



Complex Formation Capabilities of Pyrogallol Based Dipodal ligand MEP with trivalent metal ions: A Potentiometric and Spectrophotometric Investigation

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ABSTRACT

This research demonstrated and analyzed the complexation capabilities of the dipodal chelator N¹,N³-bis(2-((E)-2,3,4-trihydroxybenzylidene)amino)ethyl)malonamide (MEP) with heavy metal ions, viz., Al³⁺, Fe³⁺, and Cr³⁺, by engaging potentiometric and spectrophotometric methods. The whole experiment was carried out in a pH-dependent manner in a highly aqueous medium with a pH range of 2 to 11. The potentiometric and spectrophotometric results suggest the highest binding affinity of the chelator MEP with Al³⁺ metal ions among all three metal ions under study, with a stability constant value of log $\beta = 27.13$.

Keywords: Potentiometry, Association constant, Complexation, Spectrophotometric, Pyrogallol.

INTRODUCTION

During last few years, a lot of research's has been made by the scientific fraternity to precisely detect and quantify the concentration of various essential trace elements for human health (like Fe, Cu, Zn, etc.) and substantially toxic elements (Cd, Hg, and Pb)¹⁻³. In general, potentially harmful elements, are the ones that are present in a low amount but are responsible for being a major source of environmental contaminants⁴. Intoxication of metal ions from man-made and sometimes natural and

anthropogenic sources leads to their accumulation in the local environment, causing various health-related threats to humans and other animals⁵. Among, various trace elements, aluminum, iron, and chromium have the highest biological importance for the functioning of various metabolic pathways in humans⁶. On the other hand, these elements can pose significant risks to human health and ecosystems when present in excessive amounts⁷. Few reports suggest that the overconsumption of these elements can cause various related health issues, including neurological disorders, respiratory



problems, and the development of cancer⁸. It has been found that an excess amount of aluminium in the body can lead to various disorders like fibrosis, chronic renal failure, Alzheimer's and Parkinson's disease, bone malfunctioning, and respiratory trace dysfunction⁹⁻¹². Research has also shown that high aluminum concentrations can negatively impact both fish and algae, ultimately reducing harvest productivity^{13,14}.

To better understand the extent of their toxicity, it is essential to examine their specific properties, like routes to human exposure, toxic kinetics, general toxicity mechanisms, and potential regulatory measures¹⁵. The primary route of exposure to trivalent metal ions, such as aluminum, iron, and chromium, for the general population is usually through ingestion with food and water¹⁶. Further, secondary routes of exposure, such as inhalation, can occur through environmental contamination or occupational settings¹⁷. Therefore, it becomes crucial to first understand the potential toxicity of trivalent metal ions and develop effective strategies to mitigate their harmful effects on human health and the environment. Furthermore, accurate detection and quantification of trivalent metal ions in various matrices, such as water, soil, and biological samples, is vital for assessing their potential risks and implementing appropriate control measures.

In order to design molecular probes for the detection of these trace elements, understanding their chemical binding ability is of pivotal importance. For example, Al^{3+} has strong hydration capacity, and as a hard acid, it can show virtuous interactions with hard bases¹⁸. Further, in the last few years, it has been found that a lot of efforts have been made to tailor hard-base sites (i.e. nitrogen and oxygen) based sensors for enhanced detection of these trivalent metal ions¹⁹. Among all, organic compound-based molecular probes, Schiff-base may be the ideal coordinating sphere for the recognition of these trivalent metal ions.

Schiff bases, owing to their unique physicochemical properties, high binding ability, better stability, and ease of removal/purification tendency, have attracted numerous scientific interests for their potential application as molecular probes for the efficient detection of various metal ions²⁰⁻²². In medicine and pharma sectors, metal-

schiff base frameworks have been thoroughly investigated as powerful anticancer, antifungal, antibacterial, and antiviral drugs^{15,23,24}. Despite of their extraordinary properties, their hydrolysis and poor solubility in aqueous medium limit their efficacy for their potential application in the detection of various environmental and biological samples²⁵. Till date, the work is still in its early stages for the estimation of stability constants of that type of molecules in an aqueous solvent with a range of pH²⁶⁻²⁷. Therefore, it becomes imperative to design and analyze novel Schiff bases with greater solubility, better binding abilities, enhanced photo-physical characteristics, and stable coordination capabilities with metal ions.

