

Synthesis and spectroscopic and biological activity for binuclear complexes with Mn(II),Fe(II) and Zn(II) with ligand type N₂O₂

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Abstract

In this work, the *m*-phenylene diamine and resorcinol have been used in the synthesis ligand [*m*-phenylene bis(azo resorcinol)] tetradentate type (N₂O₂).

The tetra dentate ligand was reacted with the metal ions Mn^(II),Fe^(II)and Zn^(II) in (1:1) mole ratio via reflux in Ethanol using Et₃N as a base to give binuclear complexes of genral formula [M₂(L)₂(H₂O)₂]. The synthesized compounds were characterized by spectroscopic methods [I.R, UV-VIS and A.A] along with melting point, chloride content and conductivity measurements. These studies revealed an octahedral geometries for Mn^(II) , Fe^(II) and Zn^(II) complexes.

The ligand and its complexes exhibited biological activity against the Bacillus(G⁺) strain and the E.coli(G⁻) strain.

Introduction

Attention have been paid during the last decade the chemistry of the metal complexes of ligands containing nitrogen and oxygen as donor atoms⁽¹⁾, this could be due to the stability of such ligand complexes⁽²⁾ and its biological activity along with oxidation catalysis and electro chemical analysis^(3,4). *m*-Phenylenediamine, also called 1,3-diaminobenzene, is an organic compound with the formula C₆H₄(NH₂)₂. It is an isomer of *o*-phenylenediamine and *p*- phenylenediamine. It is a colourless solid. *m*-Phenylenediamine is used in the preparation various polymers including aramid fibers, epoxy resins, wire enamel coatings and polyureaelastomers. Other uses for *m*-phenylenediamine include as an accelerator for adhesive resins, and as a component of dyes for leather and textiles *m*-phenylenediamine is a "coupling agent", used to produce blue colors.⁽⁵⁾

Resorcinol is benzene-1,3-diol⁽¹⁾, It compound prepared by alkali fusion of 1,3 benzene disulphonic acid. Resorcinol is produced when any of a large number of resins⁽²⁾. It is one of the main natural phenols in argan oil⁽³⁾

.Resorcinol compound had medical uses as an antiseptic and disinfectant, and is used 0 to 10% in ointments in the treatment of chronic skin diseases such as psoriasis, hidradenitis suppurativa, and eczema of a sub-acute character, and in prescription treatments at higher concentrations.⁽¹⁾ Resorcinol is also used as a chemical intermediate for the synthesis of pharmaceuticals and other organic compounds.⁽²⁾ Azo compounds are used in a variety of cosmetic⁽³⁾ and as a food coloring⁽⁴⁾, and its biological activity along with oxidation catalysis and electro chemical analysis^(5,6). The aim of the present study is synthesis, characterise and evaluate the metal complexes as antibacterial agent as promising addition of new class as metal based drugs.

Experimental

Chemicals used were analytical grades; metals were used as chloride salts. I.R data were recorded as (KBr) disc using shimadza 4100s FTIR spectro photometer in the range (4000-400) cm⁻¹. (UV-VIS)spectra were obtained at 20 °C for 10⁻³ M solution in DMF using a shimadzu 160 spectrophotometer in the range (200-900) nm using quartz cell and electrical conductivity measurements of complexes were recorded at (20 °C) for (10⁻³-10⁻²) M solution in DMF as solvent using a pw 9026 digital conductivity meter. . The metal content of complexes determined by absorption technique, using shimadza (A.A) 680 G atomic absorption spectrophotometer. The chloride content for complexes was determined by potentiometric titration method using (686 - titro processor - 660), Dosinatmetrm Swiss. And melting points were obtained using an electrothermal apparatus Stuart. All measurements were obtained in Ibn-sina company. 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 (E.coli) and one Gram⁺ positive (Bacillus) bacterial strains.

Synthesis of Ligand [m- phenylene bis(azo resorcinol)] [H₂L]

m-phenylenediamine hydro chloride (1.8g, 10 mmole) was dissolved in warm mixture of 10 ml con. HCl and 10 ml distilled water contained in 200 ml beaker kept in ice salt bath (0-5)°C whilst stirring vigorously, m-phenylenediamine hydro chloride will separate in a finely divided crystalline form. Solution of sodium nitrate (1.38g, 20 mmole) in 10 ml of water was added slowly with stirring to an end – point with potassium iodide – starch paper.

Resorcinol (2.2g, 20 mmole) was dissolved in a solution of potassium hydroxide (0.56g, 10 mmole) in 10 ml water, then cooled in ice bath and added to the diazotized solution with stirring. Concentrated hydrochloride acid was added slowly and with vigorous stirring, and the filtered with gentle suction, washed with distilled water free acid and dried upon filter – paper in the air. Yield percent (81%) and dec. (120)°C.

