

A Study on Complexation Equilibria and Spectrophotometric Determination of CrIII, MnII and FeIII with Thiourea Monophosphazene Derivative

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ABSTRACT

The absorption spectra and acid-base characteristics of 1-phenyl-2,2-(dianilino-N-phenylthiourea) monophosphazene, H₂MPZ, were studied in water-ethanol media. The equilibrium constants, molar absorptivities, stability constants of the complexes of CrIII, MnII and FeIII with the ligand H₂MPZ have been determined spectrophotometrically in 10% ethanol at 25⁰C and I = 0.1M NaNO₃. The complexation equilibria in solution were characterized using the graphical logarithmic analysis of the absorbance-pH graphs. The micro-determination of the concerned metal ions was evaluated by spectrophotometry based on the proposed complex formation M(H₂MPZ) and M(HMPZ)₂ respectively. The effect of a number of interferent cationic and anionic ions was also discussed.

INTRODUCTION

There is currently an necessary interest in preparing and studying complexes of cyclodiphosphazane derivatives and their acyclic analogues⁽¹⁻³⁾. The coordination chemistry of four-membered cyclodiphosphazanes has been studied to a lesser extent than that of their acyclic analogues⁽⁴⁻⁸⁾. Cyclodiphosphazanes exhibit different coordination behavior in their transition complexes⁽⁵⁾. The authors suggested that the bonding modes in these compounds involve coordination to the metal ion via their phosphorus atoms forming monodentate and bridged bidentate complexes. On the other hand, the hydrolytically unstable 1,3-diaryl-2,2,2,4,4-hexachlorocyclodiphosphazanes were established and stabilized through their interaction with KSCN followed by the addition of aromatic amines to give amino derivatives of substituted thiourea monophosphazenes⁽⁹⁾. This class of nitrogen-phosphorus compounds, in contrast to cyclodiphosphazanes, behaves differently in the mode of coordination with transition metals^(10,11). Since no studies have yet been reported on the complexation equilibria of the transition metal ions with

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thiourea monophosphazenes (H_2MPZ), our present work is devoted in this direction.

EXPERIMENTAL

Chemicals and Reagents

All chemical used were of analytical reagent grade and need no further purification. De-ionized water and pure ethanol were used in preparing solutions. 1-Phenyl-2,2-(dianilino-2-N-phenylthiourea) monophosphazene derivative, H_2MPZ , was prepared according to the method of Ibrahim et al⁽⁹⁾. The prepared compound was checked by elemental analysis and IR spectra which were compatible with the published results⁽⁹⁾. A stock solution ($5 \times 10^{-3} M$) of thiourea monophosphazene was prepared by dissolving the requisite amount in pure ethanol and diluted as required to the working solutions. A stock solutions of the metal ions, Cr III, Mn II, Fe III ($5 \times 10^{-3} M$) were prepared by dissolving accurate quantities of their chloride or nitrate salts in de-ionized water and diluted as necessary. The metal ions concentrations were standardized by EDTA titration⁽¹²⁾. Solutions of diverse ions used for interference studies were prepared from Analar products of nitrates, acetate or chlorides salts of the metal ions and potassium or sodium salts of the anions to be tested.

Measurements

pH-metric measurements were carried out using a MV87 digital pH-meter with an accuracy of ± 0.005 units. The pH-meter was calibrated regularly before use with standard buffer solution of pH 4.00 ± 0.01 and 7.00 ± 0.01 at $20^\circ C$. All measurements were performed in the presence of 10% ethanol (v/v) at $25^\circ C$. The pH values of the partially ethanolic solutions were corrected as given by Douheret⁽¹³⁾.

The UV-VIS and IR spectra were recorded by the instruments described before⁽¹⁴⁾.