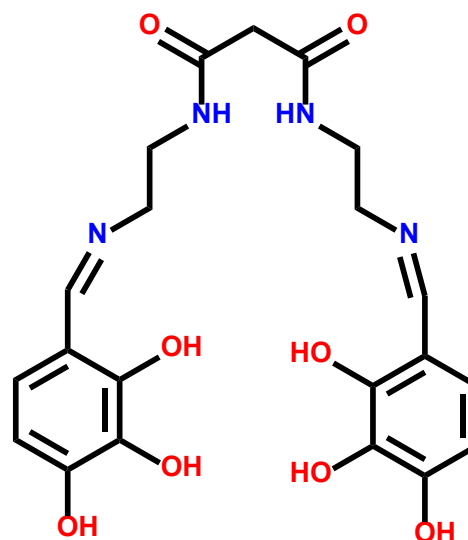


Fig. 1. Graphic illustration of the Chelator MEP

In the current study, we have demonstrated the complexation behavior of MEP (N^1,N^3 -bis(2-(2,3,4-trihydroxybenzylidene)amino)ethylmalonamide) as illustrated in Fig. 1 with trivalent metal ions viz. Al^{3+} , Fe^{3+} , and Cr^{3+} by employing potentiometric and spectrophotometric techniques. Further, so as to analyze the pH-responsive complexation behavior of ligand MEP, we have analyzed the binding abilities of ligand MEP in a pH range of 2-11 mimicking acidic, neutral and basic conditions. The results demonstrate the excellent complexation ability of ligand MEP with all trivalent metal ions, and specifically best for Al^{3+} with the highest formation constant value ($\log \beta = 27.11$) among all. The purpose of this work is to give a comparative experimental investigation of the formation constant and stability of chelate MEP

with (Al^{3+} , Fe^{3+} , and Cr^{3+}) metal ions. Further, this research provides the fundamental understanding needed to develop novel molecular probes for the recognition of (Al^{3+} , Fe^{3+} , and Cr^{3+}) metal ions present in different environmental, biotic, and industrial sources.

MATERIALS AND METHODS

DMSO was acquired from sigma aldrich, while metal salts were bought from Merck. Ultra-pure De-ionized water with an $18.2 \text{ M}\Omega\text{cm}^{-1}$ electrical resistivity was used to prepare the solutions. Due to DMSO's solubility, a 9:1 v/v water-DMSO mixture was prepared, and this solvent mixture was utilized in all pH titrations. Our group synthesized the chelator ligand MEP²⁸. An Evolution 201 UV-Vis spectrophotometer with a quartz cuvette manufactured by Thermo fisher was used for the spectrophotometric analysis. The Orion Star A111 pH meter (make Thermo Scientific) and the 8102BNUWP Ultra-Electrode (make Ross) were employed on all the pH titrations. Calibration was carried out all the instruments using buffer solutions in accordance with a predetermined process.

Potentiometric Measurements

In order to study the complexation ability of the MEP to form metal complexes, a double-walled titration flask at a temperature of 25°C , was used in all the pH titration studies. The pH titrations were carried out using an 8102BNUWP Ultra-Electrode (make Ross) and a pH meter. To achieve precise pH results, the electrode was calibrated using a well-established method²⁹⁻³⁰. To investigate the complex formation tendency of the synthesized ligand with Al^{3+} , Fe^{3+} , and Cr^{3+} , a 1:1 metal-ligand solution of 10^{-4} M concentration was titrated with 0.1M KOH. Based on calculated formation constants ($\log \beta$) of metal complexes, the prediction was made that different pH values would lead to the formation of different species. Analyzing data with Hyperquad 2008³¹, a software for curve fitting, the pH titration study (pH 2-11) were considered in order to find the equilibrium constants.

Spectrophotometric Measurements

For spectrophotometric titrations, the same protocols were followed as for potentiometric titrations. In this, a (9:1) water-DMSO solution

containing 10^{-4} M MEP and metal ions was acidified with 0.1 M HCl. Further, to maintain the ionic strength of the solution, KCl was used of molarity 0.1M. The final solution was titrated against a freshly made, standardized KOH (0.1 M) solution in the pH ranges of 2 to 11. To ensure consistent results, the temperature was held at 25°C during the experiment using a thermostat-controlled, glass-jacketed container. Stability constant values were then determined by analyzing the titration data points with HYPSPPEC software³².