Synthesis of Complexes

Synthesis of the $[Mn(II)(L)_2(H_2O)_4](1)$ complex

(0.1 g, 0.0 mmol) of $MnCl_2 \cdot 4H_2O$ in (10 ml) ethanol was added drop wise to a solution of $[H_2L]$ (0.170 g, 0.0 mmol) dissolved in (10 ml) hot ethanol, the PH of the reaction mixture was adjusted by adding Et_3N in equivalent quantity, and the reaction mixture was allowed to reflux for 2 hrs. The mixture was cooled in an ice bath, brown precipitate was collected, washed several times with absolute ethanol and dried, yield (81%), m.p (290-300) °C dec.

Synthesis of $[Fe(II)(L)_2(H_2O)_4](2)$ and $[Zn(L)_2(H_2O)_4](3)$ complexes:-

These complexes were obtained in a similar method to that mentioned in the preparation of complex (1): using $FeCl_2 \cdot 6H_2O$ and $ZnCl_2 \cdot 6H_2O$. The quantity of the compounds were 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 m-phenylenedi diazonium salt and two equivalent of resorcinol at low temperature, scheme (1). The I.R spectrum of the ligand showed bands at $(3209)cm^{-1}$ and $(3066)cm^{-1}$ which could be attributed to $\nu(OH)-s-$ and $\nu(OH)-a-$ hydroxyl groups respectively, also the spectrum showed bands at $(1560)cm^{-1}$ and $(1475)cm^{-1}$ which could be attributed to $\nu(N=N)$ stretching ortho and meta respectively. Finally the band at $(1236)cm^{-1}$ could be attributed to $\nu(C-O)$ phenolic. The (U.V-Vis) spectrum for the ligand is shown in Fig (1), the results were summarized in Table (3). The Figure exhibited three intense absorption peak at $(263)nm$, $(304)nm$ and $(419)nm$ which assigned to $(n-\pi^*)$, $(n-\pi^*)$ and $(\pi-\pi^*)$ transition respectively.

Synthesis of the complexes

The reaction of the ligand $[H_2L]$ with Mn(III), Fe(II) and Zn(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.(3, 4 and 5). The bands at $(1560)cm^{-1}$ and $(1475)cm^{-1}$ in the free ligand which assigned to $\nu(N=N)$ stretching ortho and meta was shifted to lower frequencies and appeared at $(1508, 1473)cm^{-1}$, $(1502, 1473)cm^{-1}$ and $(1504, 1473)cm^{-1}$ indicated the formation of the complexes (1), (2) and (3)^{(10),(11)} respectively.

These bands were assigned to $\nu(N=N)$ stretches of reduced bond order, this can be attributed to delocalization of metal-electron density into the ligand π -system (HOMO-LUMO)⁽¹²⁾. The phenolic (C-O) stretching vibration appeared at $(1236)cm^{-1}$ in the free ligand was shifted to lower frequencies and appeared

at $(1230)cm^{-1}$, $(1230)cm^{-1}$ and $(1234)cm^{-1}$ in the complexes (1),(2) and (3) respectively, indicating a weak linkage between oxygen of phenolic group and the metal ions^{(17),(18)}. This shift confirms the participation of phenolic oxygen in the (C-O-M) bond. The spectra of the complexes showed the appearance of new bands at $(570)cm^{-1}$, $(570)cm^{-1}$ and $(570)cm^{-1}$ refer to $\nu(M-N)$ bond for complexes (1), (2) and (3) respectively. The bands confirm also the coordination of the azo nitrogen atom to metal center^{(19),(20)}. Finally the bands at $(432)cm^{-1}$, $(432)cm^{-1}$ and $(432)cm^{-1}$ may be assigned to $\nu(M-O)$ 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 $(260)nm$ due to ligand field and two peaks at $(304)nm$ and $(416)nm$ may assigned to (C.T) transition, while the weak peak at $(630)nm$ was assigned to (d-d) electronic transition type (${}^1A_{1g} \rightarrow {}^3T_{1p}$) suggesting Octahedral geometry around the metal ion. This result is in agreement with that reported by Abu-EL-Reash and Co-workers⁽²¹⁾. On the other hand the complex(2) showed three intense absorption peaks at $(269)nm$, $(304)nm$ and $(416)nm$ assigned to ligand field and (C.T) transitions respectively, while a weak peak at $(730)nm$ was assigned to (d-d) electronic transition type(${}^1E_g \rightarrow {}^3T_g$) suggesting octahedral geometry around Fe²⁺ ion. This result is in agreement with that reported by Kumar and Co-workers⁽²²⁾. Finally the complex(3) showed a peak at $(210)nm$ was assigned to ligand field, while the peak at $(420)nm$ was assigned to (C.T) transition⁽²³⁾. The metal ion Zn of complex belong to d^{10} system and this metal do not show (d-d)⁽²⁴⁾, suggestion to an octahedral geometry around the zinc(II) ion⁽¹⁹⁾. The molar conductance of the complexes in DMF lie in the range $(26.58-12,20 Ohm^{-1}cm^2 mol^{-1})$, Table(4), indicated that complexes (Mn^(II), Fe^(II) and Zn^(II)) are all non-electrolyte⁽²⁵⁾.

