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Synthesis and Characterization of Chromium (III) Schiff base complexes: Antimicrobial activity and its Electrocatalytic sensing ability of catechol

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Abstract:

A series of acyclic Schiff base chromium (III) complexes were synthesized with the aid of microwave irradiation method. The complexes were characterized on the basis of elemental analysis, spectral analysis such as UV-Visible, Fourier transform infrared (FT-IR), nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR) spectroscopies and electrospray ionization (ESI) mass spectrometry. Electrochemical analysis of the complexes indicates the presence of chromium ion in +3 oxidation state. Cr (III) ion is stabilized by the tetradentate Schiff base ligand through its nitrogen and phenolic oxygen. From the spectral studies it is understood that the synthesized chromium (III) complexes exhibits octahedral geometry. Antimicrobial activity of chromium complexes was investigated towards the Gram positive and Gram negative bacteria. In the present work, an attempt was made to fabricate a new kind of modified electrode based on chromium Schiff base complexes for the detection of catechol at nanomolar level.

Key words: Microwave synthesis, chromium (III) Schiff base complex, antimicrobial activity, electrocatalytic sensor, catechol.

1. Introduction

The great interest was shown to synthesis Schiff base and their transition metal complexes due to its numerous applications such as metal chelating agents, heterogeneous and homogenous

catalysts, antimicrobial agents, in trace metal analysis, pesticides, antitumor agents, spectrophotometric and fluorimetric agents and in solar cells [1-14]. Chromium Schiff base complexes has received much attention because of the +3 oxidation state of the chromium metal ion, since the +3 oxidation state of chromium ion is more stable with d^3 configuration and less toxic than +6 chromium ion [15, 16]. Chromium metal has a vital role for maintaining the glucose tolerance factor (GTF) in the normal carbohydrate and lipid metabolism. Insufficient amount of chromium(III) ion consumption may lead to type II diabetes and cardiovascular diseases [17].

In chemical synthesis, the use of microwave irradiation becoming popular when compared to conventional synthesis, owing to its advantages such as shorter reaction time, high yield, low energy consumption and ecofriendly nature. The reactants are slowly activated by external heat energy in conventional heating method, due to this the heat energy is first passing through the walls of the vessel and then it reaches the reagents and reactants. In this way the energy that reaches the reacting substance is inefficient and slow. But in microwave irradiation, the microwaves are directly coupled with the reacting molecules and leads to rapid rise in temperature. As a result, in microwave irradiation reaction occurs at faster rate, because of two types of motion (dipole rotation and ionic conduction). The time duration of a chemical reaction is reduced from hours to minutes, i.e., rate of the reaction is very fast. In microwave method, the amount of solvent required for a chemical reaction is very less when compared with the conventional method. Considering all these facts in our work, we have carried out our reactions with the aid of microwave irradiation [18, 19].

In this present work, we have prepared five salen derivatives of chromium complexes and investigated the antibacterial activities and electrocatalytic sensing ability towards catechol. Electrochemistry of the complexes have direct relation with the structure and oxidation states of

the metal ions. Catechol is mainly found in wastewater discharged from industries, which may produce serious environmental pollution with mutagenesis alteration, decreased liver function and renal tube degeneration in humans. It is also present in human urine and one of the byproduct of the cell metabolism. Hence it becomes important to determine the levels of catechol present in environment and as well as in human body. In literature, so many analytical methods are available for sensing of catechol, to name a few, fluorimetric, spectrophotometric, chromatography and electrochemical methods [20], the electrochemical method is preferred owing to its advantages like cost effective, sensitivity and selectivity. In the present study for the first time, we have utilized the synthesized salen chromium complexes as a sensing platform for catechol determination.

Experimental

2.1 Reagents

All chemicals and reagents used were of AR grade and were used without purification. The $CrCl_3.6H_2O$ was purchased from Alfa Aesar. 5-methylsalicylaldehyde was synthesized by following the literature method [21]. All the diamines, [N,N-bis-(3-aminopropyl)ethylenediamine, diethylenetriamine, N,N-bis-(3-aminopropyl)piperazine, tris-(2-aminoethyl)amine, N,N-bis-(3-aminopropyl)-1,3-propanediamine] were purchased from Sigma Aldrich. TBAP was purchased from Fluka and recrystallized in hot methanol. All other solvents and reagents were obtained commercially and were used without further purification.

2.1.1 General synthesis of 5-methylsalicylaldehyde

A mixture of glycerol (150 g, 1.63 mol) and boric acid (35 g, 0.57 mol) was heated for 30 min at 170 ^{o}C to expel water. Then a mixture of 4-methylphenol (25 g, 0.23 mol) and hexamethylenetetramine (25 g, 0.18 mol) was added. The mixture was stirred for 15 min. The thick brown liquid obtained was allowed to cool to 110 ^{o}C. A solution of concentrated sulphuric

acid (30 mL) in water (70 mL) was added and the whole mixture was boiled in a current of steam. The product was collected by steam distillation. The product was recrystallized from 80% ethanol. Yield: 8.2 g (26%), M.P.: 55 ^{o}C [21].

2.2 Instrumentation

Elemental analyses were carried out on a Perkin–Elmer CHN- 2400 elemental analyzer. FT-IR measurements (KBr Pellets) were carried out on a Bruker-Tensor27 FT-IR. Electronic absorption spectra were measured on a Perkin-Elmer Lambda 600 UV–Visible spectrophotometer. NMR measurements were performed on Bruker 300 MHz NMR, $CDCl_3$ as a solvent and TMS as an internal reference. Electrospray ionization mass spectra of the complexes were performed on a Quan-Tof (Q-Tof) mass spectrometer. Electron paramagnetic resonance (EPR) studies were carried out in the Bruker X-Band CW EPR spectrometer (9.4GHz). The electrochemical analysis were carried out using CHI 1103A electrochemical workstation, with three electrode system, using glassy carbon electrode as working electrode, platinum wire as counter electrode, Ag/AgCl as a reference electrode, tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. Cyclic voltammetry was carried out in acetonitrile as solvent. All voltammetric measurements were carried out after nitrogen purging for 20 minutes.

2.3 Preparation of Chromium Schiff base complex modified GCE

Prior to electropolymerization, the GCE was subjected to the pre–treatment and sequentially polished with alumina slurries of different sizes to attain mirror finish. Then the polished GCE was ultrasonicated in double distilled water for 15 min. The electrochemical pre-treatment of the electrode was carried out, first by applying a fixed potential of +0.5 V versus SCE for 300 s, followed by potential cycling between -1.5 and +1.5 V at a scan rate of 50 mVs^{-1} for 20 cycles in 0.1 M sulphuric acid and acetonitrile solution. After that, the chromium Schiff base

complex film was successfully generated on the surface of the clean GCE via the following electrochemical polymerization procedure. 0.1 M of chromium complex was prepared in acetonitrile and tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. After the successful electropolymerization on the GCE, the film was washed with double distilled water and the electrocatalytic response of the modified electrode was evaluated using 0.1mM of catechol in 0.1 M Phosphate buffer solution (PBS) at pH 7 as the background electrolyte.

2.4. Preparation of the Schiff bases

Schiff bases were prepared by microwave assisted method [16]. All the diamines [N,N-bis-(3-aminopropyl)ethylenediamine, diethylenetriamine, N,N-bis-(3-aminopropyl)piperazine, tris-(2-aminoethyl)amine, N,N-bis-(3-aminopropyl)-1,3-propanediamine] were condensed with 5-methylsalicylaldehyde by the following procedure (Scheme-1). 1mM methanolic solution of diamine was added drop wise to a stirred solution of 2 mM 5-methylsalicylaldehyde in 5 ml methanol. This mixture was then irradiated in the microwave oven at 320 W for 10-12 minutes. After the irradiation, the mixture was cooled to room temperature, then it was kept for 12 h at 10 ^{0}C. The obtained coloured solid products were filtered and washed with cold ethanol and dried overnight in a desiccator. All the Schiff bases were recrystallized using 1:1 methanol and dichloromethane as solvent.