Table 1: Comparative analysis of the of the ligand's (MEP) complexation behaviour against Al^{3+} , Fe^{3+} and Cr^{3+} metal ions; data shows the formation constant ($\log \beta$) values obtained using A = potentiometric and B = spectrophotometric techniques

Trivalent Ions	Reactions	Formation Constant ($\log \beta$)	
		A	B
Al^{3+}	$\text{Al} + \text{MEP} \rightleftharpoons \text{AlMEP}$	27.11	27.13 ± 0.02
	$\text{Al} + \text{MEPH}_2 \rightleftharpoons \text{AlMEPH}_2$	12.87	12.87 ± 0.00
Fe^{3+}	$\text{Fe} + \text{MEP} \rightleftharpoons \text{FeMEP}$	24.98	24.99 ± 0.01
	$\text{Fe} + \text{MEPH}_2 \rightleftharpoons \text{FeMEPH}_2$	13.50	13.49 ± 0.01
Cr^{3+}	$\text{Cr} + \text{MEP} \rightleftharpoons \text{CrMEP}$	26.18	26.20 ± 0.02
	$\text{Cr} + \text{MEPH}_2 \rightleftharpoons \text{CrMEPH}_2$	16.12	16.12 ± 0.00

RESULTS AND DISCUSSION

Co-ordination Behavior of MEP

In order to investigate the complexation ability of the MEP with the trivalent metal ions, viz., Al^{3+} , Cr^{3+} and Fe^{3+} , potentiometric, and UV-Visible spectroscopic titrations were conducted. Briefly, for analyzing the process through potentiometric titrations, metal ions, and ligand MEP were taken in a 1:1 molar ratio at $25 \pm 1^\circ\text{C}$. Further, KCl of molarity 0.1M, is employed to balance the strength of ions in the highly aqueous reaction medium consisting of water and DMSO in a 99:1 ratio. Fig. 2 demonstrates the potentiometric titration curve of MEP with the metal ions, viz., Al^{3+} , Fe^{3+} and Cr^{3+} respectively, in a varying pH range from 3-11. It was observed that, after attaining a pH > 10, turbidity appeared in the solution. The observation of turbidity can be inferred to the occurrence of hydrolysis of the ligand MEP and causing saturation in the potentiometric curves after pH >10. We included data points up to pH 10 for all calculations in this study.

Further, in order to hypothesize the formation of species during the complexation

reaction between metal ions and ligand MEP, calculations were performed for the ML, MLH₂, species where M = Al³⁺, Cr³⁺, and Fe³⁺, and the finest suitable model was attained and optimized. Additionally, the Hyperquad 2008 program was used to calculate the overall stability constants (log β) for each complex; the results are displayed in Table 1. Further, the results obtained about the species distribution and their overall stability constant formed in the solution were again re-evaluated for the ligand MEP, and additionally evaluated were the ligand MEP's interactions with the ions of trivalent metals through the spectrophotometric technique.

