



## A pH Responsive and Selective Complex Formation Analysis of Catechol based Dipodal Chelator ligand N1,N3-bis(2-(((Z)-2,3-dihydroxybenzylidene)amino)ethyl) Malonamide with Trivalent Metal Ions

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### ABSTRACT

In the present study, we have explored the binding abilities of powerful dipodal chelator ligand N1,N3-bis(2-(((Z)-2,3-dihydroxybenzylidene)amino)ethyl)malonamide (MEC) to trivalent metal ions. We have investigated the coordination behavior of the dipodal ligand MEC with the trivalent metal ions Al<sup>3+</sup>, Fe<sup>3+</sup>, and Cr<sup>3+</sup> in aqueous media ranging from pH 2 to 11, employing potentiometry and spectrophotometry techniques. Results shows the higher binding ability of Cr<sup>3+</sup> metal ion among all metal ions with largest formation constant value, log  $\beta = 28.56$ .

**Keywords:** Stability constant, Chelate, Formation constant, Spectrophotometry, Binding affinity, Schiff's base.

### INTRODUCTION

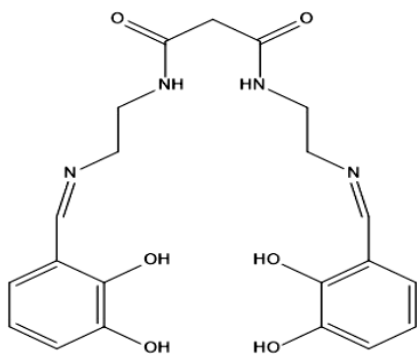
From the past few decades, synthesis of novel molecular systems for detection of metal ions from transition and post-transition series have attracted numerous scientific interest to study and analyze the various biological and environmental processes<sup>1-3</sup>. Among all elements, few trivalent metal ions like Cr<sup>3+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> are

of great importance and have found numerous applications. The role of Cr<sup>3+</sup> in the metabolism of biological active components like carbohydrates, lipids, fats, various proteins, and several essential nucleic acids makes its quite important and a vital component in a balanced diet for both humans and animals<sup>4-8</sup>. In has also been found in several studies that Cr<sup>3+</sup> deficiencies can severely affect the lipid metabolism which can further leads to abnormal



diabetic levels<sup>9,10</sup>. On the other hand, excessive Cr<sup>3+</sup> consumption can cause toxicity to cellular level and may hugely affect the basic cellular structure<sup>11,12</sup>.

Additionally, chromium is employed in various industrial operations like electroplating, preparing chromate, tanning leather, and metal polishing. Due to excessive application and poor disposal strategies of trivalent metal ions in industrial and agricultural sector, they have emerged as a chief source of environmental pollutants. Among all trivalent metal ions, Cr<sup>3+</sup> cause severe toxicity to environment even at very low concentrations<sup>13</sup>. Therefore, it becomes imperative to selectively detect Cr<sup>3+</sup> ions in biological and environmental samples at lower concentration levels with high precision. Recently, a lot of efforts have been made to fabricate devices made of novel molecular systems for precise detection of trivalent metal ions in biological and environmental spheres.



**Fig. 1. Schematic representation of the dipodal chelator ligand N1, N3-bis(2-(((Z)-2,3-dihydroxybenzylidene)amino)ethyl) malonamide**

Schiff bases owing to their capabilities to selectively combine with metal ions to form stable complexes as well as their high reaction potential with particular metal ions have emerged as potential molecular systems for detections of metal ions in biological systems. They can be used for developing synthetic enzymes as well as for potentiometric detection of homogeneous and heterogeneous processes such as those involving polymers, colors, and chemical framework<sup>14</sup>. Edifices of metal ions with Schiff bases have been extensively studied as potent antiviral, anticancer, antibacterial, and antifungal agents in medicine and pharmaceuticals<sup>15-17</sup>. Due to their insoluble nature and hydrolysis in a water medium, very little work has been done to determine the formation constants of these frameworks in a

solution. There is still plenty of room to synthesize novel Schiff bases that exhibit more promising binding capabilities, photo physical properties, and beneficial coordination conduct with metal ions of organic relevance. This can be accomplished by modelling and improving the stability of their binding domains. One of the strategies is the proton exchange between hydroxyl oxygen and imine nitrogen in excited states, which, depending on the dissolvable pH and extremity, can result in either an enol-imine form or a keto-amine form<sup>18</sup>.