Biological screening

In our study the synthesised compounds have been screened for their antibacterial activity against the bacillus (G^+) and E.coli (G^-) strains by the agar diffusion technique⁽²⁶⁾. 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), and Figs. 10 and 11, compounds (1), (2) and (3) exhibited biological activity against E.coli (G^-) (In hibition zone= 4, 1.5 and 2 mm). but the compounds (1), (2) and (3) exhibited biological activity against Bacillus (G^+) (Inhibition zone = 1.5, 2,5 and 3 mm).

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

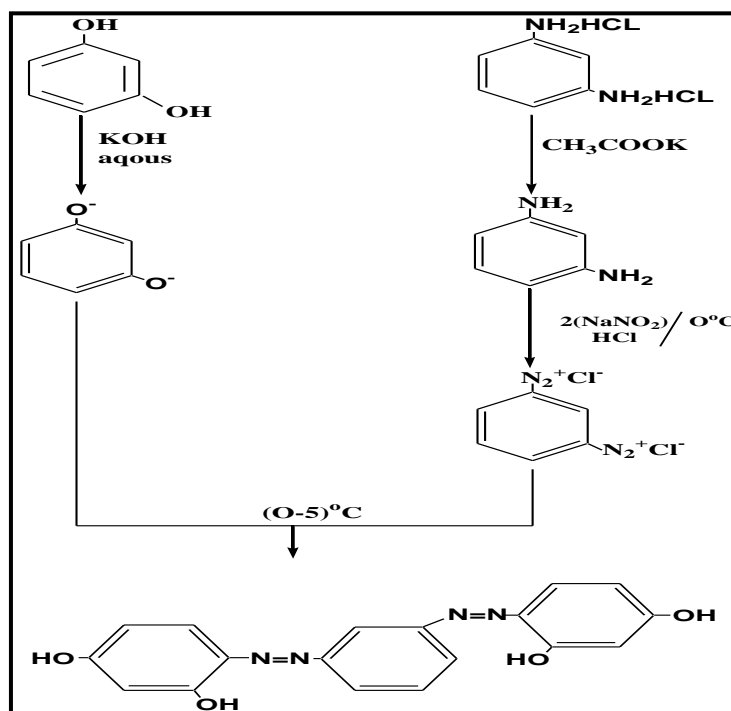
Compound	Bacillus(G^+)	E.coli(G^-)
Control	0,5	0,5
Ligand	1	1
[Mn.(II)(L).(H ₂ O) ₅]	1,5	4
[Fe.(II)(L).(H ₂ O) ₅]	2,5	1,5

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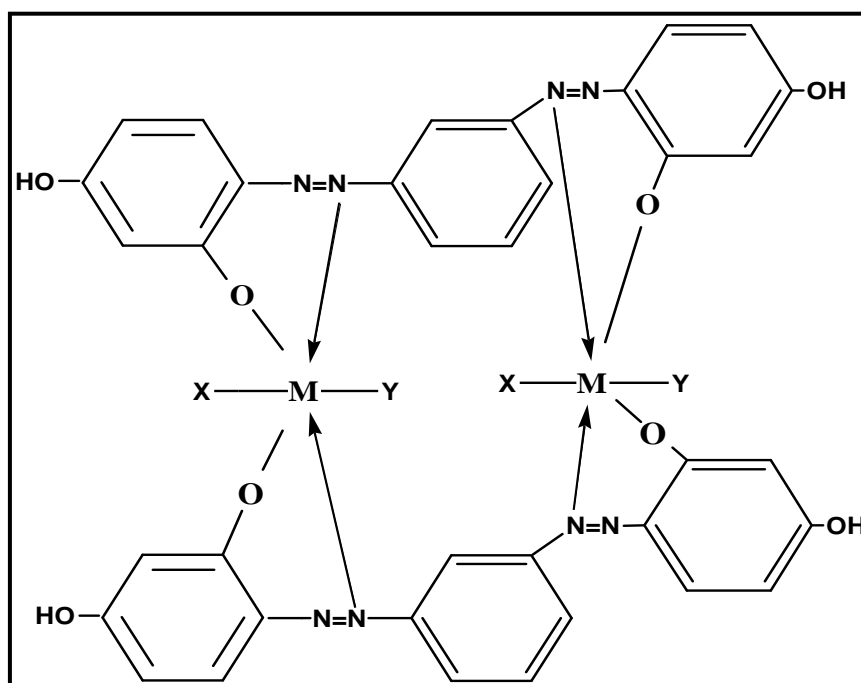
[Zn ₂ (II)(L) ₂ (H ₂ O) ₂]	٣	٢
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Scheme(1):The preparation of the ligand [H $_2$ L]



