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# Synthesis, Characterisation and biological activity for binuclear complexes with Co(II), Cu(II) and Zn(II) with new ligand m-phenylendi(azo-2-naphthol) ligand type $N_2O_2$.

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## Abstract

In this work, the(m-phenylenediamine) and (2-naphthol) have been used in the synthesis of tetradentate ligand [m-phenylenedi(azo-2-naphthol)][$H_2L$] type ($N_2O_2$). The ligand was refluxed in the ethanol with the metal ions [Co(II), Cu(II) and Zn(II)] salts, using triethyleamine as a base in (2:2) molar ratio to give the binuclear complexes. These complexes were characterised by (A.A), F.T.I.R, (U.V-Vis) spectroscopies, along with conductivity, chloride content and melting point measurement. These studies revealed an octahedral geometries for Co(II), Cu(II) and Zn(II) complexes with the general structure [$M_2(L)_2(H_2O)_4$]. The ligand and its complexes exhibited biological activity against the Bacillus(G+) strain and the Pseudomonase(G-)strains.

Keyword: m-phenylene, azo, 2-naphthol

## Introduction

The naphthols are naphthalene homologues of phenol, with the hydroxyl group being more reactive than the phenols, they can be used in production of dyes and in organic synthesis[1], pigments, fluorescent whiteners, tanning agents, antioxidants and antiseptics[2].

2-naphthol compounds had medical uses as a counterirritant in alopecia, also as an anthelmintic and as an antiseptic in treatment of scabies[3]. Azo compounds are among the most popular synthetic dyes, especially in the clothing and fashion industry. Typically, azo dyes are also used in a variety of cosmetics[4] and as a food coloring[5], and its biological activity along with oxidation catalysis and electro chemical analysis[6,7]. In the recent past, number of studies have highlighted the use of azo compounds in various significant applications[8,9]. The aim of the present study is synthesis, characterisation and evaluate the metal complexes as antibacterial agent as promising addition of new class of complexes as metal based drugs.

## Materials and Methods

All chemicals used supplied from Fluka and Merck companies and used without any further purification. Infrared spectra were performed using a Shimadzu (FT–IR)–8400S spectrophotometer in the range (4000 – 400 $cm^{-1}$). Spectra were recoded as potassium bromide discs at Ibn-sina company. The electronic spectra of the compounds were obtained using a (U.V.–Visible) spectrophotometer type Shimadzu 160, in the range (200–900 nm) using quartz cell of (1.0)cm length with concentration ($10^{-3}$) mole $L^{-1}$ of samples in DMF at 25°C, and electrical conductivity measurements of the complexes were recorded at (25°C) for ($10^{-3}$–$10^{-5}$)M solutions of the samples in DMF using a PW 9526 digital conductivity meter. The chloride content determined using potentiometric titration method on 686–Titro Processor–665 Dosim A–Metrohm/Swiss, and melting point obtained using an electrothermal apparatus Stuart, and metals were determined with a Shimadzu (A.A.) 680G atomic absorption spectrophotometer, all measurements were obtained in Ibn Sina company. Antibacterial screening was done at central laboratory in biological department, college of science, university of Baghdad, using agar diffusion technique. The compounds were screened for their in vitro antibacterial activity against Gram-negative of psedomonase and Gram-positive of Bacillus bacterial strains.

**1-Preparation of the precursor m-phenylenediazo.**

M-phenylenediamine (2.0 g, 18 mmol.) was dissolved in warm mixture of 15 ml. of concentrated hydrochloric acid and 15 ml. of water contained in 250 ml. beaker, kept in ice-salt bath (0-5) °C whilst stirring vigorously, m-phenylenediamine hydrochloride will separate in a finely divided crystalline form. A cold solution of sodium nitrite (2.48 g, 36 mmol.)in 16 ml. of water was added slowly and with stirring to an end-point with potassium ioded-starch paper.

**2-Preparation of the ligand m-phenylenedi(azo-2-naphthol)[$H_2L$].**

2-naphthol (5.0 g, 36 mmol.) was dissolved in a solution of sodium hydroxide (7.0 g)in 25 ml. water, then cooled in ice bath and added to the diazotized solution with stirring. Concentrated hydrochloric acid was added slowly and with vigorous stirring, and then filtered with gentle suction, washed with water until free acid and dried upon filter-paper in the air, the yield percent (74%), m.p.(240 °C) dec.