In light of the aforementioned perspective, the current work examined the behavior of MEC (as shown in Fig. 1) in terms of coordination with the trivalent metal ions Al<sup>3+</sup>, Fe<sup>3+</sup>, and Cr<sup>3+</sup> in a series of pH variation broadly in acidic, neutral and basic conditions. This study aims to provide the comparative experimental analysis of stability and formation constant of ligand MEC with trivalent ions and this study will provide the basis for application of ligand MEC for precise extraction of these metal ions from various environmental and industrial sources.

## MATERIALS AND METHODS

Metal salts were purchased from CDH and Rankem, and DMSO was bought from Loba Chemie. Solutions were prepared employing ultrapure milliQ water with a resistivity of 18.2 milli ohm cm<sup>-1</sup>. Due to DMSO's solubility, all potentiometric titrations were conducted in a 9:1 v/v mixture of water and DMSO. Dipodal chelator ligand MEC was procured from NanoZest Incorporation, India. Spectrophotometric analysis was carried out utilizing a quartz cuvette and an ThermoScientific company made Evolution 201 UV-Vis spectrophotometer. Further, Thermo Scientific made pH meter model: Orion Star A111 and Ross made Ultra-Electrode Model: 8102BNUWP were used for the potentiometric titrations, and both instruments were calibrated according to a set procedure using buffer solutions.

### Potentiometric Measurements: Determination of Protonation and Formation Constants

In order to investigate the synthesis of metal complexes and their respective formation constants, potentiometric titration analysis was carried out at 25°C by using a double-walled titration flask. Further, the pH titration analysis was performed using a pH meter and Ross Ultra combination pH electrode. To

correctly and precisely read the pH, the electrode calibration was carried out using the traditional method. Briefly, the complex formation capabilities of metal–ligand complex is studied by titrating a 1:1 metal–ligand solution of  $1 \times 10^{-4}$  M against 0.1 M KOH, for each set of synthesized ligand with  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Cr}^{3+}$ . Further, the value of formation constants ( $\log\beta$ ) for each of metal–ligand complexes were calculated, and distinct species that formed at various pH values were anticipated. To determine the equilibrium constants, the titration data between pH range 2–11 were refined using the non-linear least square refinement programme Hyperquad 2006<sup>19</sup>.

### Spectrophotometric measurements

Similar procedures to those used for potentiometric titrations were used for spectrophotometric titrations. These titrations involved adding 0.1 M HCl to an  $\text{H}_2\text{O}$ : DMSO (9:1, v/v) solution containing ligand and metal ions ( $1 \times 10^{-4}$  M) to make it more acidic, and 0.1 M KCl to keep the ionic concentration/strength constant. The final product was titrated in a pH range of 2 to 11 against a freshly prepared, standardized KOH solution of 0.1 M. A thermostat glass jacketed jar was utilized to keep the temperature in the spectrophotometric titrations at 25°C throughout the experiment. The values of binding constants were calculated employing HYPSPPEC software by analyzing the titration data points<sup>20</sup>.