Where : M =Mn(II), Fe(II), Zn(II)

When: M = Mn X= H $_2$ O Y= H $_2$ O

M = Fe X= H $_2$ O Y= H $_2$ O

M = Zn X= H₂O Y= H₂O

Fig.(1): The proposed structure of the complexes

Table (2) : The microanalysis result and some physical properties for the ligand [H₂L] and its complexes

Compound	Formula	M.wt	Color	m. p. (°C)	Yield %	Chloride Content	Metal Found , Calculate
H ₂ L	C ₁₃ H ₁₃ N ₂ O ₂	250	orange	dec 120	81	Nil	-
[Mn ₂ (II)(L) ₂ (H ₂ O) ₂]	C ₂₇ H ₂₇ N ₄ O ₄ Mn ₂	877,8	brown	dec(290-300)	81	Nil	13,9 (13,3)
[Fe ₂ (II)(L) ₂ (H ₂ O) ₂]	C ₂₇ H ₂₇ N ₄ O ₄ Fe ₂	879,8	Dark brown	dec(300-303)	76	Nil	14,1 (13,6)
[Zn ₂ (II)(L) ₂ (H ₂ O) ₂]	C ₂₇ H ₂₇ N ₄ O ₄ Zn ₂	898,7	Dark orange	dec(300-305)	80	Nil	15,02 (15,7)

Table (3) Infrared spectral date (wave number ν)cm⁻¹ for the ligand [H₂L] and its complexes

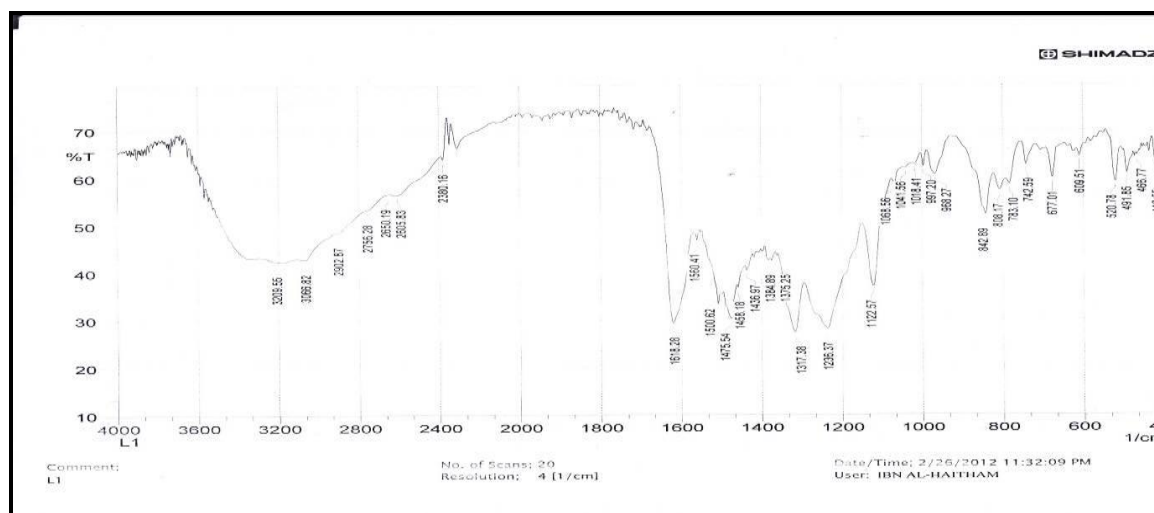
Compound	ν (N=N) _{orth} ν (N=N) _{meta}	ν (O-H) _z ν (O-H) _γ	ν (C=C) Aromatic	ν (C-O)	ν (M-N)	ν (M-O)
H ₂ L	1560 1475	3209 3066	1618	1236	-	-
[Mn ₂ (II)(L) ₂ (H ₂ O) ₂]	1508 1473	3464 3450	1562	1230	570	432
[Fe ₂ (II)(L) ₂ (H ₂ O) ₂]	1502 1473	3429 3398	1616	1230	570	432
[Zn ₂ (II)(L) ₂ (H ₂ O) ₂]	1504 1473	3414 3350	1616	1234	570	432

Table (4) Electronic spectral date for the ligand [H₂L] and its complexes Molar Ratio and Molar Conductivity