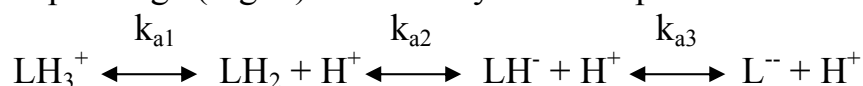
Standard Method

A solution of the metal ions under consideration containing 20-80 μg of each ion was introduced into 25 ml calibrated flask and 2.5 ml of each of H_2MPZ ($3 \times 10^{-4} M$) and 0.1 M $NaNO_3$ were added. The pH was adjusted at 9.28, 3.20, 7.77 for Cr III, Mn II and Fe III respectively and the solutions were completed to the mark with de-ionized water keeping the ethanol percentage at 10% (v/v). After thoroughly mixing, the absorbances were measured at 333, 323, 325 nm for Cr III, Mn II and Fe III respectively against a reagent blank similarly prepared but containing no metal ions.

RESULTS and DISCUSSION

Acid-Base Equilibria of H₂MPZ in 10% Ethanol

The absorption spectra of partially ethanolic solutions (10% v/v) H₂MPZ (6x10⁻⁵M) in a series of Thiel buffer solutions of pH values 1.7-11.6 were recorded as the dependence absorbance = f(λ) at an ionic strength 0.1M NaNO₃. The spectra display mainly two absorption bands at 213 and 250 nm pointing to the existence of two different absorbing species at least (see Fig. 1). Though, the spectral changes of H₂MPZ with pH at different wavelengths show three isosbestic points indicating the presence of three acids-base equilibria in solution for the reagent. In solution of pH < 3.0, the compound exists in the cationic form H₃MPZ⁺ due to protonation whilst the molecular form predominates at pH 3.5-6.26. The mono- and bi-anionic forms are the dominant species at pH 6.3-8.5. The possible existence of the three equilibria at the pH range (Fig. 2) under study can be represented as:



The change of absorbance with pH was utilized for the determination of the pK_a values of the ligand by the half-height and the limiting absorbance methods⁽¹⁵⁾ and the results are depicted in Table 1. The pK_a values were also confirmed potentiometrically using the method of Irving and Rossotti⁽¹⁶⁾ and the results agreed well with that of spectrophotometry.

Table (1) pK_a Values at λ_{max} = 254nm for H₂MPZ Ligand in 10% v/v Ethanol.

| Method | pK _{a1} | pK _{a2} | pK _{a3} |
|----------------------------------|------------------|------------------|------------------|
| Half-wave height | 3.50 ± 0.012 | 5.00 ± 0.03 | 9.15 ± 0.03 |
| Limiting absorbance | 3.55 ± 0.05 | 5.09 ± .02 | 9.10 ± 0.01 |
| Graphical analysis of A-pH plots | 3.55 ± 0.06 | 5.02 ± 0.01 | 9.20 ± 0.04 |
| Potentiometry | 3.60 ± 0.03 | 4.95 ± 0.04 | 9.15 ± 0.02 |

The absorbance versus pH graphs at selected wavelengths were interpreted making use of the relationship shown in the following equation⁽¹⁷⁾:

$$\log (A - \epsilon_1 C_L) / (\epsilon_2 C_L - A) = \text{pH} - \text{pK}_a$$

where C_L is the total ligand concentration in the final solution assuming that a particular equilibrium of the form :



is the only one existing under the specified conditions. Graphical logarithmic analysis was applied to each wavelength according to the following equation⁽¹⁸⁾:

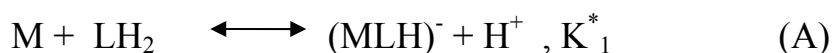
$$\sigma (\text{pK}) = \left[\frac{1}{N_{\lambda} - 1} \sum_{n=1}^{N_{\lambda}} (\overline{\text{pK}} - \text{pK}_a)^2 \right]^{1/2}$$

where $\overline{\text{pK}}$ is the mean value calculated from pK values obtained from graphs for an individual wavelength n, and N_{λ} is the number of wavelengths used. The values of pK_a obtained by this method are in good agreement with the aforementioned methods (see Table 1).