**Table 1: Equilibrium reactions and stability constants ( $\log\beta$ ) of the ligand MEC with metal ions  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  respectively, (where A stands for potentiometric titration values and B stands for spectrophotometric analysis)**

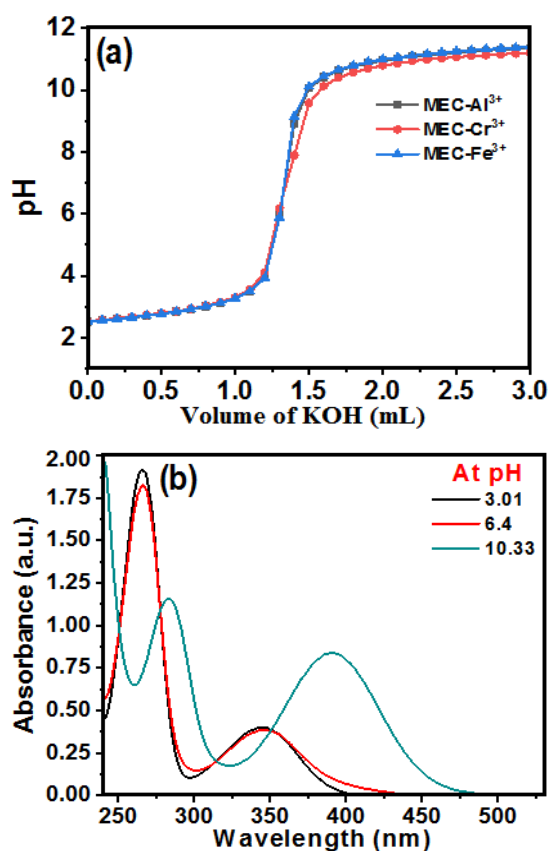
Metal Ions	Equilibrium	Log $\beta$	
		A	B
Al(III)	$\text{Al}+\text{L} \rightleftharpoons \text{AL}$	24.62	$24.62 \pm 0.01$
	$\text{Al}+\text{LH}_2 \rightleftharpoons \text{ALH}_2$	13.93	$13.90 \pm 0.03$
Fe(III)	$\text{Fe}+\text{L} \rightleftharpoons \text{FeL}$	24.99	$24.99 \pm 0.02$
	$\text{Fe}+\text{LH}_2 \rightleftharpoons \text{FeLH}_2$	15.34	$15.34 \pm 0.00$
Cr(III)	$\text{Cr}+\text{L} \rightleftharpoons \text{CrL}$	28.56	$28.55 \pm 0.01$
	$\text{Cr}+\text{LH}_2 \rightleftharpoons \text{CrLH}_2$	14.65	$14.65 \pm 0.01$

## RESULTS AND DISCUSSION

### Complexation Behavior Analysis of Ligand MEC

By using potentiometric and spectrophotometric titrations, the complex formation capabilities of the ligand MEC with trivalent transition metal ions  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Fe}^{3+}$  were examined in order to access their respective coordination properties.

Fig. 2a, demonstrates the potentiometric titrations performed in a highly aqueous media (99:1 water: DMSO mixture) at  $\mu = 0.1$  M KCl and  $25 \pm 1^\circ\text{C}$  in 1:1 metal–ligand molar ratios. The appearance of saturation in the potentiometric curves reveals the occurrence of hydrolysis and in response to hydrolysis, turbidity was developed in the solution after attaining  $\text{pH} > 10$ . As a result, in order to neglect the hydrolysis behavior after pH 10, all the calculations were carried out using data points up to pH10. Further, based on the calculations for the species  $\text{ML}$ ,  $\text{MLH}_2$ , species for  $\text{M} = \text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Fe}^{3+}$ , the best fit model was acquired and optimized. In addition, the calculations for overall stability constants ( $\log\beta$ ) for all the complexes were carried out using the Hyperquad 2008 program and results are shown in Table 1. The ligand and its interactions with the trivalent metal ions were also assessed spectrophotometrically in order to provide additional support for the different species that were produced in the solution.