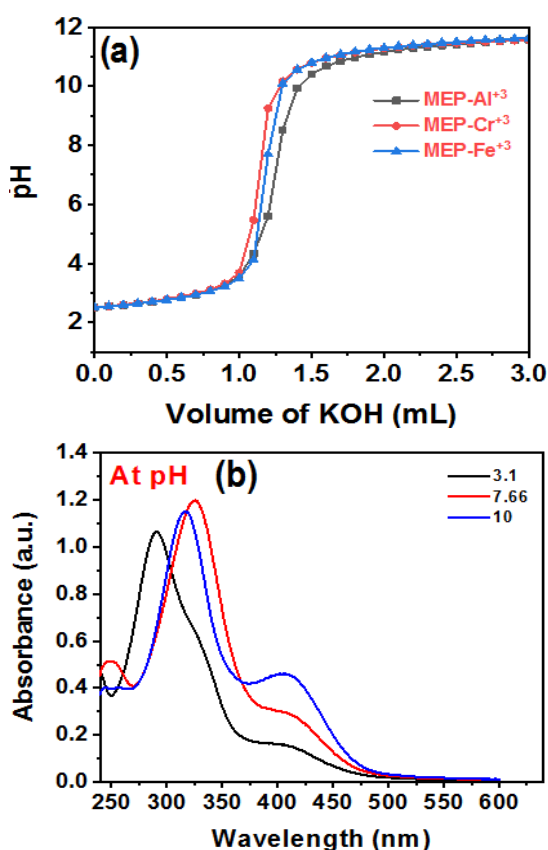


Fig. 2(a). pH titration of MEP in a range of pH environments (about 3–11) with trivalent metal ions (Al³⁺, Cr³⁺, and Fe³⁺); and b) Electronic spectral data of uncomplexed MEP in different pH range

Further, to analyze the binding ability of the dipodal MEP with Al³⁺, Cr³⁺, and Fe³⁺ metal ions spectrophotometric titrations were also carried out. Briefly, the ligand and metal ions were taken in a 1:1 ratio of concentrations, 10⁻⁴ M at temperature 25±1°C with cumulative pH ranging from 2–11, at the ionic strength of KCl, μ=0.1 M, respectively.

Fig. 2b presents the electronic spectral data for the uncomplexed ligand MEP at different pH viz., acidic, neutral and basic. Further, to analyze the complex formation tendency of ligand MEP, the spectrophotometric data for ligand MEP alone and with trivalent metal ions, viz. Al³⁺, Cr³⁺, and Fe³⁺, were compared. Fig. 3-5, reveals the appearance of the absorption spectra for ligand MEP complex with Al³⁺, Fe³⁺, and Cr³⁺ ions respectively, in varying pH ranges from 3-11, i.e., highly acidic to highly basic conditions. It was observed that in the pH ranges of 2-3, there is no variation in the electronic spectra of uncomplexed ligand MEP and that of the complexes. Further, after increasing pH, the electronic spectra of metal complexes followed distinct behavior for each metal ion, indicating the differential ability of ligand MEP to form complex with each metal ions. The complexation can be inferred from the appearance of a spectrum with changing UV-Vis wavelengths and the comparison of the ε value for free MEP and MEP-M³⁺ complex.

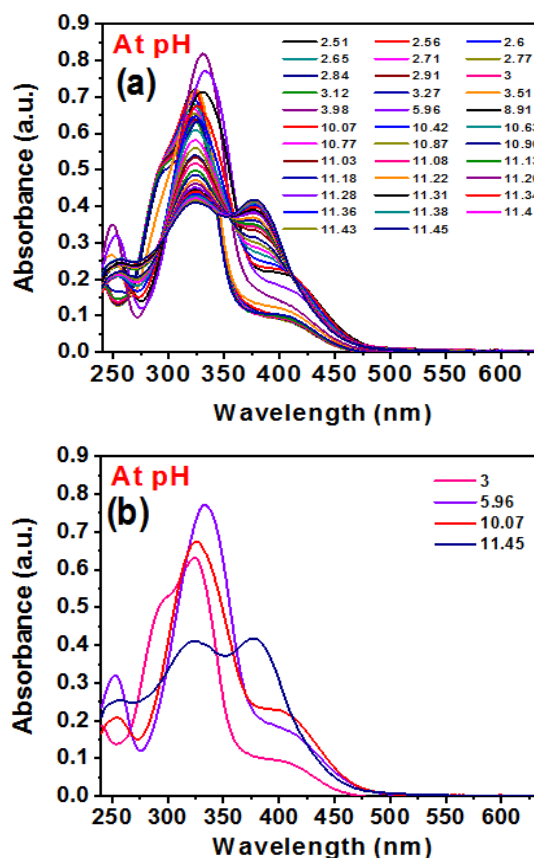


Fig. 3. Experimental electronic spectral titration of MEP with Al³⁺ metal ions in a varying pH range: a) Electronic spectra of MEP with Al³⁺ in a medium of pH (2.61–11.45), b) Electronic spectral data of MEP with Al³⁺ at selective pH (3, 5.96, 10.07 and 11.45)

