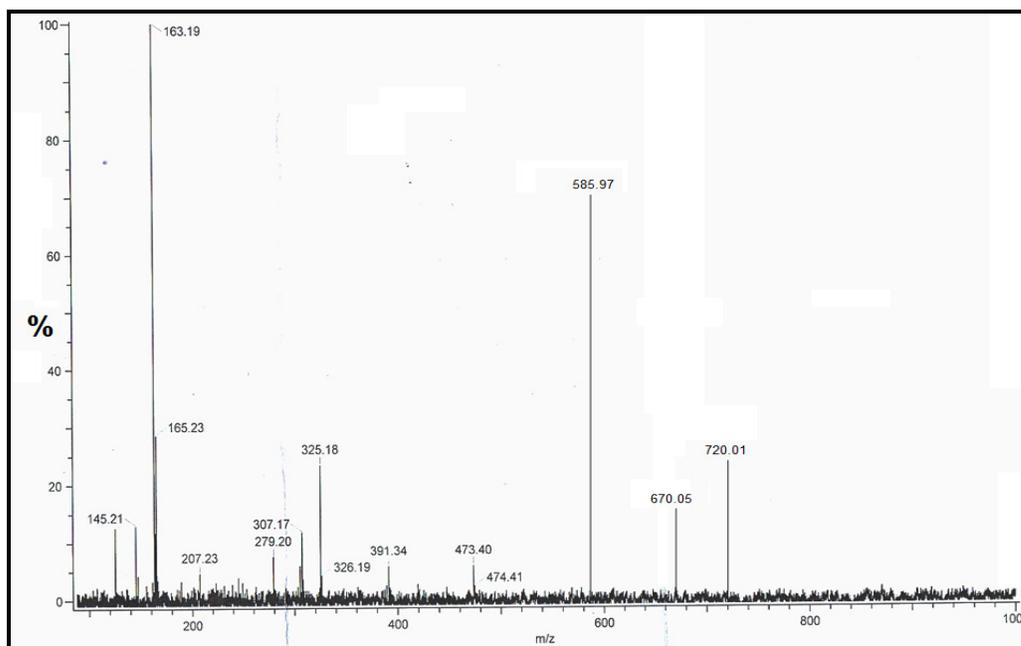


Fig 8.25. ESI-MS spectrum of Ni(II) complex (4e).