**3-Preparation of the $[Co_2(L)_2(H_2O)_4]$ complex(1).**

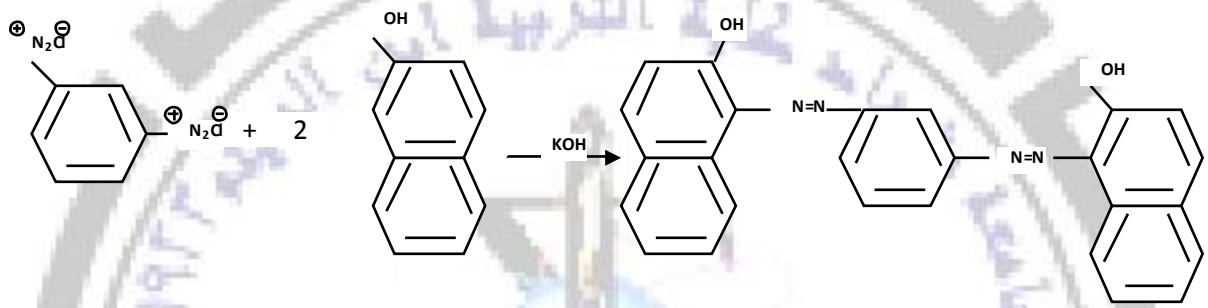
A solution of (0.1 g, 0.4 mmol.) of hexahydrated cobalt(II) chloride dissolved in 10ml. ethanol was added dropwise to a solution of [$H_2L$] (0.2 g,0.4 mmol.) dissolved in 15ml.hot ethanol, the PH of the reaction mixture was adjusted by adding triethyleamine in equivalent quantity, and the reaction mixture was allowed to reflux for 2 hours. A precipitate was formed, which was filtered off, washed several times with absolute ethanol and dried, the yield percent (86%), m.p.(over 300 °C) dec.

**4-Preparation of the $[Cu_2(L)_2(H_2O)_4]$(2) and $[Zn_2(L)_2(H_2O)_4]$(3) complexes.**

A similar method to that mentioned for the preparation of $[Co_2(L)_2(H_2O)_4]$(1) complex was used to prepare the complexes of the $[H_2L]$ with Cu(II) and Zn(II) ions.