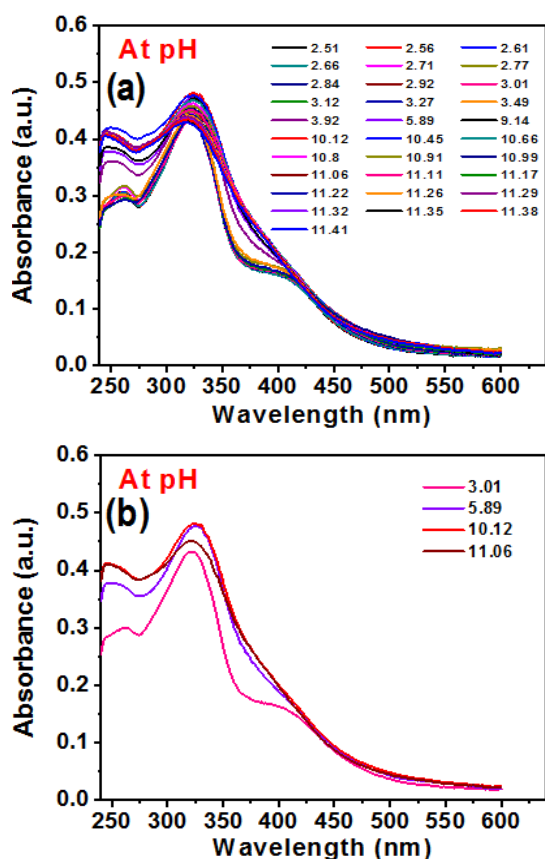


Fig. 4. Experimental electronic spectral titration of MEP with Fe^{3+} metal ion in a varying pH range: a) Electronic spectra of MEP with Fe^{3+} in a medium of pH (2.61–11.41), b) Electronic spectral data of MEP with Fe^{3+} at selective pH (3.01, 5.89, 10.12 and 11.06)

Moreover, the emergence of isosbestic spots in the spectrum suggests that the phase of equilibrium between the hydrogenated and dehydrogenated edifices of the ligand is tangled. But at pH greater than 3, a single, strong band with a high intensity at about 323 nm was visible for all of the metal complexes, demonstrating a simultaneous increase in strength with each subsequent pH rise. For example, in the case of the MEP- Al^{3+} , UV-Vis bands for the compound show a peak at $\lambda = 294.47$ nm ($\epsilon = 0.52 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$) corresponding to $\pi \rightarrow \pi^*$ electronic movement, shifting towards shorter wavelengths with a decrease in the intensity to $\lambda = 252.56$ nm ($\epsilon = 0.32 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$), an absorbance appeared at wavelength 324.14 nm ($\epsilon = 0.63 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$) corresponding $n \rightarrow \pi^*$ electronic movement, experienced shorter wavelengths and higher intensity to $\lambda = 333.18$ nm ($\epsilon = 0.77 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$) and another absorbance

appeared at wavelength 396.52 nm ($\epsilon = 0.23 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$) corresponding to charge transfer band experienced a decrease in the intensity with a trend towards higher wavelength i.e., at $\lambda = 400.84$ nm ($\epsilon = 0.185 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$) on varying pH of the solution towards neutral medium from acidic. However, when we vary the pH towards basic from neutral, UV-Vis bands of the complex at wavelength 252.56 nm ($\epsilon = 0.32 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$) corresponding to $\pi \rightarrow \pi^*$ electronic movement, show a decrease in the wavelength along with decrease in the intensity to $\lambda = 254.72$ nm ($\epsilon = 0.21 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$), absorbance appeared at wavelength 333.18 nm ($\epsilon = 0.77 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$) corresponding $n \rightarrow \pi^*$ electronic movement further shows similar variations to wavelength 325.26 nm ($\epsilon = 0.68 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$) and another absorbance at wavelength 400.84 nm ($\epsilon = 0.185 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$) corresponding to charge transfer band shows slight decrease in wavelength with an increase in the intensity to wavelength 397.16 nm ($\epsilon = 0.23 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$) correspondingly.

