

Spectroscopic and Biological activity studies of azo ligand type (N,O)and its complexes with Cr^{III},Mn^{II}and Fe^{II} ions

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Abstract

Azo derivative ligand[H₃L] have been synthesized by the reaction of diazonium salt of p-amino benzoic acid with orcinol in(1:1)mole ratio. The bidente ligand was reacted with the metal ions Mn^{II},Fe^{II}andCr^{III}in(2:1)mole ratio via reflux in ethanol using Et₃N as a base to give complexes of the general formula: [M(H₂L)₂(H₂O)_x]Cly The synthesized compounds were characterized by spectroscopic methods[I.R , UV-Vis, A.A and H¹NMR]along with melting point, chloride content and conductivity measurements. The complexes were screend for their in vitro antibacterial activity against one strain of staphylococcus as Gram(+) positive and one strain of pseudomonas as Gram(-) Negative, using the agar diffusion technique.

(2-methyl,4,6dihydroxyphenylazo)benzoicacid)

(p-aminobenzoicacid)

(N,O)

(1:2)

[M(H₂L)₂ (H₂O)X]Cly

:

| | | | |
|------------------------|---------------------|--------------------|------|
| M= Cr ^(III) | X =H ₂ O | y=Cl | n=+1 |
| M=,Mn ^(II) | X=H ₂ O | y=H ₂ O | n=0 |
| M= Fe ^(II) | X=H ₂ O | y=H ₂ O | n=0 |

-)

staphylococcus

pseudomonas

Introduction

Reaction of aryl diazonium salts that does not involve loss of nitrogen takes place when they react with phenols and aryl amines. Aryl diazonium ions are relatively weak electrophiles but have sufficient reactivity to attack strongly activated aromatic rings. The reaction is known as azo coupling; two aryl groups are joined together by azo ($-N=N-$) function⁽¹⁾. Soon after azo coupling was discovered in the mid nineteenth century, the reaction received major attention as a method for preparing dyes⁽²⁾. It has been a lot of studies related to strong association between metal complexes and antibacterial activities^{(3), (4)}. Attention has been paid during the last decade for the chemistry of the metal complexes of ligands containing nitrogen and oxygen as a donor atom⁽⁵⁾, this could be due to the stability of such ligand complexes⁽⁶⁾ and its biological activity along with oxidation catalysis and electrochemical analysis^{(7), (8)}. In the recent past, number of studies has highlighted the use of azo compounds and its complexes with transition metals in various significant applications^{(9), (10)}.

Experimental

Chemicals used were analytical grades; metals were used as chloride salts. The metal content of complexes determined by absorption technique, using Shimadzu (A.A) 680 G atomic absorption spectrophotometer. IR data were recorded as (KBr) disc using Shimadzu 4800s FTIR spectrophotometer in the range $(4000-400) \text{ cm}^{-1}$. (UV-VIS) spectra were obtained at 25°C for 10^{-3} M solution in DMF using a Shimadzu 160 spectrophotometer in the range $(200-900) \text{ nm}$ using quartz cell. Melting points were recorded on an electrothermal Stuart apparatus are not corrected. Electrical conductivity measurements of the complexes were recorded at 25°C for 10^{-3} solution in DMF as solvent using a Jenway 4071 digital conductivity meter.

The chloride content for complexes was determined by potentiometric titration method using (686-titro processor -665), Dosinatmetrm Swiss. Antibacterial screening was done at laboratories of college of science, University of Baghdad using agar diffusion technique. The metal complexes were screened for their in vitro antibacterial activity against one Gram-negative of (*Pseudomonas*) and one Gram-positive (*Staphylococcus*) bacterial strains.