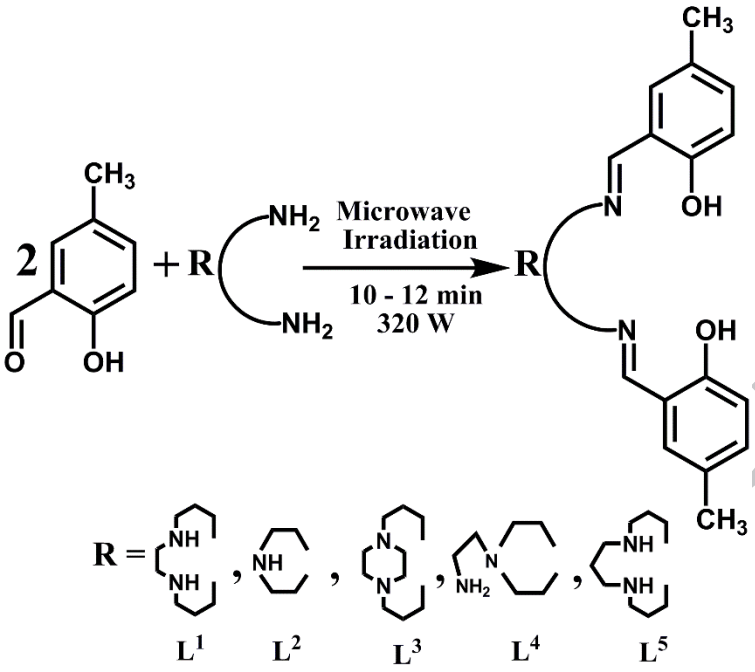
H_2L^1 = N,N'-bis(5-methylsalicylaldimine)-N,N'-bis-(2-aminoetyl)ethane-1,2-diamine;

H_2L^2 = N,N'-bis(5-methylsalicylaldimine)-N-(2-aminoethyl)ethylenediamine;

H_2L^3=N,N'-bis(5-methylsalicylaldimine)-N,N'-bis-(3-aminopropyl)piperazine;

H_2L^4 = N,N'-bis(5-methylsalicylaldimine)-tris(2-aminoethyl)amine;

H_2L^5 = N,N'-bis(5-methylsalicylaldimine)-N,N'-bis-(3-aminopropyl)ethylenediamine.



Scheme-1: Synthesis of Schiff bases.

2.3.1. Synthesis of Schiff base ligand [H_2L^1]

Greenish yellow powder, Yield: 0.689 g, 79.9 %. m.p.: 140 °C. Molecular formula ***$C_{24}H_{34}N_4O_2$***; Elemental Analysis Calc. (%): C =70.21; H =8.35; N =13.65; Exp(%): C=70.15; H = 8.28; N = 13.54. Calc av.MS (m/z) 410.27, [MH^+] 411.27. Selected IR data (KBr) (ν, cm^{-1}): 3750 ν(OH), 2925 ν(OH••••N=C), 2812 ν(C-H), 1624 ν(C=N), 1583 ν(C=C), 1357 ν(C-N), 1275 ν(C-O). ^{1}H NMR (ppm in $CDCl_3$ 300 MHz): δ 1.86 (s, 3H), 2.27 (s, 4H), 2.72 (s, 4H), 3.64 (s, 3H), 6.84–6.86 (d, 2H), 7.01-7.26 (m,3H), 8.29 (s, 1H), 8.12(s, 2H), ^{13}C NMR ($CDCl_3$, 300 MHz): 20.35, 28.00, 53.25, 55.92, 57.61, 76.74, 77.05, 116.75, 118.46, 127.51, 131.18, 132.19, 158.98, 164.97. UV–Vis spectrum in methanol: 219 nm, 256 nm, 325 nm.

2.3.2. Synthesis of Schiff base ligand [H_2L^2]

Yellow powder, Yield (0.763 g, 84%). m.p.: 156 °C. Molecular formula ***$C_{20}H_{25}N_3O_2$***; Elemental Analysis Calc (%): C = 70.77; H = 7.42; N = 12.38. Exp(%) : C = 70.57; H = 7.25; N =

12.57. Calc av.MS (m/z) 339.43, [MH^+] 340.43. Selected IR data, (KBr) (ν, cm^{-1}): 3243 ν(OH), 2946 ν(OH••••N=C), 2823 ν(C-H), 1633 ν(C=N), 1593 ν(C=C), 1490 ν(C-N), 1275 ν(C-O). ^{1}H NMR (ppm in $CDCl_3$ 300 MHz): δ 2.27(s,3H), 3.68-3.71 (m, 5H), 3.92 (s,1H), 6.82 (s, 1H), 6.85 (s, 1H), 7.01 (s,1H), 8.31 (s, 1H), 13.05 (s,1H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 49.75, 59.71, 59.87, 76.71, 77.03, 77.34, 116.68, 118.37, 127.63, 131.38, 131.53, 133.08, 133.18, 158.83, 166.47. UV–Vis spectrum in methanol: 220 nm, 257 nm, 330 nm.

2.3.3. Synthesis of Schiff base ligand [H_2L^3]

Yellow powder, Yield (0.7823, 89.9%). m.p.: 145 °C. Molecular formula $\boldsymbol{C_{26}H_{36}N_4O_2}$; Elemental Analysis Calc (%): C = 71.53; H = 8.31; N = 12.8. Exp(%) :C = 71.85; H = 8.19; N = 12.80. Calc av. MS (m/z) 436.59, [MH^+] 437.55. Selected IR data (KBr) (ν, cm^{-1}): 3325 ν(OH), 2916 ν(OH••••N=C), 2802 ν(C-H), 1625 ν(C=N), 1583 ν(C=C), 1490 ν(C-N), 1275 ν(C-O). ^{1}H NMR (ppm in $CDCl_3$ 300 MHz): δ 1.84–1.91 (m, 5H), 2.40–2.47(m,6H), 3.60–3.63 (s, 2H), 6.84–6.86 (s, 1H), 7.02–7.09 (s, 2H), 8.29 (s,1H), 13.26 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 20.35, 31.24, 47.46, 57.50, 116.73, 127.54, 131.21, 132.92, 158.93, 164.88. UV–Vis spectrum in methanol: 224 nm, 257 nm, 327 nm.

2.3.4. Synthesis of Schiff base ligand [H_2L^4]

Yellow powder, Yield (0.792 g, 86.6%). m.p.: 148 °C. Molecular formula $\boldsymbol{C_{22}H_{30}N_4O_2}$; Elemental Analysis Calc (%): C = 69.08; H = 7.91; N = 14.65. Exp. (%): C = 69.16; H = 7.82; N = 14.76. Calc av. MS (m/z) 382.50, [MH^+] 383.57. Selected IR data (KBr) (ν, cm^{-1}): 3427 ν(OH), 2925 ν(OH••••N=C), 2822 ν(C-H), 1645 ν(C=N), 1583 ν(C=C), 1490 ν(C-N), 1286 ν(C-O) . ^{1}H NMR (ppm in $CDCl_3$ 300 MHz): δ 1.55 (s, 3H), 2.27 (s, 3H), 6.82-6.85 (d, 1H), 7.00-7.20 (m, 2H), 8.31 (s, 1H), 12.96 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 20.94, 31.26, 33.80, 47.45, 49.39,

49.94, 56.61, 57.51, 76.73, 77.37, 116.57, 166.73, 118.34, 127.53, 131.43, 132.93, 158.94, 164.96. UV–Vis spectrum in methanol: 215 nm, 257 nm, 331 nm.

2.3.5. Synthesis of Schiff base ligand [H_2L^5]

Yellow powder, Yield (0.732 g, 84.6%). m.p.: 150 °C. Molecular formula ***$C_{25}H_{36}N_4O_2$***; Elemental Analysis Calc (%): C = 70.72; H = 8.55; N = 13.20. Exp. (%): C = 70.52; H = 8.36; N = 13.65. Calc av. MS (m/z) 424.58, [MH^+] 425.59. Selected IR data (KBr) (ν, cm^{-1}): 3625 ν(OH), 2915 ν(OH••••N=C), 2812 ν(C-H), 1634 ν(C=N), 1583 ν(C=C), 1480 ν(C-N), 1275 ν(C-O) . ^{1}H NMR (ppm in $CDCl_3$ 300 MHz): δ 1.84-1.87 (m, 3H), 2.27 (s, 4H), 2.71 (s, 4H), 3.63 (s, 2H), 6.84-6.86 (m, 1H), 7.01-7.10 (s, 2H), 8.29 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 28.94, 31.26, 33.80, 47.45, 49.39, 56.61, 57.51, 76.73, 77.37, 116.57, 118.45, 131.43, 132.93, 158.94, 164.90. UV–Vis spectrum in methanol: 213 nm, 256 nm, 326 nm.

2.4. Preparation of the Chromium Schiff base complexes

An absolute methanolic solution of chromium chloride ($CrCl_3.6H_2O$) [0.266 g 1 mmol] was gradually added to the stirred methanolic solution of (1mmol) Schiff base, then the solution was irradiated in a microwave oven at 320 W for 12-15 minutes. The crude product was dissolved in methanol and the solution was filtered. The filtrate was allowed to stand at room temperature for 12 h, which upon filtration yield a solid product. The resulting solid compound was recrystallized with methanol and dichloromethane in 1:1 ratio.

2.4.1. Preparation of $[Cr(L^1)(H_2O)_2]^+$

Dark green powder, Yield: 0.628 g, 85.67%. m.p.: 225-230 ^{o}C decomposition (uncorrected). Molecular formula for the complex [***$C_{24}H_{36}N_4O_4Cr$***]***Cl***. Elemental Analysis Calc. (%): C = 54.18; H = 6.82; N = 10.53; Cr =9.77; Cl = 6.66. Exp. (%): C = 54.13; H = 6.75; N = 10.56; Cr = 9.81; Cl = 6.56. Selected IR data (KBr, cm^{-1}): 3416 ν(H_2O•••Cr), 2946 ν(C-H), 1614

ν(C=N), 1479 ν(C=C), 1306 ν(C-N), 1151 ν(C-O), 527 ν(O•••Cr), 470 ν(N•••Cr). Mass spectrum: [Calc. m/z]: 496.21, [MH^+] m/z: 497.22; ESI/MS, in methanol [Exp. m/z]:514, [MH^+] m/z: 515. UV–Vis spectrum in methanol: 289 nm, 325 nm, 400 nm, 570 nm. μ_{eff} (298 K): 3.76 BM.