Furthermore, as Fig. 2b illustrates, the molar absorptivity coefficient for free ligand MEP at wavelength 291.10 nm ($\epsilon = 1.06 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$) was observed to drop suddenly when metal ions were present. This sudden drop in the molar absorptivity coefficient can be explained by the possible low absorption, which is being seen as a result of the complexation of the free ligand MEP with trivalent ions. Similar variations were also seen in the MEP ligand's absorption spectra when other two trivalent ions, such as Fe^{3+} and Cr^{3+} , were present. Table 2 shows these changes in variations of pH, indicating the related modes of complexation. While at 400nm a band is also seen in the Al^{3+} and Cr^{3+} complexes due to charge transfer, there is no extra band identified in the Fe^{3+} complex at higher wavelengths.

In order to calculate the formation constants for the MEP- M^{3+} ($\text{M} = \text{Al}^{3+}, \text{Cr}^{3+}$ and Fe^{3+}) complexes using the spectrophotometric approach, the HypSpec program was employed. Different possibilities for the formation of species were examined, and specifically, ML and MLH_2 species for Cr^{3+} , Al^{3+} , and Fe^{3+} were considered for the calculation, and found to be the best fit for the proposed model of the study. Table 1 presents the formation constants that were estimated for each species. After the careful analysis of the coordination ability of the dipodal (MEP), we found that it has shown

excellent binding efficacy with (Al^{3+} , Cr^{3+} and Fe^{3+}) metal ions in the current research. Further, there is a clear dependency on the pH of the solution, for the formation of dominating species, viz., neutral MEP-M^{3+}

complexes and protonated complexes (M-MEP-H_n) at varying pH levels. Among all MEP-M^{3+} complexes, the MEP-Al^{3+} complex has shown the highest formation constant i.e., $\text{Log } \beta = 27.11$.

Table 2: A comparison between the values of the molar absorptivity coefficient (ϵ) and the absorption wavelength for all chemical species, including free ligands MEP, MEP-Al^{3+} complex, MEP-Cr^{3+} complex, and MEP-Fe^{3+} complexes in different mediums

S. No	Molecules	pH 2-3	pH 6-7	pH 9-10
1	Free ligand MEP	$\lambda_1 = 291.10 \text{ nm}$; $\epsilon = 1.06 \times 10^4$ $\lambda_2 = 402.92 \text{ nm}$; $\epsilon = 0.16 \times 10^4$	$\lambda_1 = 248.24 \text{ nm}$; $\epsilon = 0.51 \times 10^4$ $\lambda_2 = 325.42 \text{ nm}$; $\epsilon = 1.20 \times 10^4$ $\lambda_3 = 403.64 \text{ nm}$; $\epsilon = 0.31 \times 10^4$	$\lambda_1 = 316.46 \text{ nm}$; $\epsilon = 1.15 \times 10^4$ $\lambda_2 = 391 \text{ nm}$; $\epsilon = 0.84 \times 10^4$
2	MEP-Al^{3+}	$\lambda_1 = 294.47 \text{ nm}$; $\epsilon = 0.52 \times 10^4$ $\lambda_2 = 324.14 \text{ nm}$; $\epsilon = 0.63 \times 10^4$ $\lambda_3 = 396.52 \text{ nm}$; $\epsilon = 0.23 \times 10^4$	$\lambda_1 = 252.56 \text{ nm}$; $\epsilon = 0.32 \times 10^4$ $\lambda_2 = 333.18 \text{ nm}$; $\epsilon = 0.77 \times 10^4$ $\lambda_3 = 400.84 \text{ nm}$; $\epsilon = 0.185 \times 10^4$	$\lambda_1 = 254.72 \text{ nm}$; $\epsilon = 0.21 \times 10^4$ $\lambda_2 = 325.26 \text{ nm}$; $\epsilon = 0.68 \times 10^4$ $\lambda_3 = 397.16 \text{ nm}$; $\epsilon = 0.23 \times 10^4$
3	MEP-Cr^{3+}	$\lambda_1 = 293.75 \text{ nm}$; $\epsilon = 0.43 \times 10^4$ $\lambda_2 = 321.66 \text{ nm}$; $\epsilon = 0.38 \times 10^4$ $\lambda_3 = 394.69 \text{ nm}$; $\epsilon = 0.098 \times 10^4$	$\lambda_1 = 251.84 \text{ nm}$; $\epsilon = 0.22 \times 10^4$ $\lambda_2 = 320.54 \text{ nm}$; $\epsilon = 0.52 \times 10^4$ $\lambda_3 = 395.01 \text{ nm}$; $\epsilon = 0.195 \times 10^4$	$\lambda_1 = 250 \text{ nm}$; $\epsilon = 0.23 \times 10^4$ $\lambda_2 = 319.82 \text{ nm}$; $\epsilon = 0.48 \times 10^4$ $\lambda_3 = 389.97 \text{ nm}$; $\epsilon = 0.21 \times 10^4$
4	MEP-Fe^{3+}	$\lambda_1 = 261.27 \text{ nm}$; $\epsilon = 0.30 \times 10^4$ $\lambda_2 = 321.98 \text{ nm}$; $\epsilon = 0.43 \times 10^4$ $\lambda_3 = 392.13 \text{ nm}$; $\epsilon = 0.17 \times 10^4$	$\lambda_1 = 249.68 \text{ nm}$; $\epsilon = 0.38 \times 10^4$ $\lambda_2 = 324.86 \text{ nm}$; $\epsilon = 0.48 \times 10^4$	$\lambda_1 = 245.36 \text{ nm}$; $\epsilon = 0.41 \times 10^4$ $\lambda_2 = 323.42 \text{ nm}$; $\epsilon = 0.48 \times 10^4$