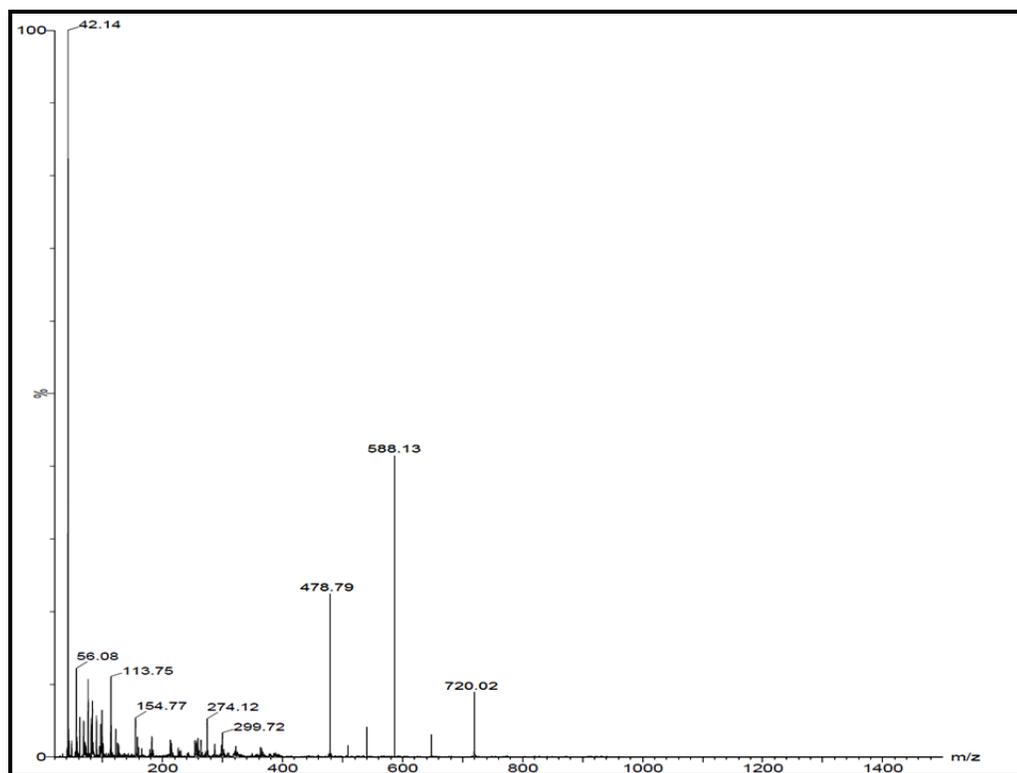


Fig 8.26. ESI-MS spectrum of Cu(II) complex (5e)

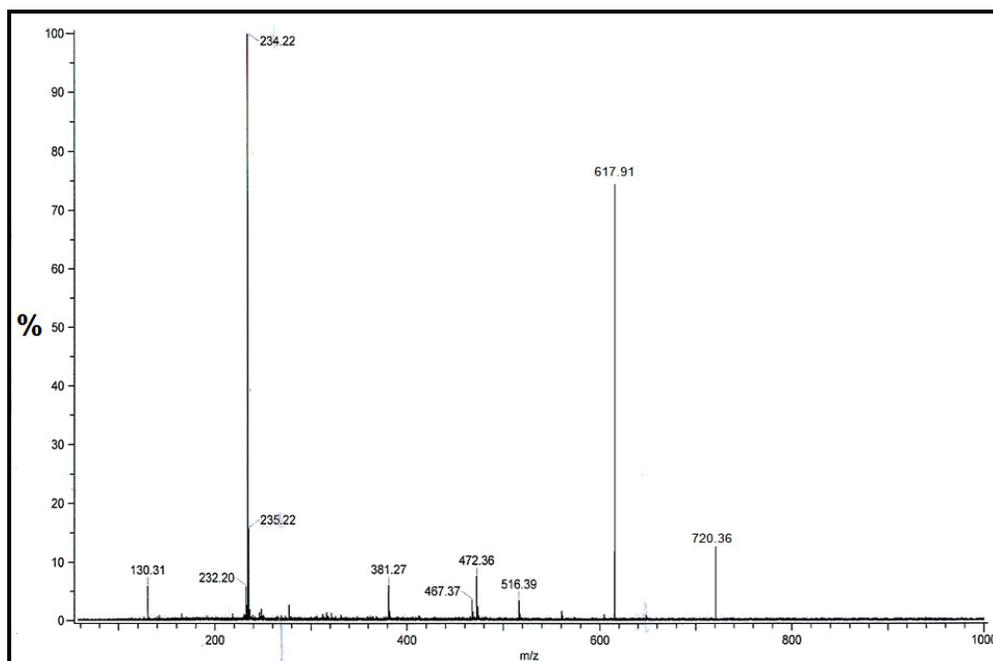


Fig. 8.27. ESI-MS spectrum of Mn(III) complex (6e).