2.4.2. Preparation of $[Cr(L^2)(H_2O)_2]^+$

Pale green powder, Yield: 0.594 g, 84.6%. m.p.: 237-240 ^oC decomposition (uncorrected). Molecular formula for the complex [$C_{20}H_{27}N_3O_4Cr$]Cl. Elemental Analysis Calc. (%): C = 52.12; H = 5.90; N = 9.12; Cr =11.28; Cl = 7.69. Exp. (%): C = 52.20; H = 6.01; N = 9.05; Cr = 11.16; Cl = 7.72. Selected IR data (KBr, cm^{-1}): 3411 ν(H_2O•••Cr), 3010 ν(C-H), 1622 ν(C=N), 1475 ν(C=C), 1300 ν(C-N), 1157 ν(C-O), 533 ν(O•••Cr), 478 ν(N•••Cr). Mass spectrum; [Calc. m/z]: 425.24, [MH^+] m/z: 426.14. ESI/MS, in methanol [Exp. m/z]: 443, [MH^+] m/z: 444. UV–Vis spectrum in methanol: 276 nm, 320 nm, 403 nm, 560 nm. μ_{eff} (298 K): 3.81 BM.

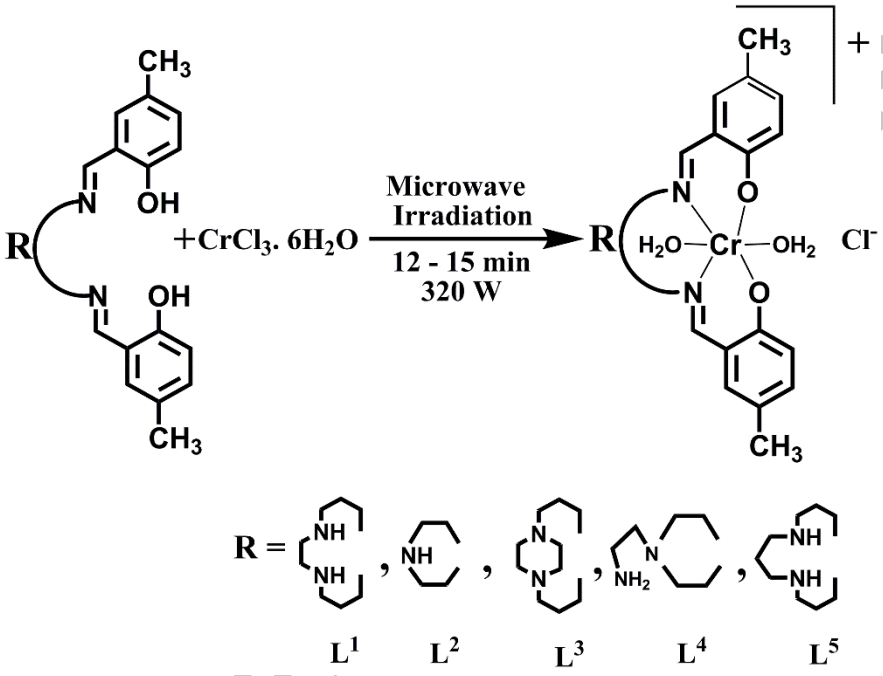
2.4.3. Preparation of $[Cr(L^3)(H_2O)_2]^+$

Brown powder. Yield: 0.625 g, 84.1%. m.p.: 218-220 ^oC decomposition (uncorrected). Molecular formula for the complex [$C_{26}H_{38}N_4O_4Cr$]Cl. Elemental Analysis Calc. (%): C = 55.96; H = 6.86; N = 10.04; Cr =9.32; Cl = 6.35. Exp. (%): C = 56.02; H = 6.84; N = 9.98; Cr = 9.28; Cl = 6.29. Selected IR data (KBr, cm^{-1}): 3411 ν(H_2O•••Cr), 2940 ν(C-H), 1618 ν(C=N), 1464 ν(C=C), 1320 ν(C-N), 1157 ν(C-O), 522 ν(O•••Cr), 446 ν(N•••Cr). Mass spectrum; [Calc. m/z]: 522.23, [MH^+] m/z: 523.23. ESI/MS, in methanol [Exp. m/z]: 550, [MH^+] m/z: 551. UV–Vis spectrum in methanol: 284 nm, 323 nm, 409 nm, 550 nm. μ_{eff} (298 K): 3.69 BM.

2.4.4. Preparation of $[Cr(L^4)(H_2O)_2]^+$

Green powder, Yield: 0.643 g, 89.1%. m.p.: 224-228 ^oC decomposition (uncorrected). Molecular formula for the complex [$C_{22}H_{32}N_4O_4Cr$]Cl. Elemental Analysis Calc. (%): C = 52.43; H = 6.40; N = 11.12; Cr = 10.32; Cl = 7.03. Exp. (%): C = 52.40; H = 6.36; N = 11.05; Cr =

10.38; Cl = 7.00. Selected IR data (KBr, cm^{-1}): 3402 ν(H_2O•••Cr), 2919 ν(C-H), 1625 ν(C=N), 1496 ν(C=C), 1280 ν(C-N), 1167 ν(C-O), 572 ν(O•••Cr), 455 ν(N•••Cr). Mass spectrum; [Calc. m/z]: 468.18, [MH^+] m/z: 469.19. ESI/MS, in methanol [Exp. m/z]:486, [MH^+] m/z: 487. UV–Vis spectrum in methanol: 253 nm, 324 nm, 410 nm, 565 nm. μ_{eff} (298 K): 3.78 BM.



Scheme-2: Synthesis of chromium Schiff base complexes.

2.4.5. Preparation of $[Cr(L^5)(H_2O)_2]^+$

Green powder, Yield: 0.496 g, 80.6%. m.p.: 230-232 ^oC decomposition (uncorrected). Molecular formula for the complex ***[$C_{25}H_{38}N_4O_4Cr$]*Cl**. Elemental Analysis Calc .(%): C = 54.99; H = 7.01; N = 10.97; Cr =9.52; Cl = 6.49. Exp. (%): C = 55.03; H = 6.98; N = 10.24; Cr = 9.55; Cl = 6.50. Selected IR data (KBr, cm^{-1}): 3422 ν(H_2O•••Cr), 2940 ν(C-H), 1618 ν(C=N), 1474 ν(C=C), 1310 ν(C-N), 1157 ν(C-O), 532 ν(O•••Cr), 478 ν(N•••Cr). Mass spectrum; [Calc. m/z]: 496.21, [MH^+] m/z: 497.22. ESI/MS, in methanol [Exp. m/z]: 514, [MH^+] m/z: 515. UV–Vis spectrum in methanol: 275 nm, 319 nm, 405 nm, 550 nm. μ_{eff} (298 K): 3.72 BM.

3. Results and discussion

Chromium (III) complexes are more stable in both solution and solid states. The yields of the synthesized complexes varied from 80 % to 89 %. The reason for yield variation may be the solubility differences between the ligand and final crude product. The resulting complexes were soluble in methanol, ethanol, DMF and DMSO. The final chromium complexes were brown and green in colour. Chromium (III) complexes have three unpaired electrons and d^3 configuration so that it shows the magnetic moment in the range of 3.69-3.81 BM. The experimental values were in good agreement with the calculated values of the complexes.

The elemental analysis was carried out for the chromium Schiff base complexes, [C,H,N] values are given in supplementary data as Table-S1, with the molecular formula, colour, melting point and yield of the complexes. The observed results have good agreement with theoretically calculated values and the given molecular formula.

3.1 IR-spectra

The significant FT-IR spectra of the free ligands and their metal complexes show various bands in the region of 400-4000 cm^{-1}, and their tentative assignments were used for the establishment of the mode of coordination. The typical FT-IR spectra of Schiff base and their metal complexes are shown in the Fig. 1(A) and Fig. 1(B) respectively. Schiff bases are capable to form coordinate bonds with many metal ions through both imine nitrogen group and phenolic oxygen group. The O–H stretching frequency of the ligand is expected from the 3500–3800 cm^{-1} region, but this frequency is displaced to the 2900–2950 cm^{-1} region due to the internal hydrogen bond between OH----N = C. These ligands are planar in structure and hence they have sufficient intramolecular distance for forming hydrogen bond [22]. In chromium(III) complexes, the band at 2900-2950 cm^{-1} broadens due to the formation of metal oxygen bond in the complex when

compared to that of Schiff base ligands. In the metal complexes a broad band at 3400-3425 cm^{-1} establish the bond formation between the chromium metal with water molecule.