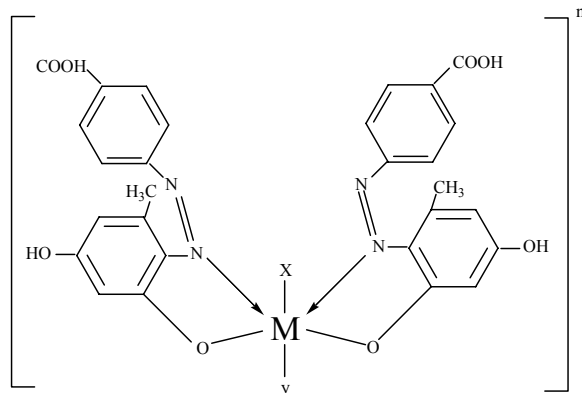
Synthesis of (2-methyl (4, 6 dihydroxy phenyl-azo) benzoic acid) [H_3L]

This compound has been synthesized according to the literature⁽¹¹⁾. P-amino benzoic acid (0.685g, 5 mmole) in dilute HCl 3 ml HCl +5ml distilled water was kept in ice bath (0°C). A drop wise addition of (0.8g), 11.5 mmole) of sodium nitrate solution with continuous stirring while the mixture at (0°C) (solution I). Orcinol (0.62 g, 5 mmole) in 10% KOH was cooled in ice bath and mixed with (solution I) with continuous stirring in the ice bath, left for 10 minutes during which dark orange precipitate was formed as shown in scheme (1). The solid residue was filtered and washed several times with distilled water until the pH of the washing water is about 7. Crystallization from ethanol afforded the desired ligand with yield (76%) and dec. ($137-140^\circ\text{C}$).

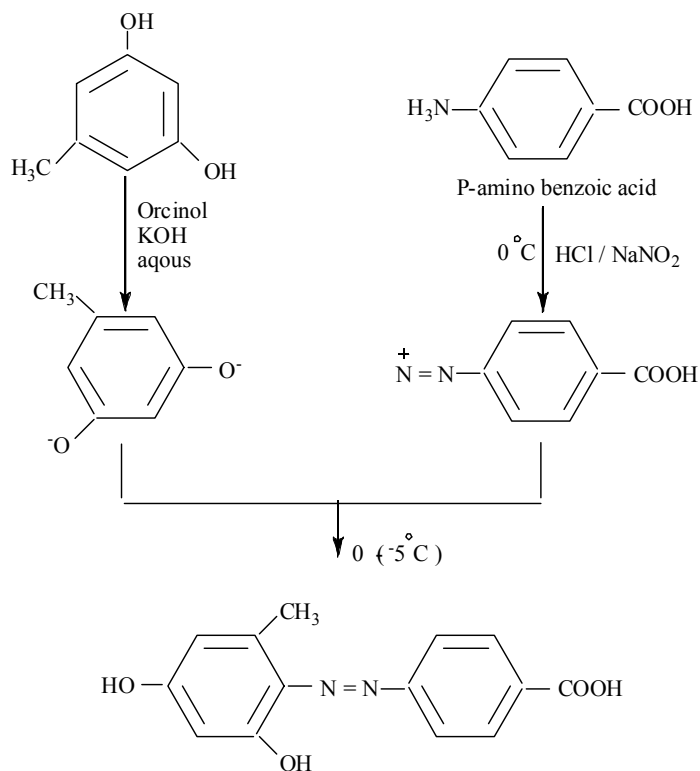
Synthesis of Complexes

Synthesis of the $[\text{Mn}(\text{II})(\text{H}_2\text{L})_2(\text{H}_2\text{O})_2](1)$ complex

(0.09g, 0.05 mmole) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in (5ml) distilled water was added drop wise to a solution of ligand (0.272g, 0.1 mmole) in 10 ml hot ethanol. Then (0.1 ml) of Et_3N was added to the mixture, which was then refluxed for 2 hrs. The reaction mixture was cooled in an ice bath, dark brown precipitate was collected, washed with cold ethanol (5ml). yield (78%) dec. (290°C).



Where : M = Cr (III), Mn (II), Fe (II)
 When: M=Cr X=H₂O y=Cl n=+1
 M=Mn X=H₂O y=H₂O n=0
 M=Fe X=H₂O y=H₂O n=0



Scheme (1): The preparation of the ligand [H₃L]

Synthesis of [Fe(II)(H₂L)₂(H₂O)₂](2) and [Cr(H₂L)₂(H₂O)₂]Cl(3) complexes:-

These complexes were obtained in a similar method to that mentioned in the preparation of complex (1): using FeCl₂.2H₂O and CrCl₃. 6H₂O. The quantity of the compounds was adjusted accordingly. Table (2) state the quantity of starting materials and some physical properties of complexes.