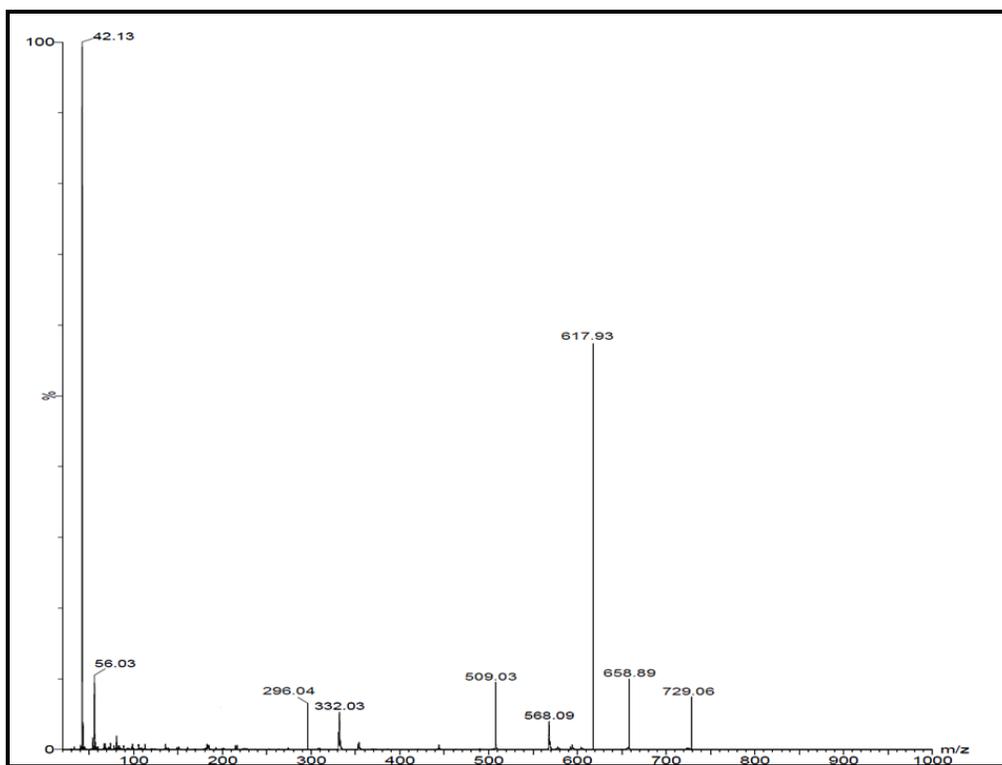


Fig 8.28. ESI-MS spectrum of Fe(III) complex (7e).

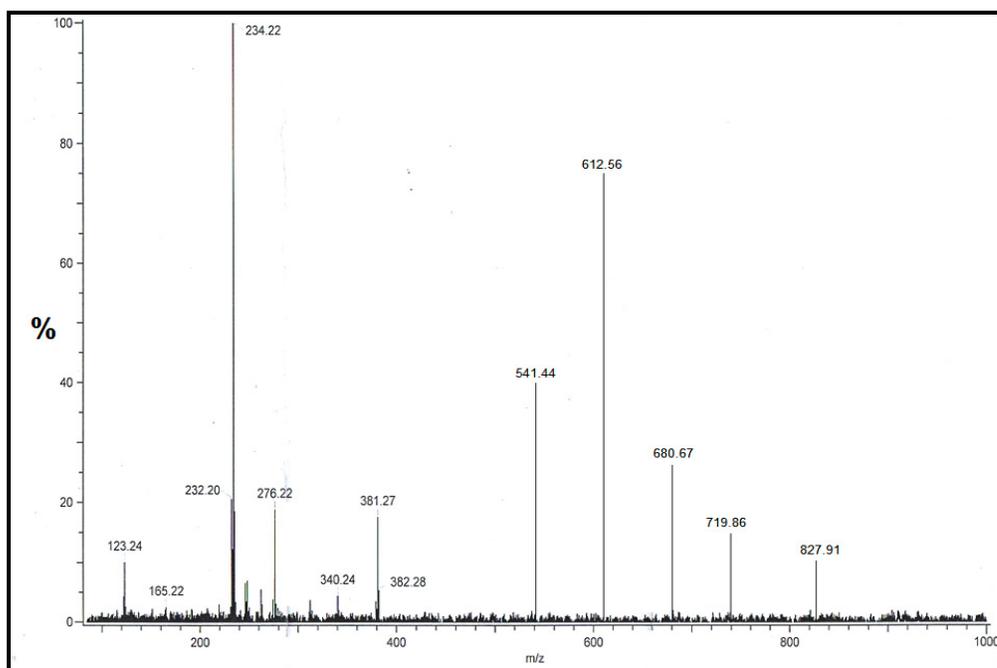
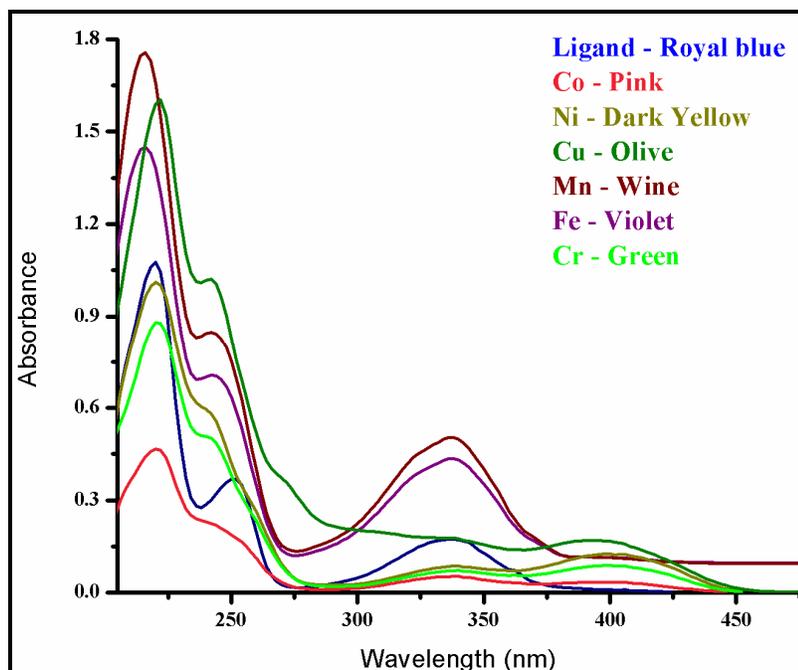