The C=N stretching vibration shows a peak in the region of 1592–1640 cm^{-1} as reported for same kind of ligands [23]. The free Schiff ligands exhibit the characteristic band of C=N in the region of 1620-1650 cm^{-1}, while in the complexes the C=N stretching vibration were observed in the region of 1600-1630 cm^{-1}. The shift of C=N stretching vibration in lower region, shows that decreasing the C=N bond order and the coordination of imine nitrogen lone pair with the metal ion. The stretching frequency of phenolic C–O exhibits a weak band within the range of 1100 –1240 cm^{-1} as reported for acyclic Schiff ligands [24].This C – O band for the Schiff bases present in the region of 1080 – 1200 cm^{-1} and for the complexes this band exhibits in the region of 1162 – 1250 cm^{-1} . This higher shift in the stretching frequency of C – O generally shows the formation of a bond between phenolic oxygen with the chromium metal ion. The bands in the region of 400–600 cm^{-1} gives evidence for the bond between chromium metal ion with the nitrogen and phenolic oxygen atom of Schiff bases. The band at 520–580 cm^{-1} is established to Cr–O bond formation in complex at the mean while a band at 440-480 cm^{-1} is established to Cr–N bond formation in the complex. These bands are newly exhibited in the complexes, which are not present in the spectrum of the free ligand [24].

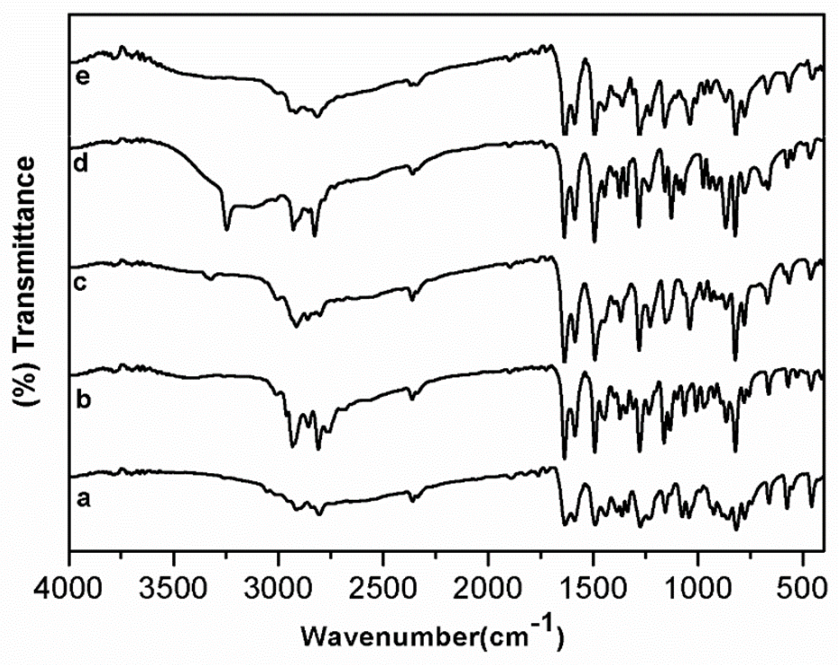


Fig-1 (A): FT-IR spectra of Schiff base ligands (a) $[H_2L^1]$; (b) $[H_2L^2]$; (c) $[H_2L^3]$; (d) $[H_2L^4]$; (e) $[H_2L^5]$.

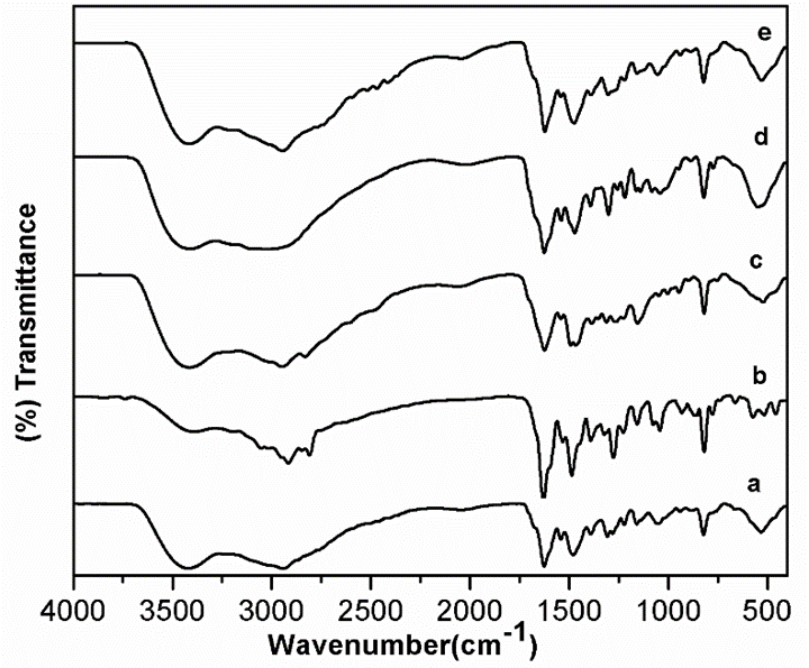


Fig-1(B): FT-IR spectra of chromium Schiff base complexes (a) $[CrL^1(H_2O)_2]^+$; (b) $[CrL^2(H_2O)_2]^+$; (c) $[CrL^3(H_2O)_2]^+$; (d) $[CrL^4(H_2O)_2]^+$; (e) $[CrL^5(H_2O)_2]^+$.

3.2 Electronic spectra

The electronic spectra of the Schiff base and its complexes are shown in Fig-2. In these spectra the benzene ring shows characteristics observation band at 210-220 nm due to $\pi \rightarrow \pi^*$ transition in C=C in free ligands, but the auxochromes and chromophores in substituted benzene ring shows red shift, this band appears at 280-285 nm in complex. A band exhibit in the region of 255-257 nm shows the $n \rightarrow \pi^*$ transition of the C=N chromophores, but this band appeared in complexes in the region of 320-325 nm. The red shift explains that the non-bonded electrons having a weak electrostatic interaction with the central metal ion. In the free ligands at 325-330 nm an absorption was appeared, this band exhibit due to the $\pi \rightarrow \pi^*$ transition of the C=N chromophores. In the electronic spectra a low intensity broad band obtained in the region of 400 - 410 and 550 - 570 nm, it is attributed to the d–d transitions of the Cr(III) ion. In the chromium complexes two transitions bands are observed, they are $^4T_{2g} \leftarrow {}^4A_{2g}$ (ν_1), and $^4T_{1g} \leftarrow {}^4A_{2g}$ (ν_2), the third transition $^4T_{1g}$ (P) $\leftarrow {}^4A_{2g}$ (F) which could not be identified, it lies in the ligand field. The corresponding energy levels for the transitions are 17544-18182 and 24390–25000 cm^{-1} respectively. The spectral transitions suggest that the geometry of the complex is octahedral around the central Cr^{3+} ion [25].

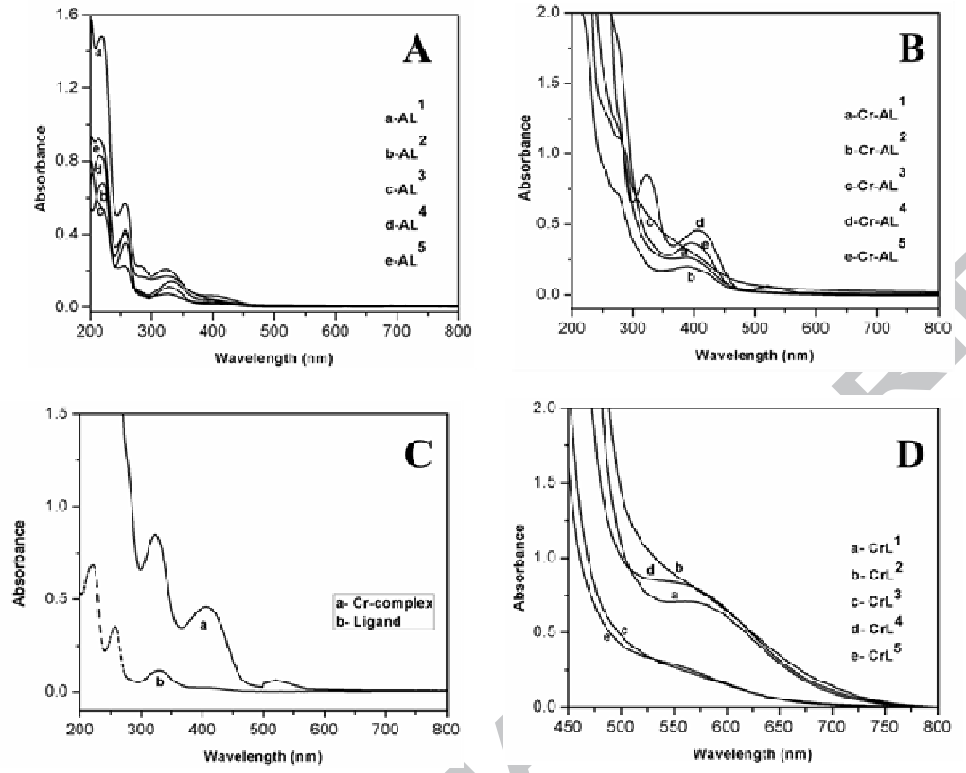


Fig-2: (A) UV-Visible spectra of Schiff base, (B) UV-Visible spectra of chromium Schiff base complexes, (C) Comparison UV-Visible spectra of Schiff base and its chromium complex and (D) UV- Visible spectrum for d-d transition.