Results and Discussion

Synthesis of the Ligand

The ligand was prepared in high yield using one equivalent of P- amino benzoic diazonium salt and one equivalent of orcinol at low temperature, scheme (1). The I.R spectrum of the ligand showed bands at (3236) cm⁻¹, (3479)cm⁻¹ and (3417)cm⁻¹ which could be attributed to $\nu(\text{OH})_{-4}$ - $\nu(\text{OH})_{-6}$ and carboxylic hydroxyl groups respectively, also the spectrum showed bands at (1689) cm⁻¹ and (1423) cm⁻¹ which could be attributed to $\nu(\text{C}=\text{O})$ carboxylic and $\nu(\text{N}=\text{N})$ azo compound, the bands at (1504) cm⁻¹ and (1477)cm⁻¹ could be attributed to $\nu(\text{C}=\text{C})$ of acid and orcinol rings. Finally the band at (1157) cm⁻¹ could be attributed to $\nu(\text{C}-\text{O})$ phenolic. The (U.V-Vis) spectrum for the ligand is shown in Fig (5), the results were summarized in Table (4). The Figure exhibited two intense absorption peak at (250) nm and (411)nm which assigned to ($\pi-\pi^*$) and ($n-\pi^*$) transition respectively.

Synthesis of the complexes

The reaction of the ligand [L] with Cr(III), Mn(II) and Fe(II) salts was carried out in ethanol. The analytical and physical data Table (2) and spectral data Table (3) and Table (4) are compatible with the suggested structure Fig(1). The I.R spectra of the complexes (1),(2) and (3) are shown in Figs.(2,3 and 4). The band at (1423)cm⁻¹ in the free ligand which assigned to $\nu(\text{N}=\text{N})$ stretching was shifted to lower frequencies and appeared at (1404) cm⁻¹, (1388)cm⁻¹ and (1392) cm⁻¹

¹ indicated the formation of the complexes (1),(2) and (3)^{(12),(13)} respectively. These bands were assigned to $\nu(\text{N}=\text{N})$ stretches of reduced bond order, this can be attributed to delocalization of metal-electron density into the ligand π -system (HOMO-LUMO)⁽¹⁴⁾. The phenolic (C-O) stretching vibration appeared at (1157)cm⁻¹ in the free ligand was shifted to higher frequencies and appeared at (1165) cm⁻¹, (1165) cm⁻¹ and (1161)cm⁻¹ in the complexes (1),(2) and (3) respectively, indicating a weak linkage between oxygen of phenolic group and the metal ions^{(13),(15)}. This shift confirms the participation of phenol oxygen in the (C-O-M) bond.

The spectra of the complexes showed the appearance of new bands at (578) cm⁻¹, (567) cm⁻¹ and (586) cm⁻¹ refer to $\nu(\text{M}-\text{N})$ bond for complexes (1), (2) and (3) respectively. The bands confirm also the coordination of the azo nitrogen atom to metal center^{(16),(17)}. Finally the bands at (445) cm⁻¹, (549) cm⁻¹ and (541) cm⁻¹ may be assigned to $\nu(\text{M}-\text{O})$ band of complexes(1),(2)and(3)respectively.

These confirm also the coordination of the phenolic oxygen atom to metal center. The (U.V-Vis) Spectra for the complexes are shown in Figs.(7),(8) and (9), the results were summarized in table (3). The complex (1) showed an intense absorption peak at (239) nm due to ligand field and high peak at (347) nm may assigned to (C.T) transition, while the weak peak at (820) nm was assigned to (d-d) electronic transition type($^4\text{A}_2\text{g} \rightarrow ^4\text{T}_2\text{g}$) suggesting Octahedral geometry around the metal ion. This result is in agreement with that reported by Abu-EL-Reash and Co-workers⁽¹⁸⁾. On the other hand the complex (2) showed two intense absorption peaks at (262)nm and (421)nm assigned to ligand field and (C.T) transitions respectively, while a weak peak at (721) nm was assigned to (d-d) electronic transition

type(${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$) suggesting octahedral geometry around Mn^{+2} ion. This result is in agreement with that reported by Kumar and Co-workers⁽¹⁹⁾. Finally the complex (3) showed a broad peak at (415) nm was assigned to overlap of ligand field and (C.T) transition, while the weak peak at (674)nm was assigned to (d-d) electronic transition type (${}^5T_{2g} \rightarrow {}^5E_g$) suggesting octahedral geometry around Fe^{+2} ion. This result is in agreement with that reported by West and Coworkers⁽²⁰⁾. The molar conductance of the complexes in DMF lie in the range(38.6-78.2 $Ohm^{-1}cm^{-2} mol^{-1}$) ,Table(4) ,indicated that complexes(Mn and Fe) are all non-electrolyte while Cr complex having molar ratio of 1:1⁽²¹⁾