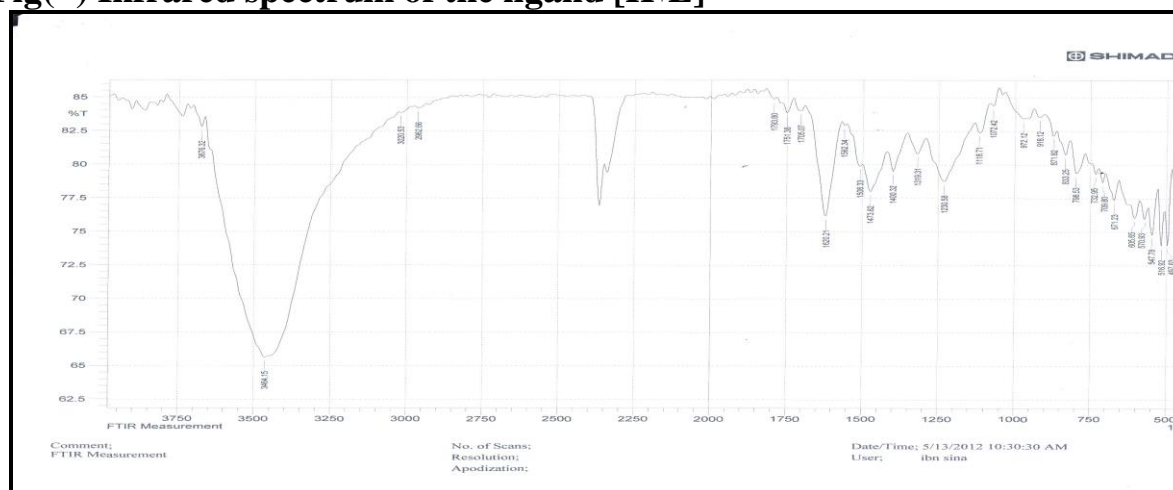
Compound	λ nm	ϵ max molar ⁻¹ cm ⁻¹	Assignment	Ratio	Λ_m S.cm ² .mol ⁻¹	Coordination
Ligand	263 304 419	362 217 130	(n- π^*) (n- π^*) (π - π^*)	-	-	-
[Mn ₂ (II)(L) ₂ (H ₂ O) ₂]	265 304 416 635	586 233 127 86	Ligand field (C.T) (C.T) (⁶ A _{1g} → ⁶ T _{1pr})	Non elec.	14,5	Octahedral

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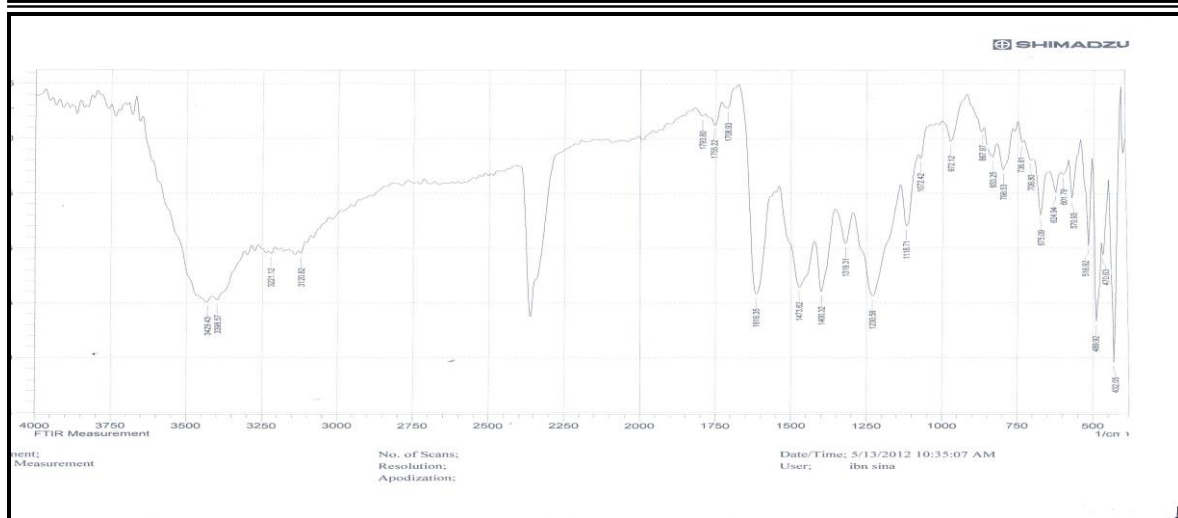
[Fe ₂ (II)(L) ₂ (H ₂ O) ₂]	٢٦٩ ٣٠٤ ٤١٦ ٧٣٠	٤٣٢ ٢٢٠ ١٢١ ٩٣	Ligand field (C.T) (C.T) (¹ E _g → ¹ T _{2g})	Non elec.	١٢,٢٥	Octahedral
[Zn ₂ (II)(L) ₂ (H ₂ O) ₂]	٢١٠ ٤٢٥	٣١٨ ١٠٩	Ligand field (C.T)	Non elec.	٢٦,٥٨	Octahedral