Fig 8.29. ESI-MS spectrum of Cr(III) complex (8e).

### 8.3.5. Electronic absorption spectral and magnetic moment studies

The UV-Visible spectra of the Schiff base and its metal complexes (as shown in Fig 8.30.) were recorded at ambient temperature using methanol as solvent. The LH (**2e**) 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 (**3e**, **4e** and **5e**), the bands that appeared below 350 nm were ligand centred transitions ( $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$ ). The Co(II) complex (**3e**) showed a shoulder at 398 nm which was attributed to the combination of  ${}^2B_{1g} \rightarrow {}^1A_{1g}$  and  ${}^1B_{1g} \rightarrow {}^2E_g$  transitions and supporting square planar geometry [47, 48]. The complex (**3e**) showed magnetic moment of 2.32 B.M. due to an unpaired electron. The Ni(II) complex (**4e**) 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 (**5e**) displayed  $d \rightarrow \pi^*$  metal-ligand charge transfer transition (MLCT) at the region 395 nm was assigned for 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 **5e** was 1.82 B.M. consistent with the presence of an unpaired electron [52]. In the UV-Visible spectra of Mn(III) complex (**6e**) three bands at 339, 243 and 216 nm were observed. Due to its  $d^4$  electronic structure; electronic transition was assigned to  ${}^5T_{2g} \rightarrow {}^5E_g$  which proposed that the metal centre was effectively coordinated by ligand in octahedral environment [53, 54]. The observed magnetic moment was found 4.84 B.M. for Mn(III) complex (**6e**). The Fe(III) complex (**7e**), ( $d^5$  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 **7e** suggested high spin configuration of the metal ion with five unpaired electrons [55]. UV-visible spectrum of the Cr(III) complex (**8e**) 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 [56, 52]. Again the complex **8e** showed magnetic moment of 3.93 B.M. corresponding to three unpaired electrons.