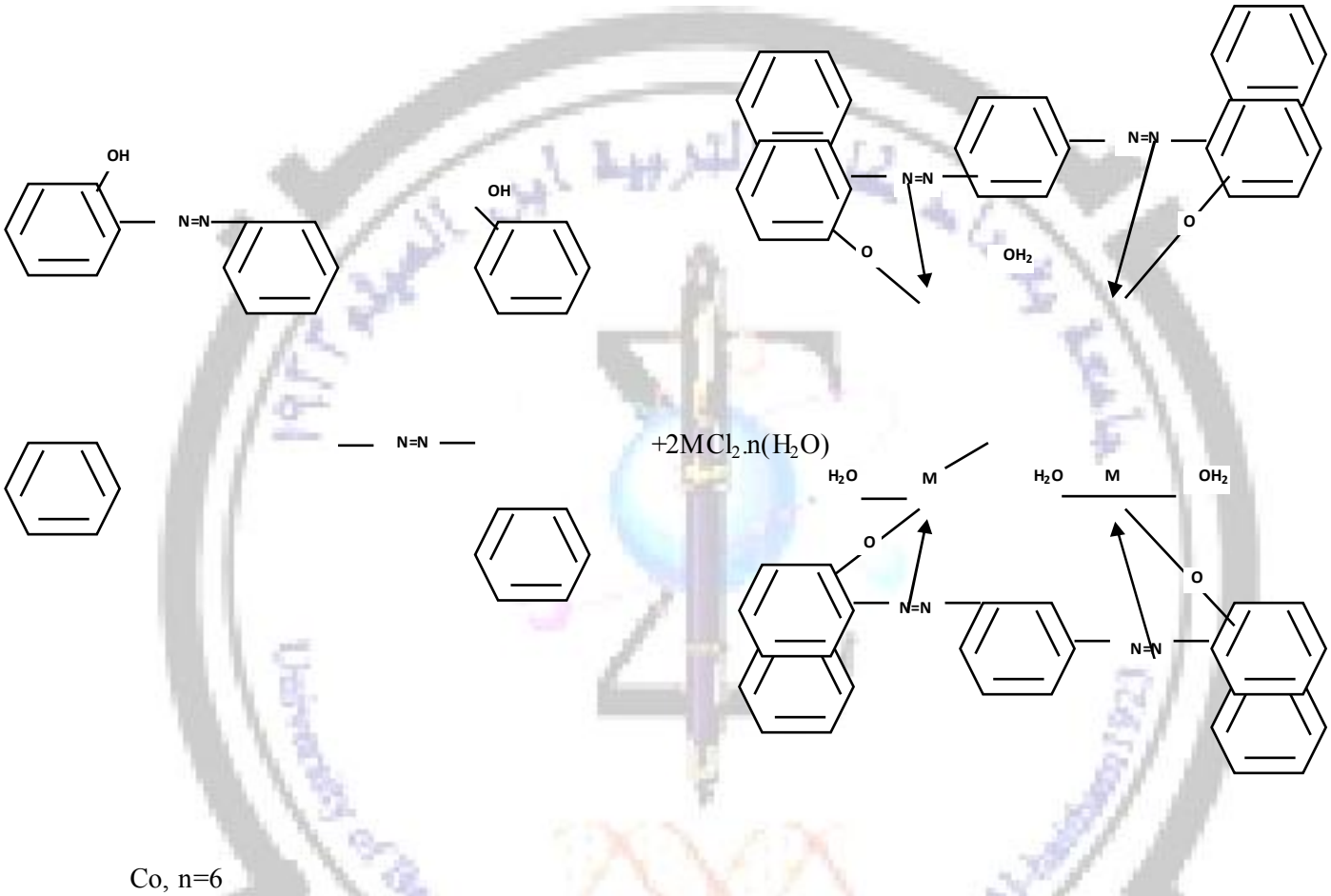
## Results and Discussion

The ligand $[H_2L]$ was obtained in high yield by the addition reaction using one equivalent of m-phenylenediazonium and two equivalent of 2-naphthol, where a potentially tetradentate new cyclic ligand type $N_2O_2$ donor atoms have been synthesised. The ligand contains two labile proton $[H_2L]$ and by removing these protons an anionic(-2) tetradentate system is formed. The ligand was prepared according to the route shown in the Scheme 1.




**Scheme 1 preparation of the ligand $[H_2L]$**

All complexes were prepared with similar method by refluxing the ligand $[H_2L]$ with the corresponding metal chloride salt in ethanol, as a solvent, and triethyleamine, as a base where the pure complexes were formed Scheme 2




Co, n=6

Cu, n=2

Zn, n=0

Scheme 2 Preparation route of the metal complexes.

**Infrared spectral data**

I.R. spectral data for the ligand [$H_2L$] and 1, 2 and 3 complexes are shown in Figs.(1,2,3 and 4) respectively . The important infrared bands for the ligand and the produced complexes with their assignments are listed in Table (1).

The I.R. spectrum for [$H_2L$] displayed band at 3028$cm^{-1}$ assigned to the aromatic ν(C-H) stretching while a broad band at 3464$cm^{-1}$ can be attributed to ν(OH) stretching and the absence of this band in all complexes indicates the deprotonation followed by complexation[10], while appearance of bands at (3444, 3429 and 3433) and at(991,995 and 991)$cm^{-1}$ for complexes 1, 2 and 3 respectively assigned to coordinated aqua($H_2O$)ligands. The two bands at (1554 and 1496)$cm^{-1}$ which can be attributed to ν(N=N) stretching ortho and meta respectively in the spectrum of the free ligand, were shifted to a lower frequencies and appeared at (1500,1446), (1500,1473) and (1500,1481)$cm^{-1}$ for complexes 1, 2 and 3 respectively, the shift to lower frequency may be due to delocalisation of metal electron density into the ligand π-system(HOMO→LUMO), indicating the coordination of nitrogen atom to the metal ions[11,12]. On the other hand, the band at 1315$cm^{-1}$ which attributed to the ν(C-O) stretching vibration in the spectrum of the free ligand, was shifted to a lower frequencies and observed at 1253, 1300 and 1300$cm^{-1}$ for the complexes 1, 2 and 3 respectively, this shift in the ν(C-O)vibration confirms the coordination of nitrogen of the ligand through the oxygen atom to the metal ion[13,14]. Finally the complexes exhibited bands at the ranges 462-497 and 524-555$cm^{-1}$ which could be assigned to the ν(M-O) and ν(M-N) stretching vibration modes respectively.