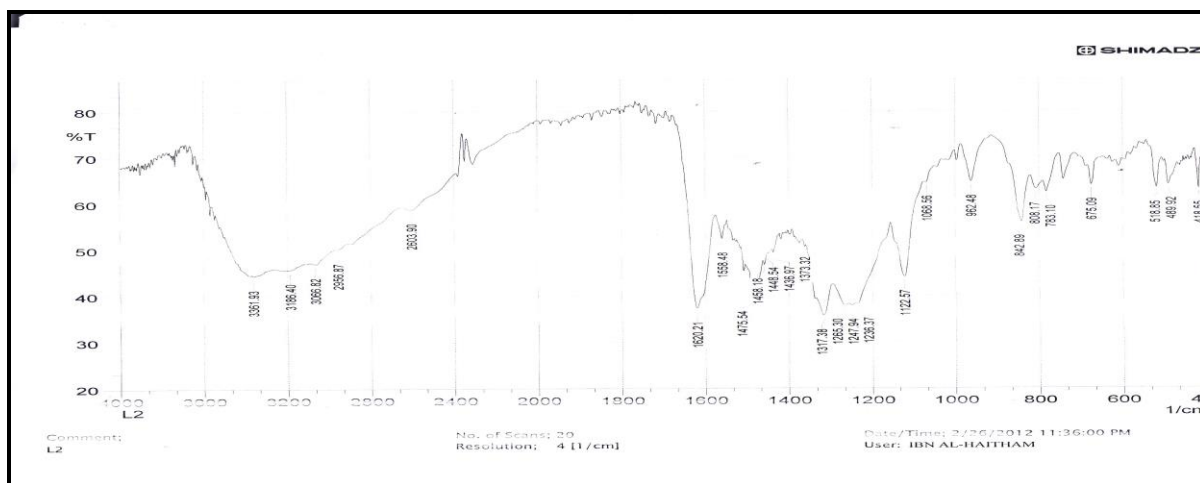
Fig(٢) Infrared spectrum of the ligand [H₂L]



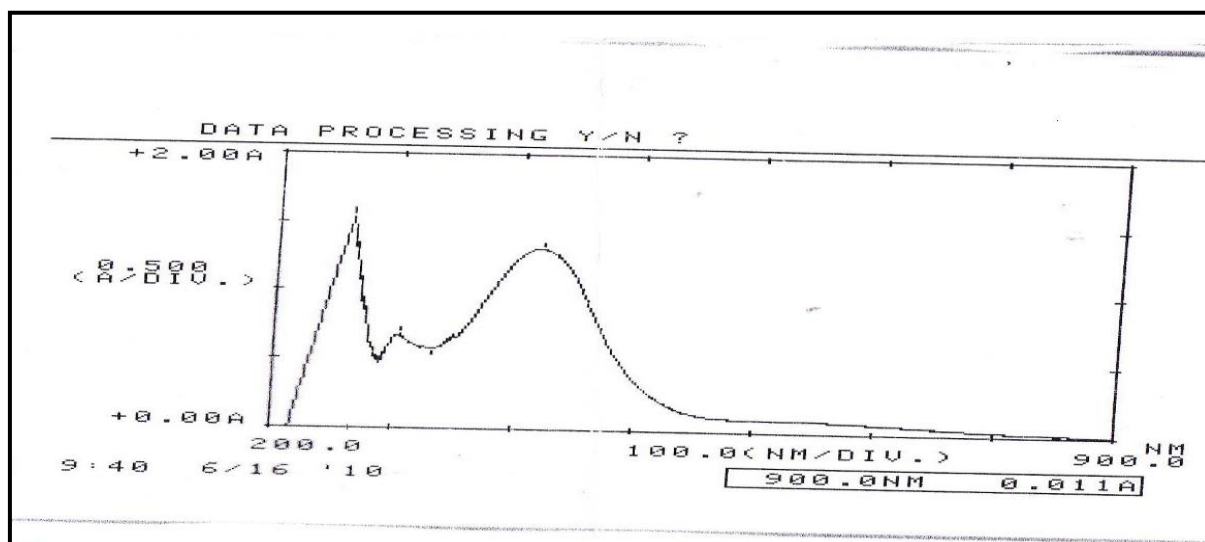
Fig(٣) Infrared spectrum of [Mn₂(II)(L)₂(H₂O)₂]