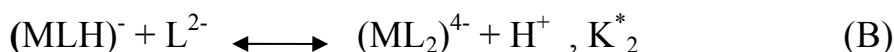
Complexation Equilibria

The equimolar reaction of CrIII, MnII or Fe III ions and H_2MPZ in solution was studied at different hydrogen ion concentrations. The spectra in Figs.3-5 reflect unambiguously the formation of two complexed species in the pH ranges 4.0-10.5 , 3.5-9.0 and 4.0-11.0 for Cr III, Mn II and Fe III respectively . The absorbance - pH graphs (Figs. 6-8) show two sufficiently separated inflections in the aforementioned pH ranges denoting the existence of two ranges of complexation equilibrium in solution for the three metal ions probably as a consequence of a stepwise transition of two complexes. The second rising part of these graphs is assumed to correspond to further ligand species coordinated to the first complex. The shapes of the second descending part of all graphs are nearly similar and rapidly decreased in absorbance due to a hydrolysis effect.

By following the process of complexation of the metals under study and the ligand H_2MPZ taking in consideration its pK_a values, it can be assumed that the neutral form of the ligand (LH_2) is the prevalent ligand species at the pH ranges of the first complexation 3.5-7.0, 3.5-5.0 and 4.5-7.0 for Cr, Mn or Fe and the mono-protonated complex is formed according to the general equation:



The analysis of the absorbance-pH graphs for the equimolar concentrations of components at the pH ranges of the first chelates and by using the appropriate transformations^(19,20), yields the best fit for equilibrium (A) and the formation of MLH complex species. The second complexation equilibrium is attained at pH 8.0-10.5, 6.5-10 and 8.0-10.5 for Cr, Mn and Fe which means that the predominant complexed ligand species is the bi-anionic form (L^{2-}) according to the equation:



In analyzing the second ascending part of the graphs at the respective pH ranges, it was found that equilibrium (B) and the formation of $\text{M}(\text{LH})_2$ species can be proved and characterized reliably. In the above equations, K_1^* and K_2^* are the equilibrium constants which are related to the stability constants, β_n , by the expression⁽²¹⁾:

$$\beta_1 = K_1^* \cdot K_{a1}^{-1}$$

$$\beta_2 = \beta_1 K_1^* \cdot K_{a2}^{-1}$$

The calculated values of the molar absorptivities, equilibrium and stability constants of the two types of complexes for the studied metal ions are cited in Table(2).

Table (2) Mean values of equilibrium, $\log k^*$, Stability, $\log\beta$, Constants and Molar Absorptivities, ϵ , of $\text{M-H}_2\text{MPZ}$ Complexes at 25°C , $I = 0.1\text{M NaNO}_3$

| method | $\text{Cr}^{3+}, \lambda_{318}$ | $\text{Mn}^{2+}, \lambda_{320}$ | $\text{Fe}^{3+}, \lambda_{325}$ |
|-------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| M.R.(1:1) | 8.03×10^3 | 4.42×10^3 | 3.70×10^3 |
| (1:2) | 5.34×10^7 | 3.86×10^7 | 1.96×10^7 |
| C.V. (1:1) | 3.81×10^4 | 4.28×10^3 | 3.10×10^7 |
| (1:2) | 5.19×10^7 | 2.78×10^7 | 1.90×10^7 |
| Log k_1^* | 0.30 | 0.04 | -0.11 |
| Log k_2^* | -5.31 | -5.21 | -5.35 |
| β_1 | 3.91 | 3.65 | 3.51 |
| β_2 | 7.73 | 7.57 | 7.29 |
| ϵ | 2.10×10^3 | 2.42×10^3 | 4.22×10^3 |

The data reveal that the order of stability for the formed complexes fall in the the order: $\text{Cr}^{3+} > \text{Mn}^{2+} > \text{Fe}^{3+}$.