**(U.V.-Vis.) spectra**

(U.V.-Vis.) spectra and molar conductivity measurement for the ligand and its complexes 1, 2 and 3 were shown in Table (2), and the U.V.-Vis. spectra were shown in Figs.(5,6,7 and 8) respectively. The U.V.-Vis. spectrum of [$H_2L$] exhibited intense absorption peak at 305nm due to the (π → π*) transition, and peak at 486nm related to(n→ π*) transition[15], The U.V.-Vis. spectrum of complex 1, exhibited a high intense peak at 240nm due to the (π → π*) transition and peak at 312nm which refer to the(n→ π*) transition, while a peak at 495nm which refer to the (C.T.)transition. Finally the peak at 687nm may be due to ($^4T_1g^{(F)} \rightarrow {}^4A_2g^{(F)}$) transition[16], corresponding to an octahedral geometry around the cobalt(II) ion. The U.V.-Vis. spectrum of complex 2, exhibited a peak at 212nm due to the(π → π*) transition, a peak at 242nm due to (n→ π*) transition, and a peak at 368nm which refer to the (C.T.) transition, while a peak at 507nm due to ($^2B_1g \rightarrow {}^2B_2g$) transition[16], corresponding to an octahedral geometry around the cupper(II) ion. The U.V.-Vis. spectrum of complex 3 exhibited a peak at 207nm due to the (π → π*) transition, a peak at 242nm due to (n→ π*)transition, and a peak at 287nm which refer to (C.T.) transitions[16], the metal ion Zn(II) of this complex belong to $d^{10}$ system and this metal do not show (d-d)transition[16], suggesting to an octahedral geometry around the zinc(II) ion[17].

The molar conductance of the complexes in DMF lie in the 3.01-5.45 $S.cm^2.mole^{-1}$ range, indicating their non-electrolytic behavior[18].

**Biological screening : The antibacterial activity test**

In our study the synthesised compounds have been screened for their antibacterial activity against the Bacillus(G+) and Pseudomonase(G-) strains by the Nutrient agar diffusion technique[19]. Each of the compounds was dissolved in DMF to give a final concentration of 0.001mg/ml, and from the data shown in Table 3, and Figs.9 and 10 , all compounds exhibited a biological activity against the Bacillus(G+) strain [inhibition zone = 20, 21, 22 and 30mm] for the ligand [$H_2L$], Co(II), Cu(II) and Zn(II) complexes respectively, also the compounds exhibited a biological activity against the Pseudomonase(G-) strain [inhibition zone = 20, 5, 5 and 25mm] for the ligand [$H_2L$], Co(II), Cu(II) and Zn(II) complexes respectively.

Table (4) represented below shows the chloride content, melting point, atomic absorption and some other physical properties for the ligand and the synthesised complexes.

## References

1- Ikeda, T.; Misawa, N.; Ichihashi, Y.; Nishiyama, S. and Tsuruya, S., (2005), " Coupling of 2-naphthol by vanadium catalyst supported liqud-phase oxidative on mcm-41", Journal of Molecular Catalysis A: Chemical, 231: 1381-1169.

2- Charles, C. (1986) W.M. Toxicology of the Eye. 3rd ed. Springfield, IL, 656.

3-Van der zee, F. P.; Lettinga ,G. and Field, J. A. (2000) The role of (auto)catalysis in the mechanism of an anaerobic azo reduction", Water Science & Technology 42: 301-308.

4- Peter Vollhardt and Neil Schore (2010) Organic Chemistry, Structure and Function, 6th Edition, W. H. Freeman.

5- Fennema, O.R. (1996) Food Chemistry, 3rd edition, CRC Press.

6- Djebbar, S.; Benali, B.; and Deloume, J. (1998) Synthesis, characterization, electrochemical behaviour and catalytic activity of manganese(II) complexes with linear and tripodal tetradentate ligands derived from Schiff bases Trans.Met. 23: 443-447.

7- Sakakibara, Y.; Okutsu S.; Enokida, T. and Tani T. (1999) Red organic electroluminescence devices with a reduced porphyrin compound, tetraphenylchlorin, Applied Physics Letters 74: 2587.

8- Maurya, RC.; Verma, R. and Singh, H. (2003) Synthesis and Physico-Chemical Studies of Some Mixed-Ligand Complexes of bis(Benzoylacetonato)copper(II) with Some Biologically Active Heterocyclic Chelating Donors, synthesis and Reactivity in Inorganic and Metal-organic Chemistry, 33: 1063-1080.

9- Maurya, RC.; Rajput, S., (2003), "Vanadium Complexes of Bioinorganic Relevance: Synthesis, Magnetic, and Spectral Studies of Some Mixed-Ligand Oxovanadium(IV) Complexes Having an N, O-Donor Environm", synthesis and Reactivity in Inorganic and Metal-organic Chemistry, 33: 1877-1894.