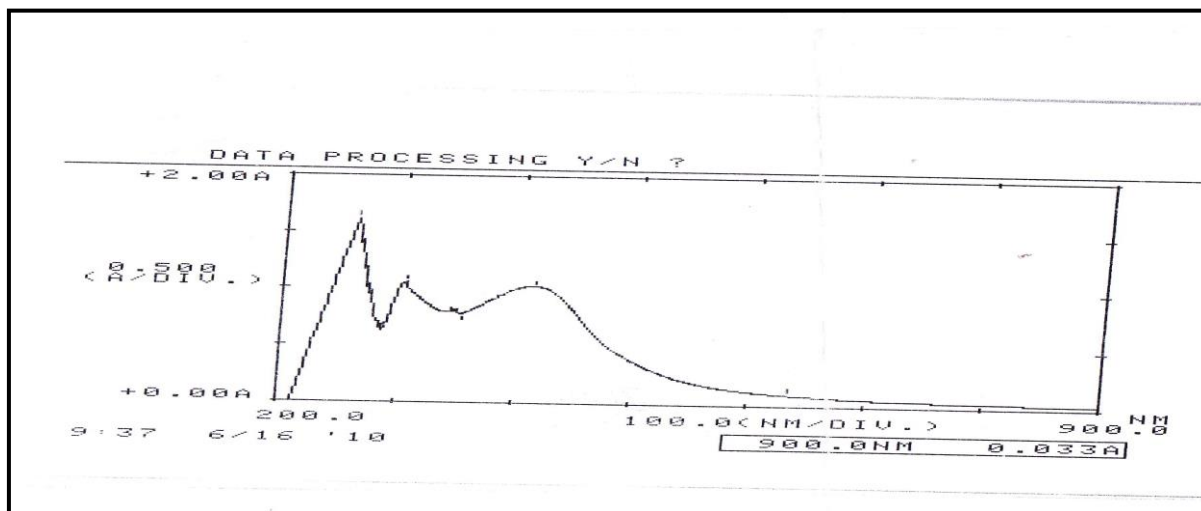
Fig(٤) Infrared spectrum of $[Fe(II)(L)(H_2O)]$



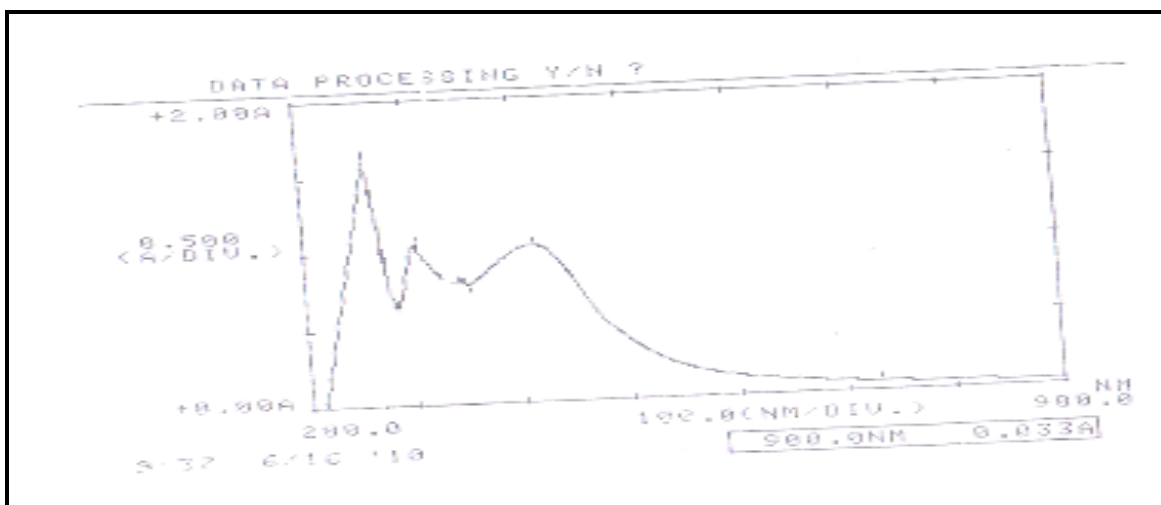
Fig(٥) Infrared spectrum of $[Zn(II)(L)(H_2O)]$



Fig(٧) Electronic spectrum of the ligand [H₂L]



Fig(٧) Electronic spectrum of [Mn(II)(L)₂(H₂O)₂]



Fig(٨) Electronic spectrum of [Fe(II)(L)₂(H₂O)₂]