The stoichiometry of $\text{M-H}_2\text{MPZ}$ complexes was further ascertained with the familiar molar ratio⁽²²⁾ and continuous variation⁽²³⁾ methods. The results shown in Fig. 9 indicate that the formed complexes have 1:1 and 1:2 (M:L) compositions at the pH studied for the three metal ions . The solid complexes were prepared and isolated in the two stoichiometric ratios 1:1 and 1:2. The characteristic IR spectral features of all complexes are the appearance of new bands at $710\text{-}775 \text{ cm}^{-1}$ due to $\nu\text{M-H}_2\text{O}$ coordinated water molecules. The bands at ~ 1350 and $\sim 1390 \text{ cm}^{-1}$ characteristic to $\nu(\text{C}=\text{S})$ ⁽²⁴⁾ and $\nu(\text{NH})$ groups in the free ligand are shifted to lower frequencies in the complexes $(10\text{-}55)\text{cm}^{-1}$. It should be noted that the spectra of all complexes show bands at $395\text{-}430 \text{ cm}^{-1}$ and $470\text{-}530 \text{ cm}^{-1}$ tentatively assigned to $\nu(\text{S-M})$ and $\nu(\text{N-M})$ ⁽²⁵⁾ stretching

vibration respectively. So, the conclusion drawn from the preceding arguments is that H₂MPZ acts as a bidentate ligand where the two binding sites are the nitrogen and sulfur atoms of NH and C=S groups .

Calibration Graphs and Reproducibility

By following the optimum conditions given under standard method in constructing calibration curves, Beer's law was obeyed over the range $1 \times 10^{-5} \text{M} - 2 \times 10^{-4} \text{M}$, $1 \times 10^{-5} \text{M} - 2.75 \times 10^{-4} \text{M}$ and $1 \times 10^{-5} \text{M} - 4 \times 10^{-4} \text{M}$ for Cr III , Mn II and Fe III respectively. Ringbom plots showed that the optimum range for the determination of Cr III , Mn II and Fe III were 1.3-10.4, 2.75-13.2 and 2.1-7.8 $\mu\text{g/ml}$ respectively. The sensitivity of the method was calculated according to Sandell⁽²⁶⁾ and was found to be 0.024, 0.022 and 0.019 $\mu\text{g cm}^{-2}$ for Cr III, Mn II and Fe III respectively. The reproducibility of the method was tested by measuring two series of solutions each containing 5 and 10 $\mu\text{g/ml}$ of each ion. The obtained relative standard deviations were 0.6 and 0.75% for Cr III, 0.7 and 0.8% for Mn II and 0.4 and 0.55% for Fe III respectively.

Effect of Diverse Ions

The effect of diverse ions on the determination of the concerned metals was performed by preparing solutions containing 100 μg of each determined ion and the various diverse ions to be tested individually under the optimum conditions. The anions used were solutions of their sodium or potassium salts whilst the cations were solutions of their chloride, acetate or nitrate salts. The tolerance limit for a given ion was taken to be the deviation of the absorbance values by more than $\pm 2\%$ from the value expected for any of the determined ion alone. The determination of the respective metals as M(H₂MPZ) and M(H₂MPZ)₂ complexes were possible in presence of Li⁺, Na⁺, K⁺ (12mg), Cd²⁺, Ni²⁺ (5mg), NO₃⁻, S₂O₃²⁻, B₄O₇²⁻ (16mg), SO₄²⁻ (7mg) and CH₃COO⁻ (5mg) without interference.

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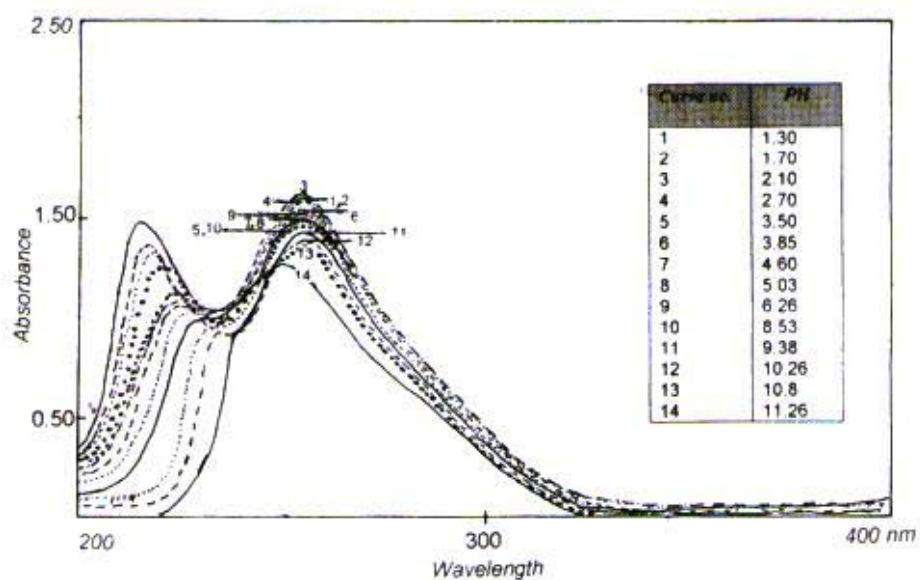