3.3 Nuclear magnetic resonance spectra

The investigation of ^{1}H NMR spectra of the free Schiff base ligands were recorded in $CDCl_3$. The ^{1}H and ^{13}C NMR spectrum of the Schiff base ligand was shown in Fig. 3. It appeared in down field from the internal reference of tetramethylsilane. In the spectra a peak appeared in the range of 12.92-13.27 ppm, which attributed to phenolic protons. Signals for the aromatic protons are appeared in the range between 6.8-7.80 ppm. The proton which present next to the imine carbon shows more downfield when compare with the other protons in the aromatic ring. In imine group, the methine protons, –N = C(H) – which exhibit the peak in between 8.28-8.32 ppm. The

peaks were appeared in the range of 2.0-4.8 ppm which is due to the presence of aliphatic protons in the substituted methyl group in phenyl ring.

The interpretation of the ^{13}C NMR spectra shows the peaks for the various carbon atoms in the Schiff base as follows; the carbons which are present in diamine –N─(CH_2)n ─N─, shows peaks in the range of 30 ppm to 60 ppm. The imine group carbon ─N=CH─ show peak at 164 ppm. The carbon which bonded to the imine group shows peak at 118 ppm. The carbon bonded with the hydroxyl group exhibit a peak at 158 ppm. The aromatic carbons in the benzene rings show peak in the range of 115-132 ppm. The substituted methyl group in the phenyl ring exhibits a peak at 25 – 28 ppm. These assignments were carried out based on the tetradentate Schiff base ligands [26- 28].

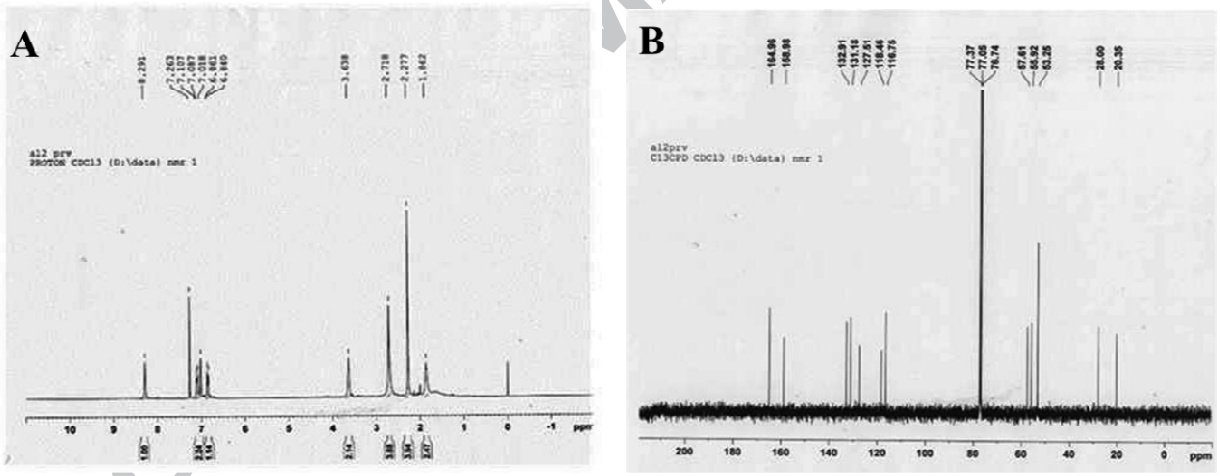


Fig. 3: (A) and (B) are ^{1}H and ^{13}C NMR Spectra of H_2L^2

3.4 ESI-MASS spectra

The ESI-mass spectra of chromium Schiff base complexes $[Cr(L^{1-5})(H_2O)_2]$ were recorded in the methanol solution at room temperature. The ESI-mass spectra of chromium complexes were

shown in Fig-4 (a) and (b). The mass spectrum exhibits multiple peaks represent the degradation of chromium complex and the proposed molecular formula of the chromium complexes were confirmed from m/z value in the mass spectrum. The molecular ion peaks of the complexes are as follows $[CrL^1(H_2O)_2]$ m/z = 514, $[CrL^2(H_2O)_2]$ m/z =443, $[CrL^3(H_2O)_2]$ m/z =550, $[CrL^4(H_2O)_2]$ m/z= 486 and $[CrL^5(H_2O)_2]$ m/z=514. The mass spectra of chromium complex support the nitrogen rule, and also confirm the stoichiometry of the metal ion and the free ligand. The molecular ion peaks show higher molecular weight than the theoretically calculated molecular weight of the complexes. The spectra shows 18 units of mass higher than the theoretical weight, it shows that the one water molecule bonded with the phenolic oxygen by hydrogen bond. The spectral data has good agreement with the proposed molecular formula of the chromium complexes, and gives the more details about the intermediates and reaction products [29, 30].

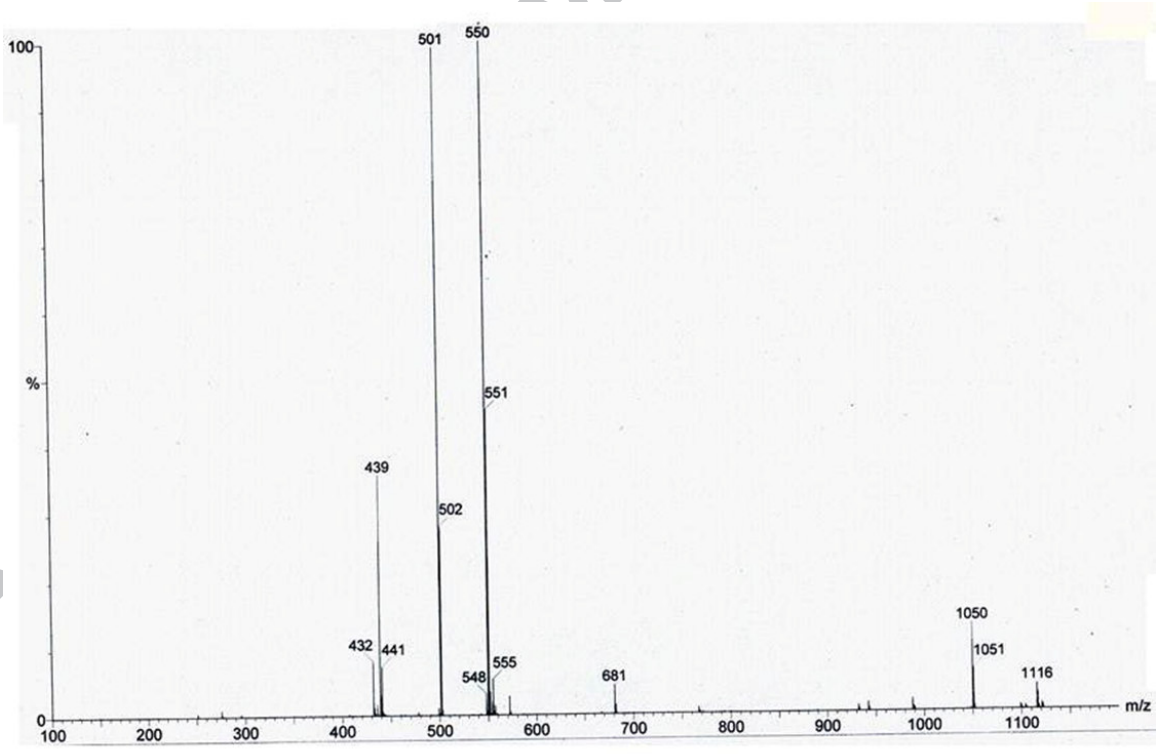


Fig-4 (a): ESI-Mass spectrum of $[CrL^3(OH_2)_2]^+$ complex.