Biological screening

In our study the synthesised compounds have been screened for their antibacterial activity against the staphylococcus (G^+) and Pseudomonas (G^-) strains by the agar diffusion technique⁽²²⁾. Each of the compounds was dissolved in DMF to give a final concentration of (0.001) mg / ml and from the data shown in Table (1), compounds (1), (2) and (3) exhibited biological activity against Pseudomonas (G^-) (In hibition zone 11 mm).While against the staphylococcus (G^+), the compound (1) and (2) have no any biological activity (Inhibition zone =zero), but the compound (3) exhibited biological activity (Inhibition zone =16 mm).

Table (1).The biological activity of the synthesised complexes

| Compound | Staphylococcus (G^+) | Pseudomonas (G^-) |
|---|--------------------------|-----------------------|
| [Cr(III)(H ₂ L) ₂ (H ₂ O) ₂]Cl | 0 | 11 |
| [Mn(II)(H ₂ L) ₂ (H ₂ O) ₂] | 0 | 11 |
| [Fe(II)(H ₂ L) ₂ (H ₂ O) ₂] | 16 | 11 |
| Control | 0 | 0 |

Table (2) : The microanalysis result and some physical properties for the ligand [H₃L] and its complexes

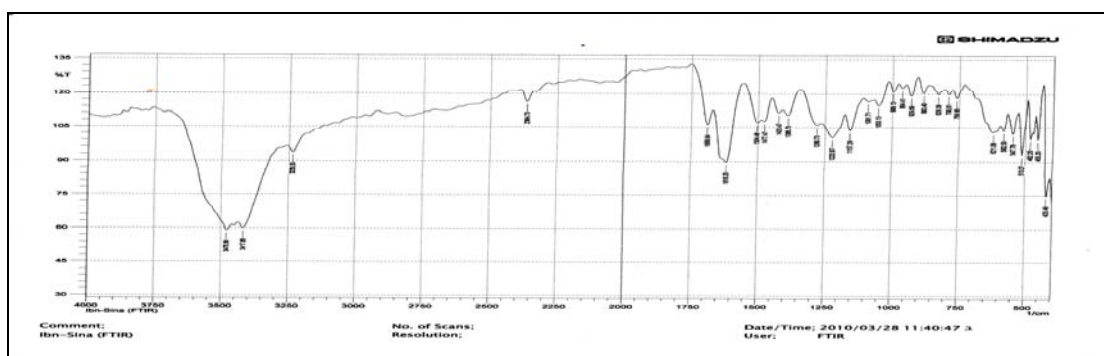
| Compound | Formula | M.wt | Color | m. p. (°C) | Yield % | Chloride Content | Metal Found , Calculate |
|--|---|-------|-------------|---------------|---------|------------------|-------------------------|
| H ₃ L | C ₁₄ H ₁₂ N ₂ O ₄ | 272 | Dark orange | Dec.(137-140) | 76 | Nil | - |
| [Cr(III)(H ₂ L) ₂ (H ₂ O) ₂] Cl | C ₂₈ H ₂₆ N ₄ O ₁₀ CrCl | 665.5 | Brown | Dec(296-300) | 80 | 1.46 | 7.01 (7.81) |
| [Mn(II)(H ₂ L) ₂ (H ₂ O) ₂] | C ₂₈ H ₂₆ N ₄ O ₁₀ Mn | 633 | yellow | Dec(287-290) | 78 | Nil | 8.5 (8.68) |
| [Fe(II)(H ₂ L) ₂ (H ₂ O) ₂] | C ₂₈ H ₂₆ N ₄ O ₁₀ Fe | 634 | Dark green | Dec(295-300) | 77 | Nil | 8.9 (8.83) |