Fig. 1 Absorption spectra of H_2MPZ $6 \times 10^{-5}M$ at different pH values in 10 % ethanol and $I=0.1M NaNO_3$

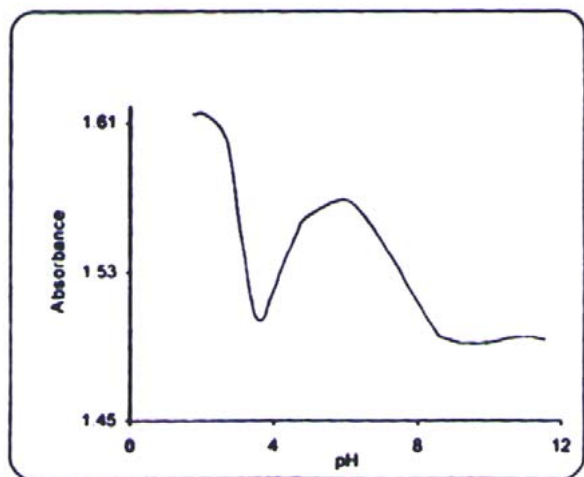


Fig. 2 Absorbance vs. pH for H₂MPZ 6x10⁻⁵M at 250 nm

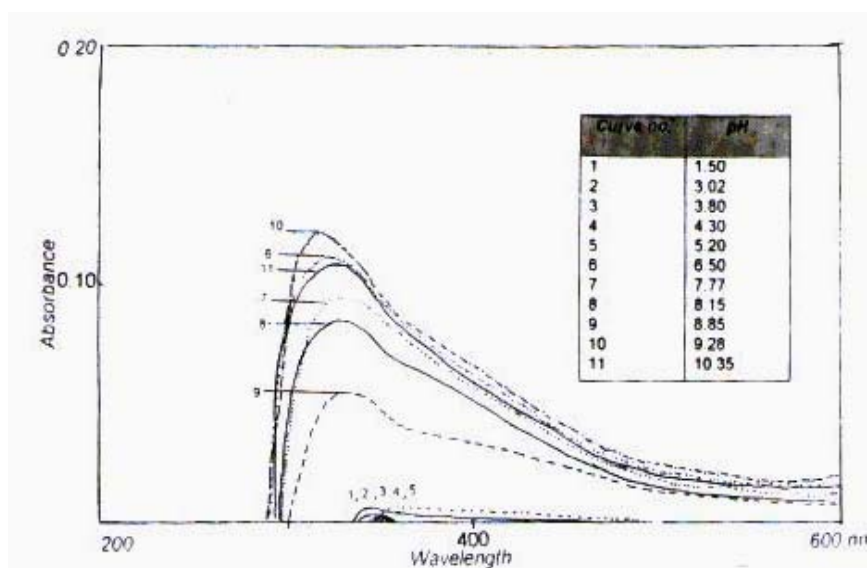


Fig. 3 Absorption spectra of H₂MPZ- Fe³⁺ complex at different pH values in 10 % ethanol and I=0.1M NaNO₃