**Fig. 2(a).** Potentiometric titration of ligand MEC with trivalent metal ions in varying pH media ranging from approximately 3–11 and (b) Absorption spectra of free ligand MEC in acidic, neutral and basic pH range

In order to access the coordination behavior of the ligand MEC with trivalent metal ions viz.  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Fe}^{3+}$  spectrophotometric titration technique was employed for confirmation of the possible complex formation in the solution. The titrations were performed in 1:1 M-L,  $[\text{L}]=[\text{M}]=1 \times 10^{-4}$  M with increasing pH ranging from 2 to 11, at  $\mu = 0.1$  M potassium chloride (KCl) and Temperature =  $25 \pm 1^\circ\text{C}$ . The electronic absorption spectra show no change in the range of pH 2-3, this pattern of electronic spectra remains same with the trivalent metal ions as shown by the ligand MEC alone. Fig. 3 to 5 reveals the appearance of absorption spectra with varying  $\lambda_{\text{max}}$  at different pH ranging from 3 to 11. The appearance of spectra with varying absorption wavelength and the comparative analysis of value for free ligand MEC and MEC-metal ion complex can be inferred for the formation of metal complexes.

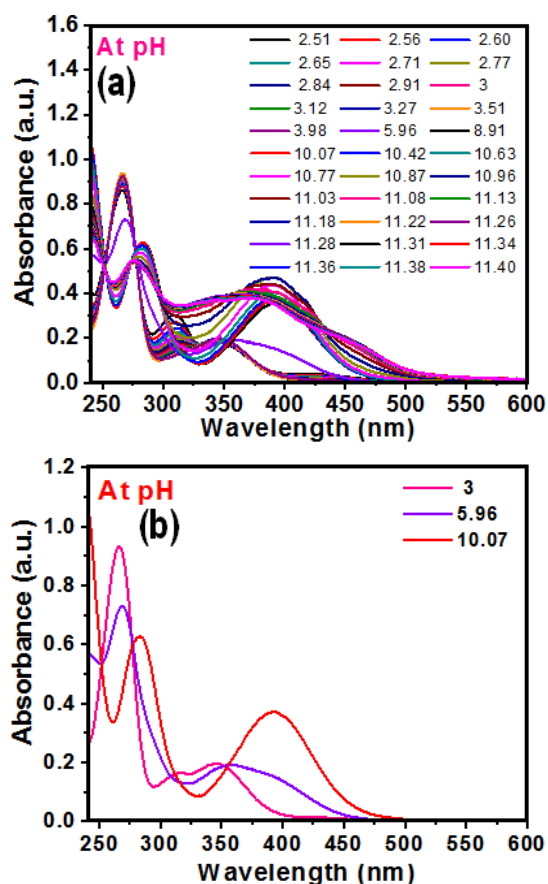


Fig. 3. Experimental absorption spectra of ligand MEC with variation in pH with  $\text{Al}^{3+}$ : a) Absorption spectra of ligand MEC with  $\text{Al}^{3+}$  in medium of pH ranging from 2.51–11.40, (b) selective representation of absorption spectra of ligand MEC with  $\text{Al}^{3+}$  in acidic, neutral and basic medium