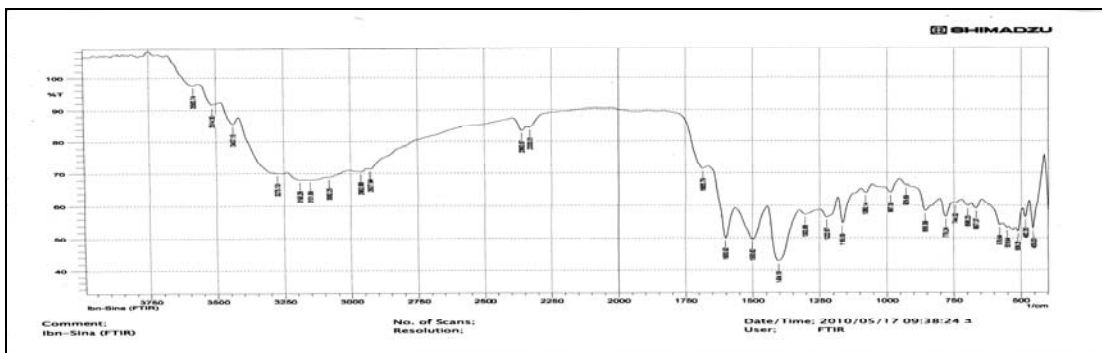
Table (3) Infrared spectral data (wave number ν) cm^{-1} for the ligand [H₃L] and its complexes

| Compound | $\nu(\text{N}=\text{N})$ | $\nu(\text{O}-\text{H})_4$ $\nu(\text{O}-\text{H})_6$ $\nu(\text{O}-\text{H})_{\text{car}}$ | $\nu(\text{C}=\text{O})$ Carboxylic | $\nu(\text{C}=\text{C})$ Aromatic | $\nu(\text{C}-\text{O})$ | $\nu(\text{M}-\text{N})$ | $\nu(\text{M}-\text{O})$ |
|---|--------------------------|---|--|--------------------------------------|--------------------------|--------------------------|--------------------------|
| H ₃ L | 1423 | 3236 3479 3417 | 1689 | 1504 | 1157 | - | - |
| [Cr(III)(H ₂ L) ₂ (H ₂ O) ₂]Cl | 1404 | 3275 3437 | 1685 | 1500 | 1165 | 578 | 455 |
| [Mn(II)(H ₂ L) ₂ (H ₂ O) ₂] | 1388 | 3290 3400 | 1700 | 1508 | 1165 | 567 | 459 |
| [Fe(II)(H ₂ L) ₂ (H ₂ O) ₂] | 1392 | 3290 3440 | 1697 | 1492 | 1161 | 586 | 452 |

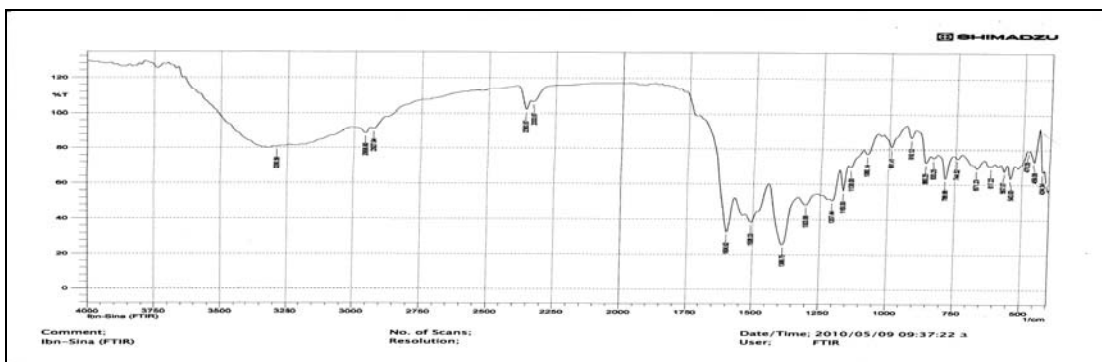
Table (4) Electronic spectral data for the ligand [H₃L] and its complexes, Molar Ratio and Molar Conductivity