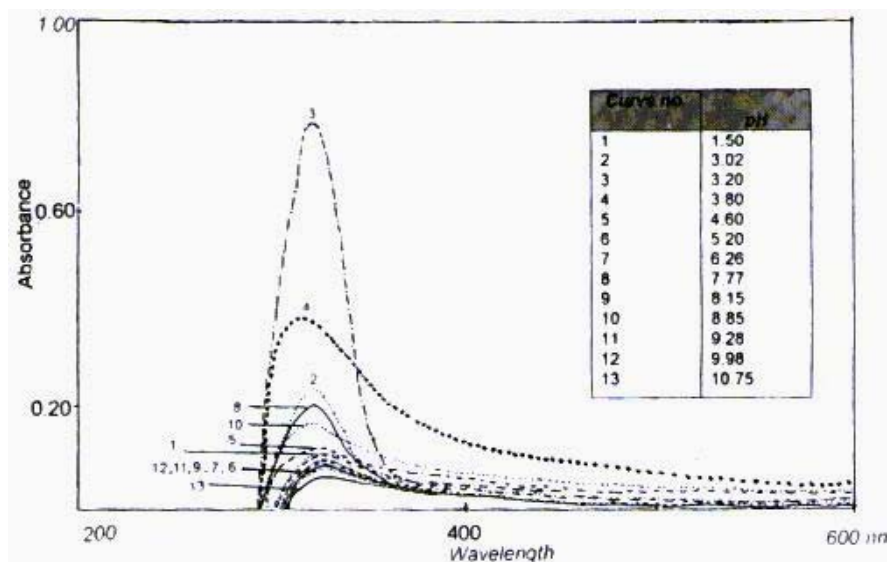


Fig. 4 Absorption spectra of H₂MPZ- Mn²⁺ complex at different pH values in 10 % ethanol and I=0.1M NaNO₃

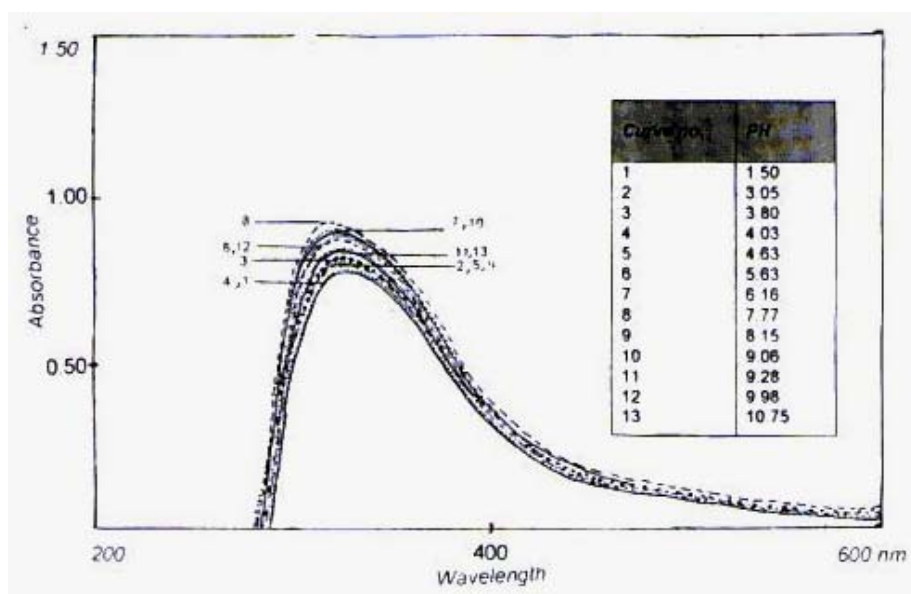


Fig. 5 Absorption spectra of H₂MPZ- Cr³⁺ complex at different pH values in 10 % ethanol and I=0.1M NaNO₃