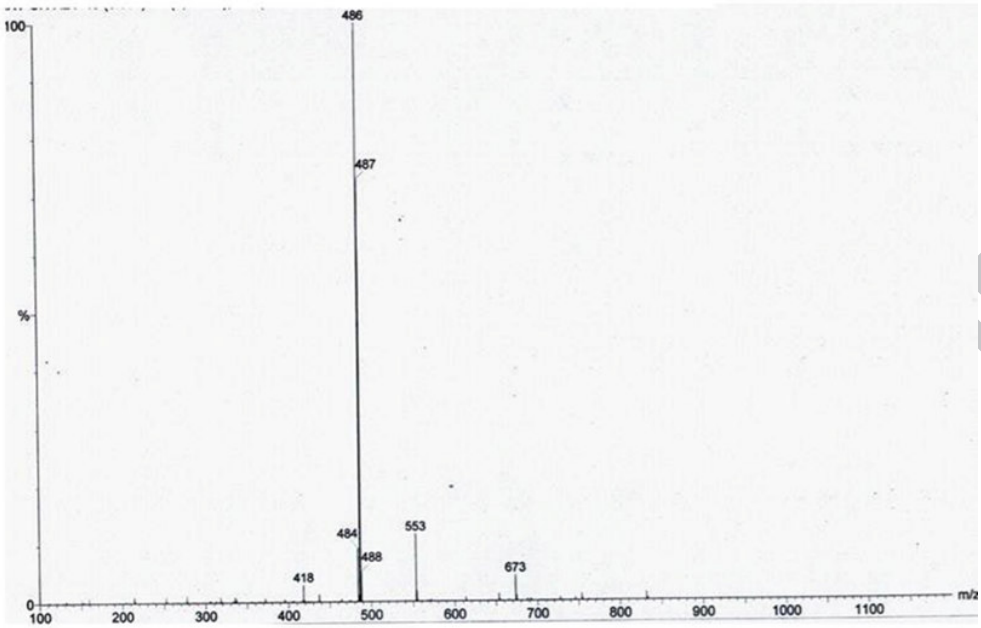


Fig-4 (b): ESI-Mass spectrum of $[CrL^{3}(OH_2)_2]^{+}$ complex.

3.5 EPR Spectral analysis

The EPR spectra of chromium complexes were recorded in methanol solution at room temperature on X-band 9.4 GHz frequency under the magnetic field strength of 3400 G. The EPR spectra show a single broad peak. The EPR spectrum was interpreted by using the simple Hamiltonian Ĥ operator.

$$\hat{H} = \beta\, B.\, g.\, S + S.D.S$$

Where, S=1, g and D are tensors, the contribution of hyperfine interaction is neglected [31].

The Lande splitting factor 'g' was calculate by the following method

$$g = 2.0024(1-4\lambda/10Dq)$$

Where λ is the orbit spin coupling constant for the metal ion in the complex [32].

The g factor for the chromium complexes were obtained 1.9784 -1.9991, with g_{iso} (2.0024) at ground state. The EPR spectra have no features characteristic signals for a binuclear complex.

From the g factor value, the octahedral geometry is thus confirmed for the aforesaid chromium complex [33, 34]. The magnetic moment of the chromium Schiff base complexes at the room temperature is 3.69 – 3.81 BM. It is understood from EPR results that the complex possess the central metal ion in d^3 electronic configuration. The magnetic momentum is also support the mononuclear and the octahedral geometry of the complex. Besides with it confirms the electronic state of the central metal ion. The typical EPR spectra are shown in **Fig-5**.

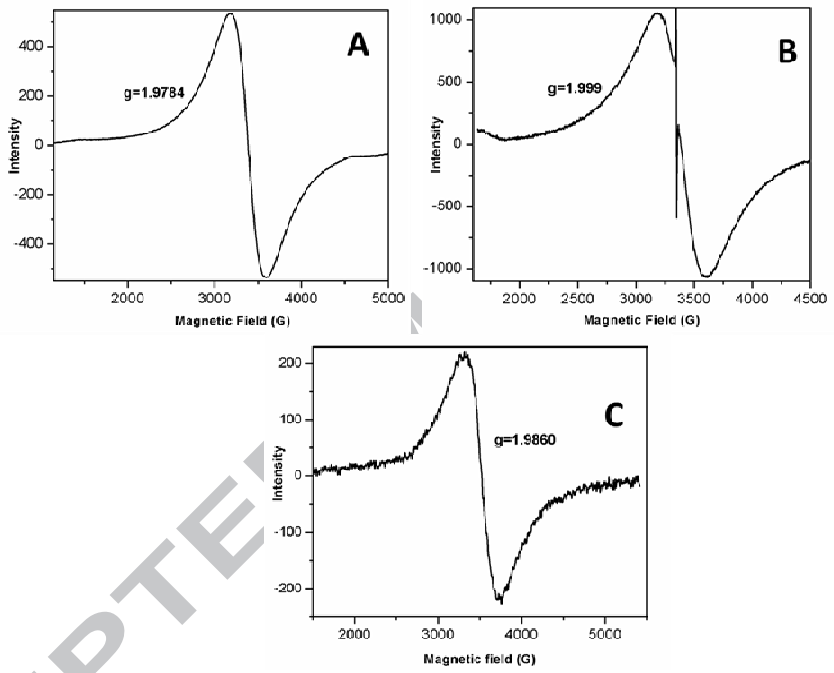


Fig-5: EPR spectra of Chromium Schiff base complexes (A) $[CrL^1(H_2O)_2]^+$; (B) $[CrL^3(H_2O)_2]^+$; (C) $[CrL^4(H_2O)_2]^+$.

3.6 Electrochemical studies of chromium complexes:

The electrochemical behavior of chromium(III) complexes were investigated in acetonitrile as solvent with TBAP as supporting electrolyte, at scan rate of 50 mVs^{-1}. The cyclic voltammogram of the chromium complexes show only reduction peak. The acyclic Schiff base ligands were also examined at the same condition it does not show any characteristic peaks. When we compare these voltammograms of ligands and complexes, the complexes only gives cathodic peaks, at the potential of -0.85 to -1.10 V, this clearly reveals that the reduction of Cr(III)/Cr(II) metal ion has occurred in the complexes. In the complexes CrL^1, CrL^4 and CrL^5 the voltammograms show an additional reduction peak at the potential range of -0.73 to -0.80 V, it may be due to the reduction of ligand center. From the cyclic voltammogram we conclude that all the chromium complexes were electrochemically active and show response in the potential range of 0.0 to −1.50 V vs Ag/AgCl. The reduction potential of the Cr(III)/Cr(II) is dependent on number of factors such as coordination number of the complex, bulkiness and hard/soft nature of the ligand [35, 36]. The corresponding cyclic voltammograms are shown in **Fig-6**.

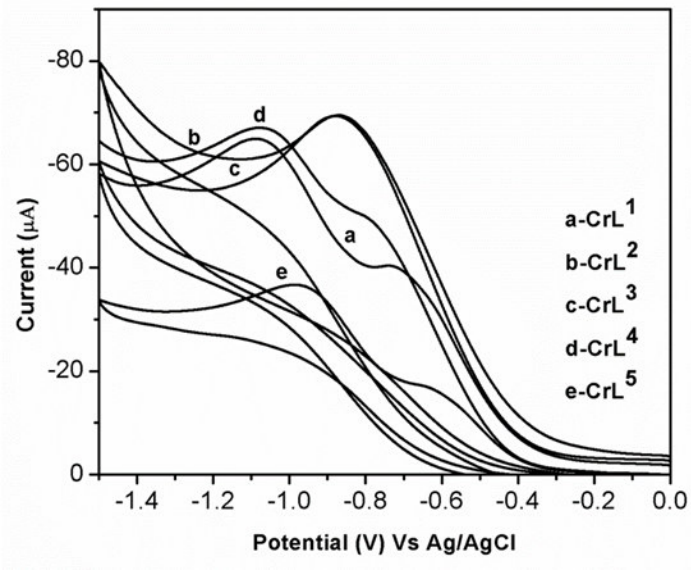


Fig-6: Cyclic voltammograms of chromium complexes in acetonitrile at the scan rate of 50 mVs^{-1}.

3.7 Antimicrobial activity:

The in-vitro antimicrobial activity of chromium Schiff base complexes were tested against the bacteria; Staphylococcus aureus (Gram positive), Escherichia coli (Gram negative) and Pseudomonas aeruginosa (gram negative) in agar medium. For the antimicrobial testing these complexes were dissolved in DMSO at the concentration of 5 mg/ml, 10 mg/ml, 50 mg/ml, 100 mg/ml and 500 mg/ml. In general procedure 50 mL of the agar was added to a petri dishes and it was allowed to solidify. The testing organism was spread evenly on the agar medium. These Petri dishes were incubated for 48 h at 30 ^{0}C. The pH range was maintained between 7.0 and 7.5. The result was observed, from the observation we conclude that the growth of microorganism were inhibited by the chromium complex solution the inhibition zones developed on the medium were measured. The antibacterial activity of the chromium complexes were determined by disc diffusion method. The inhibition values for chromium complexes are summarized in **Table-1-3**. From the study of antimicrobial activity we conclude that the $[CrL^3(OH_2)_2]^+$ has a weak activity against E. coli and P. aeruginosa. The $[CrL^5(OH_2)_2]^+$ has low inhibition activity for the S. aureus bacteria. The complex $[CrL^1(OH_2)_2]^+$ has better activity in contrast with $[CrL^3(OH_2)_2]^+$, especially against E. coli and P. aeruginosa bacteria. This activity varied due to the different ligand center in the chromium complexes. For the S. aureus $[CrL^1(OH_2)_2]^+$ has better activity in contrast with $[CrL^5(OH_2)_2]^+$. As the concentration of chromium complex increases it will increase the inhibition activity of bacterial growth. After these studies, we compare the inhibition activities of the chromium complexes with standard drug like ampicillin, its shows that the chromium complexes are not strong active antibacterial agents than the ampicillin. The lower antimicrobial activity of chromium complexes may be ascribed to the lower electronegativity and small radius of the central

metal ion [Cr(III)]. It shows that the higher electronegativity and large atomic radius will increase the activity, due to decrease in the effective positive charge on the metal complex [37].