| Compound | λ_{nm} | ϵ_{max} $\text{molar}^{-1} \cdot \text{cm}^{-1}$ | Assignment | Ratio | Molar Conductivity $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ | Coordination |
|---|-----------------------|---|---|-----------|--|--------------|
| H ₃ L | 250 411 | 302 123 | (n- π^*) (π - π^*) | - | - | - |
| [Cr(III)(H ₂ L) ₂ (H ₂ O) ₂]Cl | 239 347 820 | 582 195 107 | Ligand field (C.T) (${}^4A_{2g} \rightarrow {}^4T_{2g}$) | 1:1 | 78.2 | Octahedral |
| [Mn(II)(H ₂ L) ₂ (H ₂ O) ₂] | 262 421 721 | 413 245 89 | Ligand field (C.T) (${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$) | Non elec. | 65.6 | Octahedral |
| [Fe(II)(H ₂ L) ₂ (H ₂ O) ₂] | 415 674 | 782 111 | (C.T) (${}^5T_{2g} \rightarrow {}^5E_g$) | Non elec. | 38.6 | Octahedral |

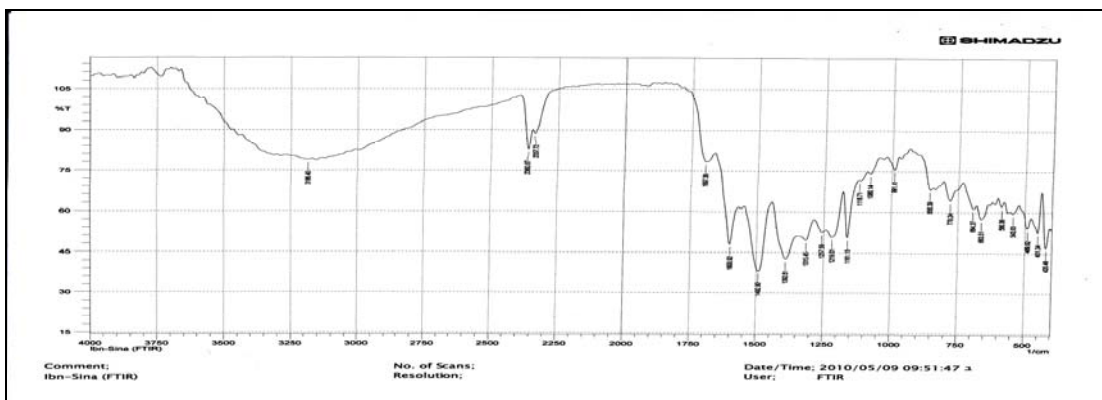
**Fig(2) Infrared spectrum of the ligand [H₃L]**



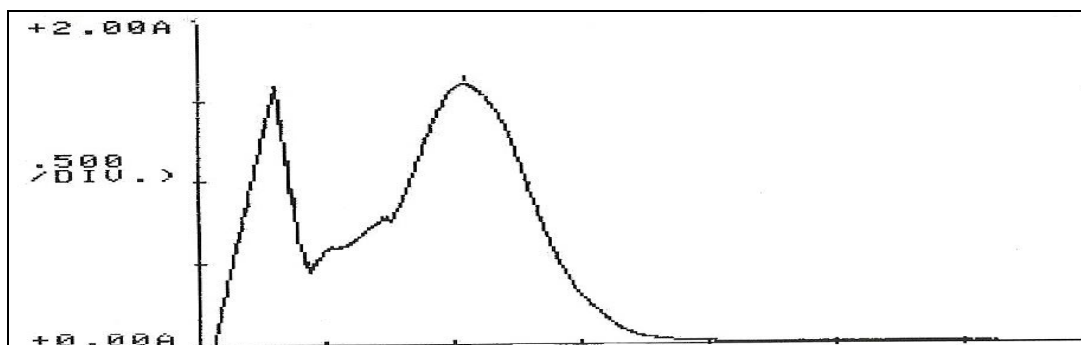
Fig(3) Infrared spectrum of [Cr(III)(H₂L)₂(H₂O)₂]Cl