Further, the appearance of turbidity after  $\text{pH} > 10$  reveals the occurrence of hydrolysis in the metal-ligand system. As a result, the data points for metal-ligand titrations were not taken into consideration for calculation after  $\text{pH} > 10$ . Furthermore, the formation of isosbestic points in the spectra can be referred to the state of equilibrium between the protonated and deprotonated structures of ligand. However, at above 3 pH, one prominent band appeared at  $\sim 266\text{nm}$  with high intensity with all the metal complexes which showed, a concomitant rise in the intensity with successive increase of pH. For instance, in case of MEC- $\text{Cr}^{3+}$  complex, absorption spectra of the complex shows a band at  $\lambda = 265.9\text{nm}$  ( $\epsilon = 0.98 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$ ) corresponding to  $\pi \rightarrow \pi^*$  transition showed a bathochromic effect to  $\lambda = 282.47\text{nm}$  ( $\epsilon = 0.63 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$ ), band at  $\lambda = 344.69\text{nm}$  ( $\epsilon = 0.21 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$ ) corresponding  $n \rightarrow \pi^*$  transition experienced a red shift to  $\lambda = 391.4\text{nm}$  ( $\epsilon = 0.418 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$ ) on changing pH of the solution from acidic to neutral whereas, on changing pH from neutral to basic, appearance of band for the ligand at  $\lambda = 282.47\text{nm}$  ( $\epsilon = 0.63 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$ ) corresponding to  $\pi \rightarrow \pi^*$  transition showed a hypsochromic effect to  $\lambda = 275.59\text{nm}$  ( $\epsilon = 0.51 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$ ), band at  $\lambda = 391.4\text{nm}$  ( $\epsilon = 0.418 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$ ) corresponding  $n \rightarrow \pi^*$  transition experienced a blue shift to  $\lambda = 344\text{nm}$  ( $\epsilon = 0.386 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$ ) respectively.

Further, it can be seen that the value of  $\epsilon$  for free ligand MEC at  $\lambda = 265.9\text{nm}$  ( $\epsilon = 1.92 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$ ) as shown in Fig. 2b and that of with metal ions, a sudden drop in the value of  $\epsilon$  was observed. This impulsive fall in the  $\epsilon$ , can be inferred to the quenching of absorption being observed due to complexation of free MEC with metal ions. Similar nature of changes were also observed in the absorption spectrum of MEC ligand in the presence of other trivalent ions viz  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  as depicted from Table 2, acidic to neutral and neutral to basic, pH range signifying corresponding mode of complexation. Though, there is no additional band occurs at higher wavelength in  $\text{Cr}^{3+}$  complex, whereas, in  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  complexes a charge transfer band is also observed above  $400\text{nm}$ .

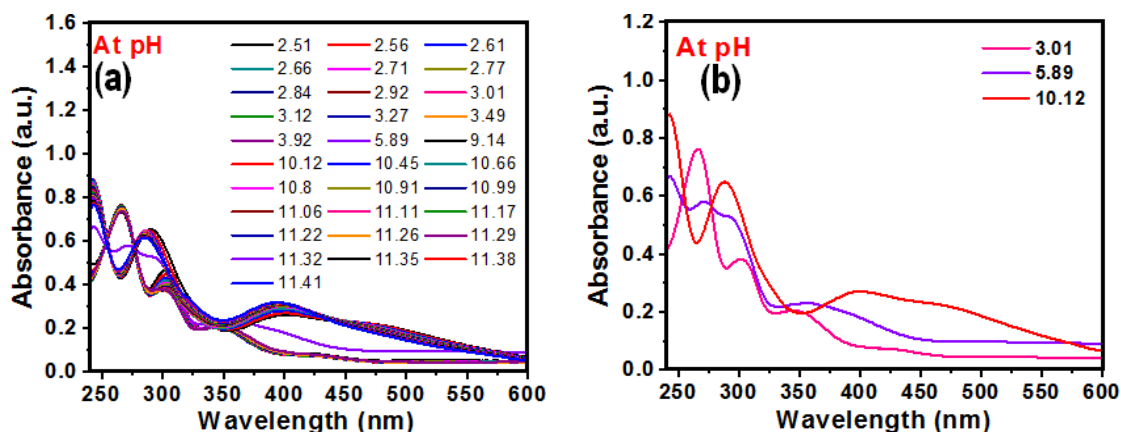


Fig. 4. Experimental absorption spectra of ligand MEC with variation in pH with  $\text{Fe}^{3+}$  metal ion+: a) Absorption spectra of ligand MEC with  $\text{Fe}^{3+}$  in medium of pH ranging from 2.51–11.41, b) selective representation of absorption spectra of ligand MEC with  $\text{Fe}^{3+}$  in acidic, neutral and basic medium