Table- 1: Antimicrobial activity of the chromium complexes against E.coli

E.coli	Zone of inhibition (mm)				
Complexes	**5 mg/ml**	**10 mg/ml**	**50 mg/ml**	**100 mg/ml**	**500 mg/ml**
$[CrL^1]^+$	23 ± 0.4	27 ± 0.1	32 ± 0.2	36 ± 0.1	41 ± 0.4
$[CrL^2]^+$	20 ± 0.2	23 ± 0.2	25 ± 0.1	30 ± 0.2	34 ± 0.3
$[CrL^3]^+$	-	-	17 ± 0.3	21 ± 0.2	26 ± 0.2
$[CrL^4]^+$	20 ± 0.2	24 ± 0.1	27 ± 0.2	32 ± 0.1	36 ± 0.2
$[CrL^5]^+$	22 ± 0.2	25 ± 0.1	28 ± 0.1	30 ± 0.2	34 ± 0.2
SD	32 ± 0.3	38 ± 0.2	43 ± 0.4	49 ± 0.2	56 ± 0.5

SD- Ampicillin drug.

Table- 2: Antimicrobial activity of the chromium complexes against S. aureus

S. aureus	Zone of inhibition (mm)				
Complexes	**5 mg/ml**	**10 mg/ml**	**50 mg/ml**	**100 mg/ml**	**500 mg/ml**
$[CrL^1]^+$	26 ± 0.1	30 ± 0.2	34 ± 0.2	39 ± 0.1	45 ± 0.4
$[CrL^2]^+$	24 ± 0.3	26 ± 0.2	28 ± 0.1	34 ± 0.1	39 ± 0.2
$[CrL^3]^+$	15 ± 0.1	19 ± 0.1	24 ± 0.2	28 ± 0.2	30 ± 0.1
$[CrL^4]^+$	23 ± 0.3	28 ± 0.3	33 ± 0.1	36 ± 0.3	38 ± 0.3
$[CrL^5]^+$	-	-	18 ± 0.1	24 ± 0.3	29 ± 0.2
SD	32 ± 0.2	39 ± 0.3	46 ± 0.2	53 ± 0.2	61 ± 0.3

SD - Ampicillin drug.

Table- 3: Antimicrobial activity of the chromium complexes against P. aeruginosa

P. aeruginosa	Zone of inhibition (mm)				
Complexes	**5 mg/ml**	**10 mg/ml**	**50 mg/ml**	**100 mg/ml**	**500 mg/ml**
$[CrL^1]^+$	18 ± 0.2	21 ± 0.2	26 ± 0.3	30 ± 0.1	36 ± 0.4
$[CrL^2]^+$	16 ± 0.1	20 ± 0.3	24 ± 0.2	27 ± 0.2	33 ± 0.3
$[CrL^3]^+$	-	-	-	-	14 ± 0.1
$[CrL^4]^+$	-	19 ± 0.2	24 ± 0.2	27 ± 0.1	30 ± 0.2
$[CrL^5]^+$	-	-	-	18 ± 0.2	24 ± 0.2
SD	35 ± 0.3	42 ± 0.3	53 ± 0.5	61 ± 0.5	70 ± 0.5

SD- Ampicillin drug.

3.8 Electrochemical Sensing

3.8.1 Electrochemical behaviors of Catechol at Cr-SBC/GCE

A solution of 0.1mM of chromium Schiff base complexes was taken for the electropolymerization in the presence of TBAP as supporting electrolyte. Chromium Schiff base complexes were polymerized on the glassy carbon electrode surface. Polymerized chromium Schiff base complexes modified GCE (Cr-SBC/GCE) was used for the detection of catechol. Fig. 7 shows the electrochemical behaviors of 0.1 mM catechol (CT) at the bare GCE and chromium complex modified /GCE in 0.1 M PBS (pH = 7). It can be observed that at bare GCE, there is a broad redox peak with ΔE_P (159 mV for CT). This indicates that the electrochemical reaction of CT at bare GCE is irreversible. For complex modified/GCE the redox peak of CT is also found to be irreversible in nature. In addition, the redox peak current has increased by about three times compared with that observed at bare GCE. It is evident that the chromium Schiff base complexes (Cr-SBC) could be an effective electrocatalyst for the redox reaction of dihydroxyphenyl compounds. This electron transfer between the electrode and analyte is facilitated by the complex and is found to be a good electrocatalyst. The modified GCE has large surface area to interact with

the analyte and thereby it enhances the electrocatalytic activity [38]. All these five complexes $[CrL^2(H_2O)_2]^+$ show better activity for the sensing of catechol. The difference in the catalytic activity of all the complexes may be due to the ligand size and nature. We have found out that the less number of subituted ligand has more sensing ability towards catechol. From this work it clearly indicates that the Cr-SBC/GCE is favorable for determination of catechol.

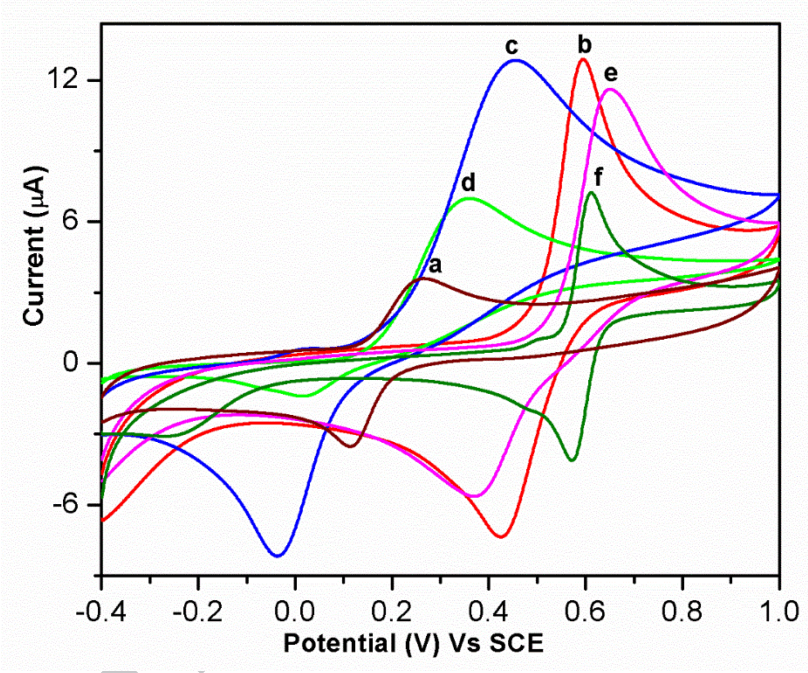


Fig-7: Cyclic voltammograms of (a) bare GCE, (b) $[CrL^1(H_2O)_2]^+$/GCE, (c) $[CrL^2(H_2O)_2]^+$ /GCE, (d) $[CrL^3(H_2O)_2]^+$/GCE, (e) $[CrL^4(H_2O)_2]^+$/GCE and (f) $[CrL^5(H_2O)_2]^+$/GCE in presence of 1×10^{-4} M CT at scan rate of 50 mV s^{-1}

3.8.2 Effect of scan rate

CVs of $[CrL^2(H_2O)_2]^+$/GCE were recorded at different scan rates in 0.1 M PBS (pH 7.0) containing of 0.1 CT. The CVs of $[CrL^2(H_2O)_2]^+$/GCE shows well-defined peaks, I_{pa} and I_{pc} increased with the increasing the scan rate from 10 to 500 mVs^{-1} (Fig - 8). The I_{pa} and I_{pc} of CT is directly proportional to the square root of the scan rate. Plots of the anodic or cathodic peak current for CT against the scan rate showed linear relationship over the range above with the regression

coefficient of 0.998 for I_{pa} & 0.997 for I_{pc}. It suggests that the redox reaction of CT is diffusion controlled. $I_{pa}(\mu A) = 0.7393\ v^{1/2}(mV\ s^{-1})^{1/2} - 0.3658$ ($R^2 = 0.998$),

$I_{pc}(\mu A) = -0.8738\ v^{1/2}(mV\ s^{-1})^{1/2} + 0.7264$ ($R^2 = 0.997$).