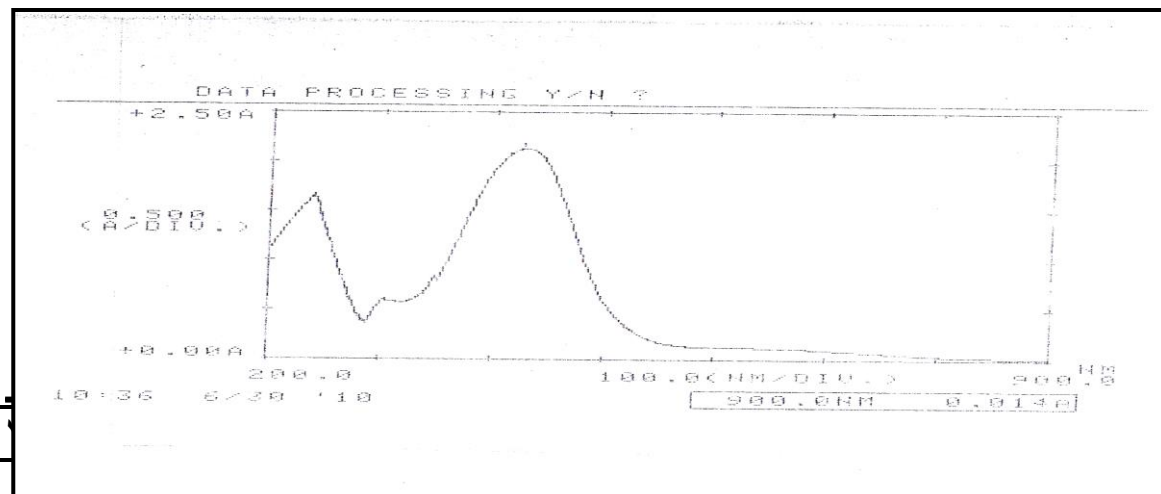


Fig.(٩) Electronic spectrum of $[Zn_2(II)(L)_2(H_2O)_4]$

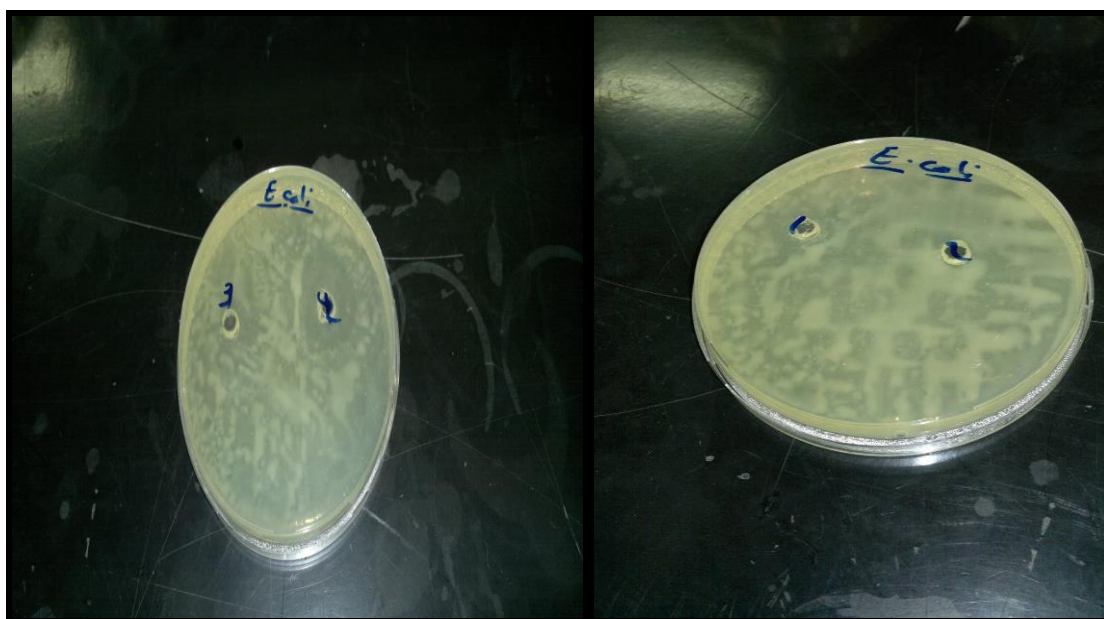


Fig.(١٠) Effect of compounds towards the E.coli



Fig.(١١) Effect of compounds towards the Bacillus

تحضير ودراسة طيفية وبايولوجية لمعقدات ثنائية النواة ب (Mn^(II), Fe^(II), Zn^(II)) مع ليكاند نوع N₂O₂

بيداء كريم سلمان

جامعة بغداد

كلية التربية- ابن الهيثم- قسم الكيمياء

الخلاصة

في هذا البحث تم استعمال m-phenylenediamine مع resorcinol لتحضير الليكاند m-phenylenebis(azoresorcinol) الرباعي السن من نوع N₂O₂ ومن ثم مفاعلة الليكاند مع املاح بعض العناصر الفلزية وباستخدام الايثانول وسطا للتفاعل ونسبة ٢:٢ وبوجود القاعدة (Et)₃N لتكوين المعقدات الثنائية النواة ذوات الصيغة العامة: [M₂(L)₂(H₂O)₄] وشخصت جميع المعقدات بالطرق الطيفية (الاشعة تحت الحمراء والاشعة فوق البنفسجية - المرئية) مع الامتصاص الذري للعناصر وقياسات محتوى الكلور ودرجات الانصهار مع التوصيلية الكهربائية. ومن النتائج اعلاه كان الشكل الفراغي المقترح لمعقدات المنغنيز والحديد والزنك هو ثماني السطوح.

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اما قياسات الفعالية البيولوجية فأظهرت ان المعقدات فعالة تجاه نوعين من البكتريا (G⁺) Bacillus ككروم موجب (G-) E.coli ككروم سالب.