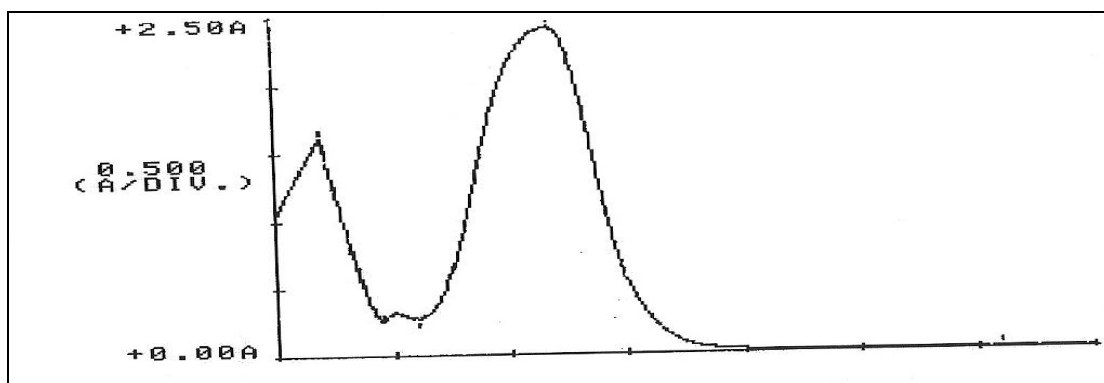
Fig(4) Infrared spectrum of [Mn(II)(H₂L)₂(H₂O)₂]



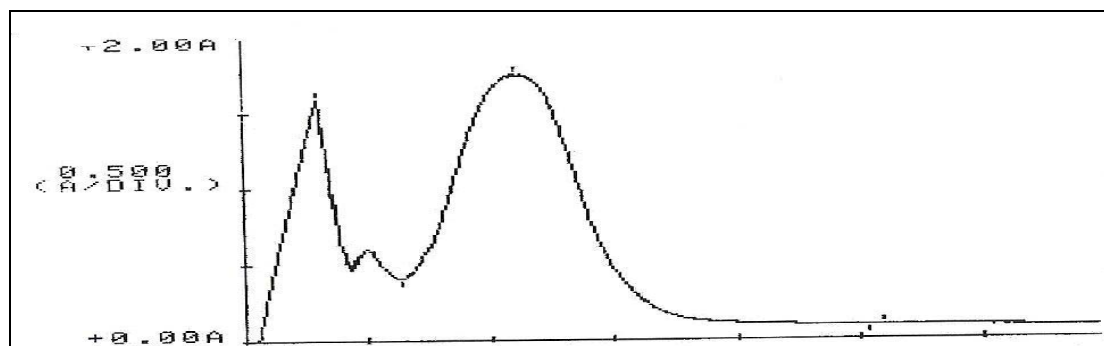
Fig(5) Infrared spectrum of [Fe(II)(H₂L)₂(H₂O)₂]



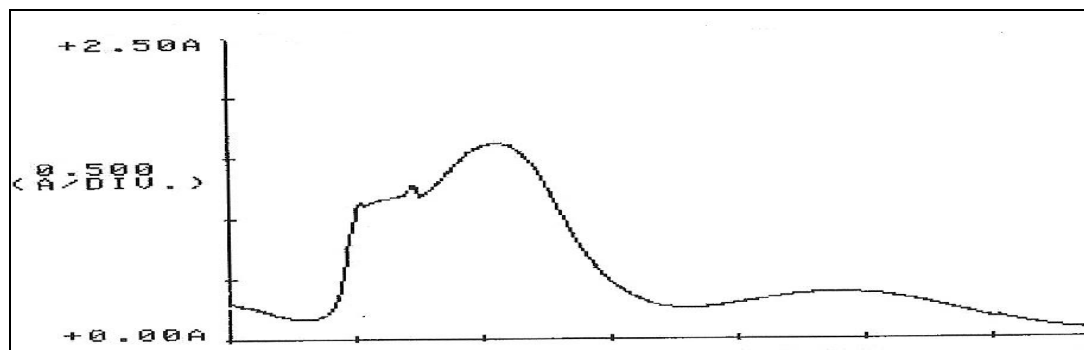
Fig(6) Electronic spectrum of the ligand [H₃L]



Fig(7) Electronic spectrum of [Cr(III)(H₂L)₂(H₂O)₂]Cl



Fig(8) Electronic spectrum of [Mn(II)(H₂L)₂(H₂O)₂]



Fig(9) Electronic spectrum of [Fe(II)(H₂L)₂(H₂O)₂]

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