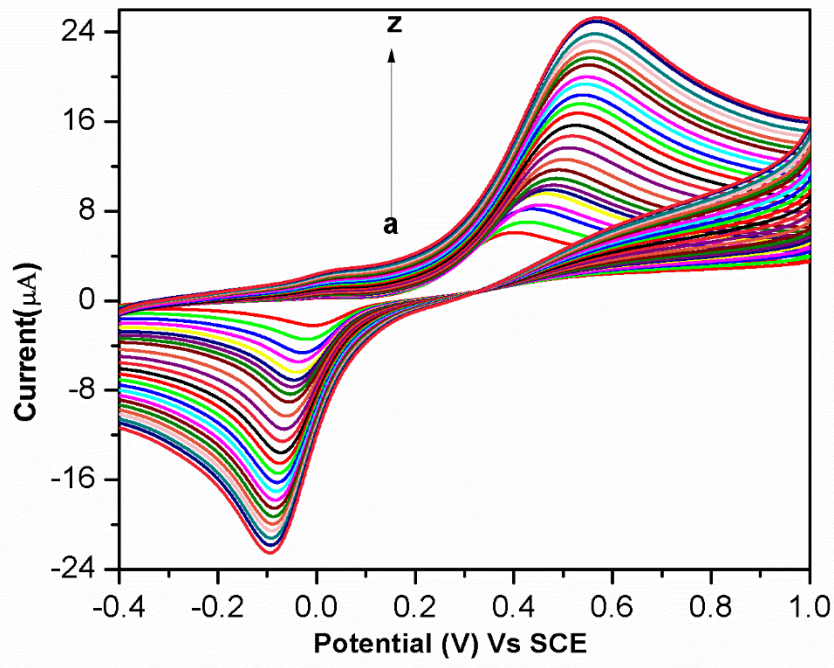
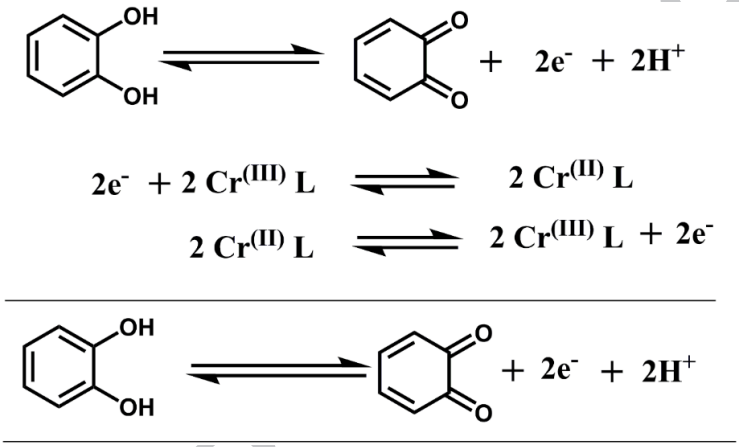


Fig-8: Cyclic voltammograms of $[CrL^2(H_2O)_2]^+$ /GCE in 1×10^{-4} M CT (pH 7.0) at the scan rate of (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, (h) 80, (i) 90, (j) 100, (k) 125, (l) 150, (m) 175, (n) 200, (o) 225, (p) 250, (q) 275, (r) 300, (s) 325, (t) 350, (u) 375, (v) 400, (w) 425, (x) 450, (y) 375 and (z) 500 mVs^{-1}.

3.8.3 Effect of pH for the electrochemical detection of CT

pH effect of the electrochemical behavior of 0.1 mM CT in 0.1 M PBS solution at $[CrL^2(H_2O)_2]^+$ /GCE was investigated by CV in a wide range of pH from 1 to 11, was shown in Fig. 9. From this we can found that the E_{pa} and E_{pc} values are negatively shifted with increase in the pH value. It shows that the E_{pa} and E_{pc} values of CT is inversely proportional to pH value. If we plot E_{pa} and E_{pc} vs pH we get the linear relationship with the regression coefficients R^2 0.998 and 0.999 respectively ($E_{pa} = 0.8276 + 0.067pH$ & $E_{pc} = 0.3828 - 0.055pH$). According to the

formula [39], $dE_p/dpH = 2.303mRT/nF$, in which, m and n are the number of proton and electron, respectively; the calculated proton and electron ratio m/n is 1.03 for CT redox reaction. It shows that the number of proton and electron involved in the redox process of CT is equal. In addition, to this the slopes of the regression equations are close to the theory value of 67.1 mV pH^{-1} for two electrons and two protons process [40]. The possible electrocatalytic reaction is shown in Scheme-3.



Scheme – 3: Electrocatalytic redox reaction of catechol (CT)

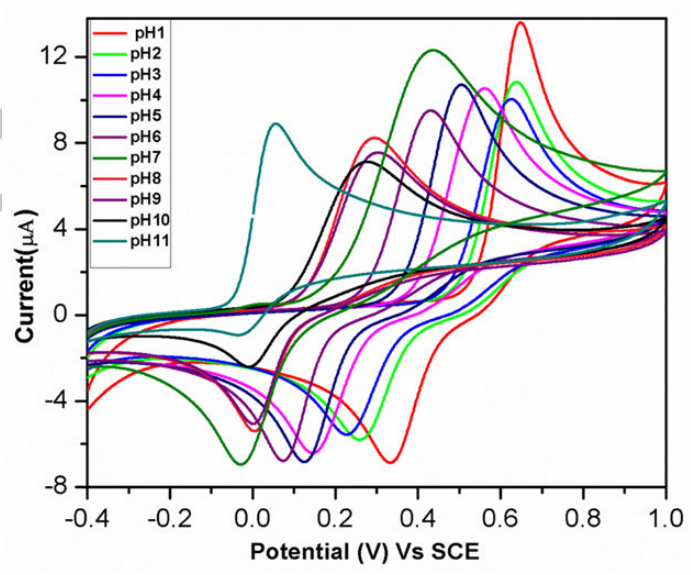


Fig – 9: CVs of 1×10^{-4} M CT in different pH value from 1 to 11 on $[CrL^2(H_2O)_2]^+$ /GCE.

3.8.4 Determination of catechol

Fabricated electrode was also evaluated for sensing of catechol quantitatively by chronoamperometric technique [41]. The chronoamperometry (CA) has higher sensitivity than CV, hence it was utilized for the determination of CT. In CA, each addition of 5 µL CT the current peak was increased that we observed in **Fig. 10.** A calibration graph of current against concentration gives a linear relationship in a range of 5 µL to 45 µL, with the R^2 value is 0.9986. $I(\mu A) = 0.2079 + 1.97\ C_{CT}$. It reveals that the concentration is proportional to the peak current (Ip). From the linear relation we can calculate the limit of detection by using the following equation [42].

$$\mathbf{LOD = 3\sigma / q}$$

Where, σ is the standard deviation and q is the slope of the calibration curve.

From the calculation we conclude that the Cr-L^2/GCE has a detection limit of 519 nM towards catechol, which clearly indicated us that this method is more sensitive for the catechol determination.

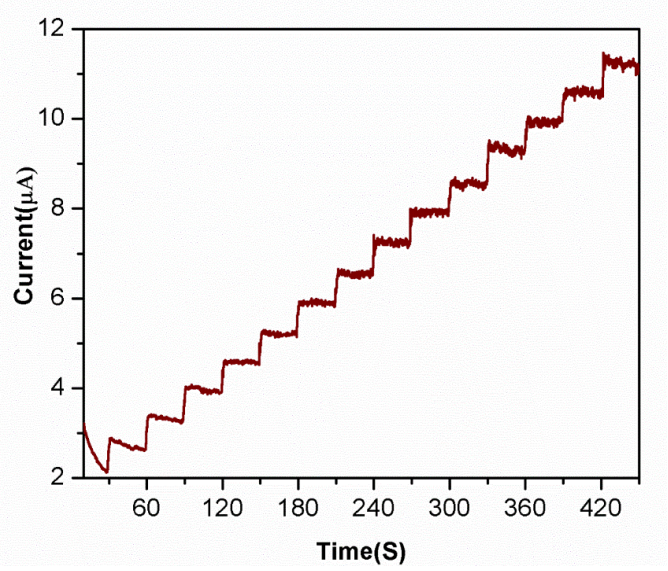


Fig - 10: Chronoamperometric responses of $[CrL^2(H_2O)_2]^+$/GCE for the successive additions of 5 µL of 1×10^{-4} M CT to 30 mL of 0.1 M PBS. Applied potential is 0.38 V.

4. Conclusion:

In this work, we have used a green synthesis method for the synthesis of all symmetrical tetradentate Schiff bases and their chromium(III) complexes. Microwave (MW) irradiation method is an efficient and environmentally friendly method to use for the various inorganic syntheses with higher yields in shorter reaction periods. The complexes were spectrally characterized and electrochemical redox behavior also tested. The geometry of the synthesized Cr(III) complexes have been proposed as octahedral based on the spectral studies. The biological activity of the Cr(III) complexes have been investigated. From the result we conclude that the complex $[CrL^{1}(OH_2)_2]^{+}$ has the better activity in contrast with $[CrL^{3}(OH_2)_2]^{+1}$. The synthesized Cr(III) complexes successfully was used for determination catechol. It gives good response for the electrochemical detection of phenolic compounds with high sensitivity. The Cr-SBC/GCE is a new platform for the detection of catechol by using Schiff base complexes. In this method we can detect at nanomolar level catechol.

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Highlights:

- Chromium (III) Schiff base complexes are synthesized by microwave irradiation method.
- Schiff base ligands formed chromium complexes through Cr-N and Cr-O bonds.
- Chromium (III) Schiff base complexes are characterized by various spectral techniques.
- Electrocatalytic sensing of catechol was investigated by the Chromium (III) Schiff base complex modified GCE.
- Chromium Schiff base complexes have good antibacterial activity.

Graphical abstract