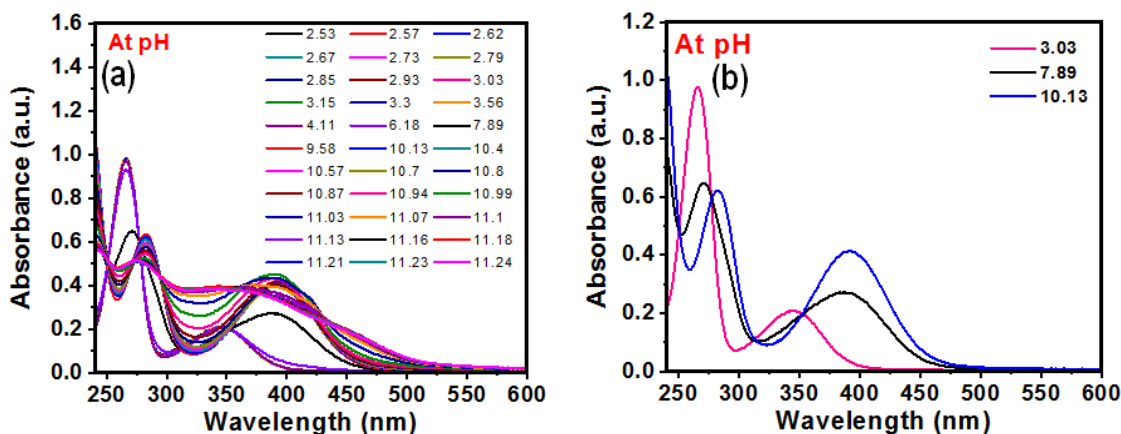


Fig. 5. Experimental absorption spectra of ligand MEC with variation in pH with  $\text{Cr}^{3+}$  metal ion+: a) Absorption spectra of ligand MEC with  $\text{Cr}^{3+}$  in medium of pH ranging from 2.53–11.24, b) selective representation of absorption spectra of ligand MEC with  $\text{Cr}^{3+}$  in acidic, neutral and basic medium

Table 2: A comparative analysis of absorption wavelength and their respective value of molar absorptivity coefficient for all chemical species like free ligand MEC,  $\text{MEC-Cr}^{3+}$  complex,  $\text{MEC-Al}^{3+}$  complex and  $\text{MEC-Fe}^{3+}$  complexes in acidic, neutral and basic medium respectively

S. No	Chemical Unit	Acidic Medium	Neutral Medium	Basic Medium
1	Free ligand MEC	$\lambda_1 = 266.39\text{nm}; \epsilon = 1.92 \times 10^4$ $\lambda_2 = 344.77\text{nm}; \epsilon = 0.40 \times 10^4$	$\lambda_1 = 266.39\text{nm}; \epsilon = 1.82 \times 10^4$ $\lambda_2 = 346.14\text{nm}; \epsilon = 0.39 \times 10^4$	$\lambda_1 = 283.43\text{nm}; \epsilon = 1.16 \times 10^4$ $\lambda_2 = 391\text{nm}; \epsilon = 0.84 \times 10^4$
2	$\text{MEC-Cr}^{3+}$	$\lambda_1 = 265.9\text{nm}; \epsilon = 0.98 \times 10^4$ $\lambda_2 = 344.69\text{nm}; \epsilon = 0.21 \times 10^4$	$\lambda_1 = 282.47\text{nm}; \epsilon = 0.63 \times 10^4$ $\lambda_2 = 391.4\text{nm}; \epsilon = 0.418 \times 10^4$	$\lambda_1 = 275.59\text{ nm}; \epsilon = 0.51 \times 10^4$ $\lambda_2 = 344\text{ nm}; \epsilon = 0.386 \times 10^4$
3	$\text{MEC-Fe}^{3+}$	$\lambda_1 = 265.75\text{nm}; \epsilon = 0.76 \times 10^4$ $\lambda_2 = 301.02\text{nm}; \epsilon = 0.39 \times 10^4$ $\lambda_3 = 345.50\text{nm}; \epsilon = 0.21 \times 10^4$	$\lambda_1 = 270.95\text{nm}; \epsilon = 0.58 \times 10^4$ $\lambda_2 = 291.90\text{nm}; \epsilon = 0.53 \times 10^4$ $\lambda_3 = 355.25\text{nm}; \epsilon = 0.23 \times 10^4$	$\lambda_1 = 287.99\text{ nm}; \epsilon = 0.65 \times 10^4$ $\lambda_2 = 399\text{ nm}; \epsilon = 0.28 \times 10^4$
4	$\text{MEC-Al}^{3+}$	$\lambda_1 = 266.39\text{nm}; \epsilon = 0.93 \times 10^4$ $\lambda_2 = 345.49\text{nm}; \epsilon = 0.20 \times 10^4$	$\lambda_1 = 268.39\text{nm}; \epsilon = 0.72 \times 10^4$ $\lambda_2 = 358.53\text{nm}; \epsilon = 0.19 \times 10^4$	$\lambda_1 = 282.71\text{ nm}; \epsilon = 0.63 \times 10^4$ $\lambda_2 = 393\text{ nm}; \epsilon = 0.37 \times 10^4$