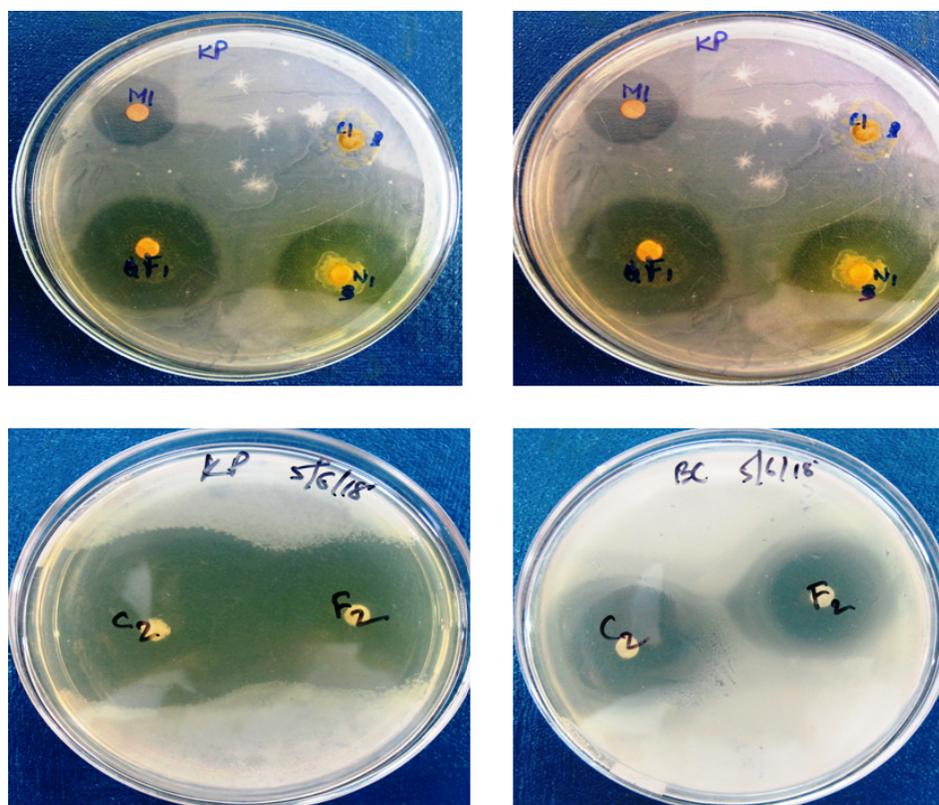
**Fig 8.30.** The UV-Vis spectra of ligand (**2e**) and its metal complexes (**3e** to **8e**).

### 8.3.6. Antimicrobial activities

Antimicrobial susceptibility tests were conducted to assess the efficacy of synthesized compounds. The seven synthesized compounds showed variable results (Fig 8.31 and Table 8.1). All the compounds except **6e** 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 (**5e**) in plates of *Klebsiella pneumoniae* while the minimum inhibition zone was produced by *Bacillus cereus*. *Staphylococcus aureus* showed maximum susceptibility for the all the samples in comparison to the other bacterial cultures. So, it was concluded that the ligand (**2e**) along with its metal complexes (**3e**, **4e**, **5e**, **6e**, **7e** and **8e**) inhibited the growth of pathogenic bacteria like *Staphylococcus aureus*, *Bacillus cereus*, *Escherichia coli* and *Klebsiella pneumoniae*.

**Table 8.1:** Antibacterial activities of the ligand (2e) and its metal complexes (3e to 8e).

Specimen	Minimum inhibition concentration (mm)			
	Gram positive		Gram negative	
	<i>E. coli</i>	<i>K. pneumoniae</i>	<i>B. cereus</i>	<i>S. aureus</i>
LH (2e)	22	18	18	25
Co(II) complex (3e)	35	21	35	36
Ni(II) complex (4e)	33	30	34	35
Cu(II) complex (5e)	28	42	20	36
Mn(III) complex (6e)	---	---	---	---
Fe(III) complex (7e)	35	30	35	38
Cr(III) complex (8e)	32	31	24	34



**Fig 8.31.** MIC of the Cu(II) complex (5e) against *K. pneumoniae* and *B. cereus*.

### 8. 4. Conclusion

In this 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 act as a potential bidentate ligand coordinating through the N-atom of azomethine and O-atom of phenolic group to the metal ions and thus formed 1:2 (M:L) complexes. Spectral and magnetic susceptibility data revealed that the ligand was arranged in square planer geometry 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 study of the synthesized compounds was performed and metal complexes have exhibited promising activity against the tested bacteria.

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## Chapter VIII

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