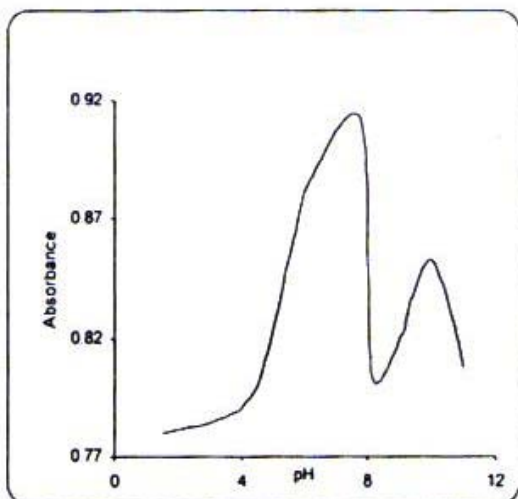


Fig. 6 Absorbance vs. pH graph for equimolar concentration 3×10^{-4} M of H_2MPZ and Fe^{3+} at 325 nm, $I=0.1\text{M NaNO}_3$ and 10% v/v ethanol

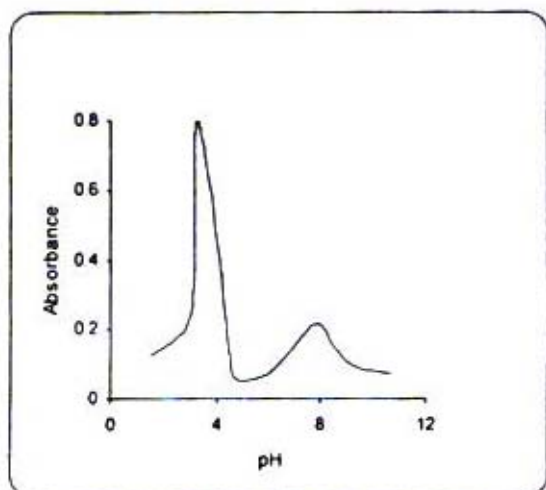


Fig. 7 Absorbance vs. pH graph for equimolar concentration 3×10^{-4} M of H_2MPZ and Mn^{2+} at 223 nm, $I = 0.1\text{M NaNO}_3$ and 10% v/v ethanol

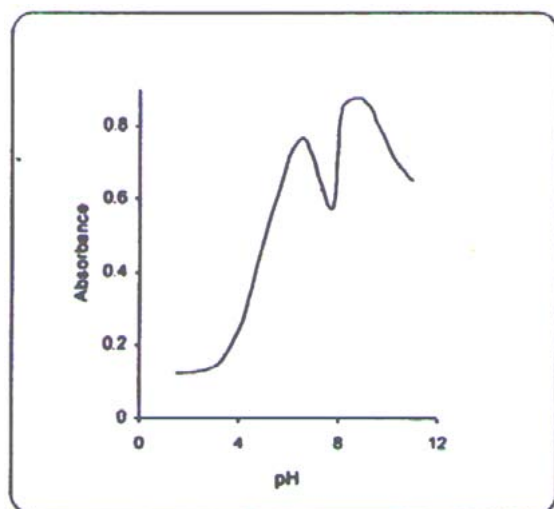


Fig. 8 Absorbance vs. pH graph for equimolar concentration $3 \times 10^{-4} \text{M}$ of H_2MPZ and Cr^{3+} at 333 nm, $I = 0.1 \text{M}$ NaNO_3 and 10% v/v ethanol

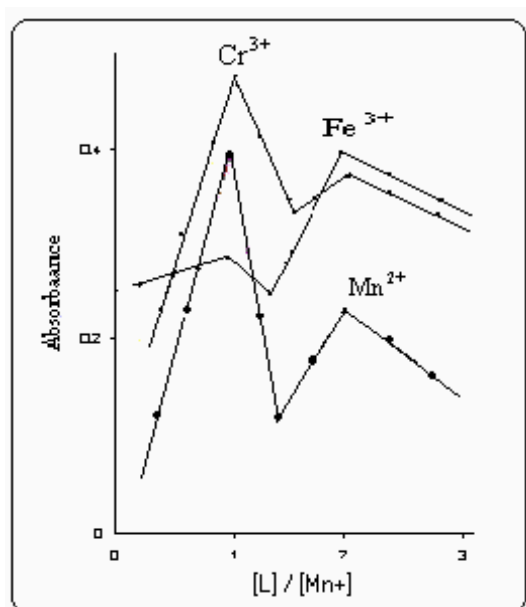


Fig. 9 Molar ratio plots of M- H_2MPZ complexes