The HypSpec program was employed to determine the formation constants of the  $\text{M}^{3+}$ -MEC complexes in the spectrometric approach. When ML and  $\text{MLH}_2$  species for  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ , and

$\text{Fe}^{3+}$  were taken into account for the calculation, the model produced the best fit curve. The values of the formation constants determined for the respective species are provided in Table 1. From the

investigation of coordination properties, we found that the ligand MEC shows high binding efficiency towards all the trivalent metal ions to form neutral ML complex to protonated complex (MLHn) at different pH condition, where protonated chromium complex (CrLH<sub>2</sub>) exhibits high binding constant (Log  $\beta$  = 28.56) compared to all other trivalent metal ions.

In a nutshell, co-ordination behavior of the ligand with the transition metal ions viz., Al<sup>3+</sup>, Cr<sup>3+</sup>, and Fe<sup>3+</sup> in 1:1 molar ratio in a range of pH 2-11 were investigated in solution by means of potentiometric and spectrophotometric methods. The ligand exhibited a strong metal chelation efficiency with the trivalent metal ions coordinating through nitrogen of imine and oxygen of Ar-OH binding sites to form ML and MLHn kind of complexes. In the ligand, the protonated metal-ligand complex species are dominant in a highly acidic medium. Out of all the complexes of ML type, Cr<sup>3+</sup>-MEC exhibited highest formation constant (log  $\beta$  = 28.56).

At pH > 10, formation of hydrolysis species occurred on account of hydrolysis of imine bonds. Considering ML, MLHn and the hydrolysis species (LH-n) in the calculations gave the best fit model to the curves obtained by using Hyperquad and HypSpec program.

### CONCLUSION

In the present study, we have reported the

pH responsive and selective complex formation capabilities of catechol based ligand MEC employing potentiometric and spectrophotometric techniques. The ligand MEC have shown excellent co-ordination capabilities with all trivalent metal ions used in this study. Further, it has shown maximum stability and formation constant (log  $\beta$  = 28.56) value for coordinating Cr<sup>3+</sup> ion. It has also been found that after pH 10 i.e. in truly basic conditions, MEC gets hydrolyzed. From the above results it can be inferred that the dipodal chelator MEC have shown remarkable coordination excellence with trivalent metal ions analyzed in the study, and their potential employment for various applications as in metallurgy, chelation therapy and sequestering agents can be beneficial for mankind.

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### Conflict of Interest

There is no conflict of interest between any author regarding any financial, personal or relationship with any organization.

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