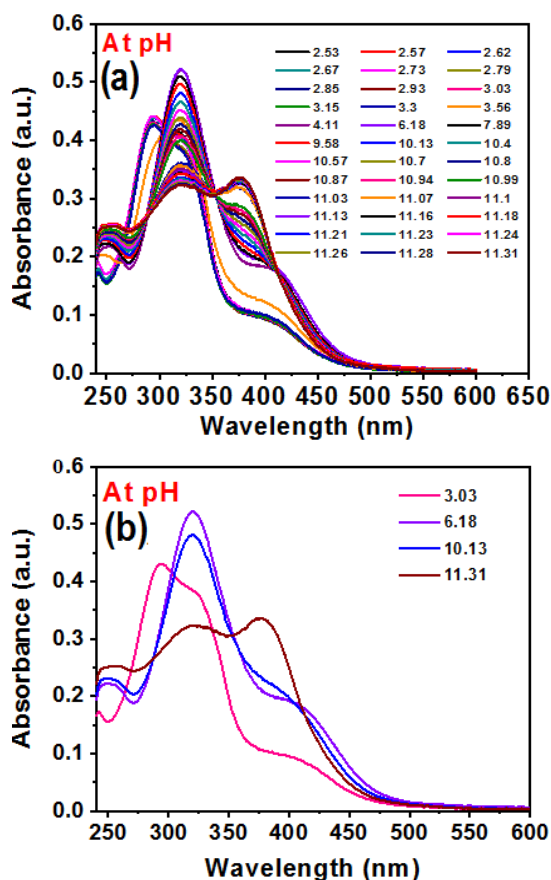


Fig. 5. Experimental electronic spectral titration of MEP with Cr^{3+} metal ion in a varying pH range: a) Electronic absorbance spectrum of ligand MEP with Cr^{3+} in medium of a pH ranges of 2.53–11.31, b) Electronic spectral data of MEP with Cr^{3+} at selective pH (3.03, 6.18, 10.13 and 11.31)

CONCLUSION

Using potentiometric and spectrophotometric techniques, the coordination ability of the dipodal (MEP) in a 1:1 molar ratio with the trivalent ions (Al^{3+} , Cr^{3+} , and Fe^{3+}) within a pH range of 2–11 was examined in solution. It was found that the metal ions were binding through the nitrogen (imine linkage) and the oxygens of the pyrogallol binding sites present in the ligand MEP to form M^{3+} -MEP and M-MEP-H_n kinds of complexes. The ligand MEP has shown remarkable binding efficiency with all studied metal ions. In a highly acidic medium, hydrogenated complex species are predominant in the ligand. Among all the complexes formed, the ligand MEP exhibits the highest formation constant value, i.e. $\text{log } \beta = 27.11$ for Al^{3+} metal ions. The aforementioned investigations examined the dipodal chelator MEP's exceptional coordination capabilities with trivalent metal ions and provided the basis for their possible use in various industrial, biological, and environmental applications like chelation therapy, sequestering agents, and environmental challenges.

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Conflict of Interest

Regarding financial and relationships to organisations, none of the authors have any conflicts of interest.

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