10- Saravanakumar, D.; Sengottuvelan, N.; Priyadarshni, G.; Kandaswamy, M. and Okawa, H. (2004) Synthesis of unsymmetrical 'end-off' phenoxo and oximinato di bridged copper(II) and nickel(II) complexes: spectral, electrochemical and magnetic properties. Polyhedron, 23: 665-672.

11- Socrates, G. (1980) Infrared Characterstic Group Frequencies, Wiley, Newyork, 32-37.

12- El-Sonbati, A.Z.; El-bindary, A.A. and Al-Sarawy, A.A. (2002) Stereochemistry of new nitrogen containing heterocyclic aldehyde. IX. Spectroscopic studies on novel mixed-ligand complexes of Rh(III)", Spectrochim Acta Part A 58: 2771-2778.

13- Sreedaran, S.; Bharathi, K.S.; Rahiman, A.K.; Rajesh, K.; Nirmala, G.; Jagadish, L.; Kaviyarasan, V. and Narayanan, V. (2008) Synthesis, electrochemical, catalytic and antimicrobial activities of novel unsymmetrical macrocyclic dicompartmental binuclear nickel(II) complexes", Polyhedron, 27: 1867.

14 – Sreedaran, S.; Bharathi, K.S.; Rahiman, A.K.; Jagadish, L.; Kaviyarasan, V. and Narayanan, V. (2008) Novel unsymmetrical macrocyclic dicompartmental binuclear copper(II) complexes bearing 4- and 6-coordination sites: Electrochemical, magnetic, catalytic and antimicrobial studies", Polyhedron, 27: 2931.

15- Samir, A.H.; Hasan, A. and Aziz, M.R. (2010)synthesis of some metal complexes of azo type ligand and evaluation of their antibacterial activity", Journal of College of Education al-mustansirya university, 1: 392-406.

16- Lever, A.B.P. (1984) Inorganic electronic spectroscopy, 2nd edn. Elesvier, New York.

17- Tajmir-Riahi, H.A. (1991) Coordination chemistry of vitamin C. part II. Interaction of L-Ascorbic acid with ZnII, CdII, HgII and MnII ions in the solid state and in aqueous solution", Journal of Inorganic Biochemistry, 42: 47-55.

18- Geary, W.J. (1971) The use of conductivity measurements in organic solvents for the characterisation of coordination compounds", Coord.Rev., 7: 81-122.

19- Shank, R.C.; Duguid, J.P.; Marmion, B.P. and Swain, R.A. (1975) Medical Microbiology the Practical of Medical Microbiology" 12th ed. Long Man Group Lted London, 2.

**Table (1): I.R. spectral data of the synthesised compounds**

| υ(M-O) | υ(M-N) | υ(C-H) aromatic | υ(C-O) | υ(C-C)naph. υ(C-C)phen. | υ(C=C)naph. υ(C=C)phen. | υ(N=N)ortho υ(N=N)meta | υ (O-H) | compound |
|---|---|---|---|---|---|---|---|---|
| - | - | 3028 | 1315 | 1450<br>1404 | 1610<br>1600 | 1554<br>1496 | 3464 | $[H_2L]$ |
| 497 | 555 | 3059 | 1253 | 1357<br>1303 | 1597<br>1550 | 1500<br>1446 | 3444<br>991<br>aqua | $[Co_2(L)_2(H_2O)_4]$ |
| 462 | 524 | 2974 | 1300 | 1400<br>1346 | 1593<br>1549 | 1500<br>1473 | 3429<br>995<br>aqua | $[Cu_2(L)_2(H_2O)_4]$ |
| 466 | 550 | 3062 | 1300 | 1400<br>1342 | 1600<br>1546 | 1500<br>1481 | 3433<br>991<br>aqua | $[Zn_2(L)_2(H_2O)_4]$ |

**Table (2): (U.V.-Vis.) spectral data and molar conductivity in DMF solution.**

| Suggested structure | Ratio | $S.cm^2 \Lambda_m mol^{-1}$ | Assignments | $\lambda$ | compound |
|---|---|---|---|---|---|
| | | – | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$ | 305<br>486 | $[H_2L]$ |
| octahedral | Non-electrolyte | 5.45 | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$<br>C.T.<br>$^4T_1g^{(F)} \rightarrow {}^4A_2g^{(F)}$ | 240<br>312<br>495<br>687 | $[Co_2(L)_2(H_2O)_4]$ |
| octahedral | Non-electrolyte | 3.01 | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$<br>C.T.<br>$^2B_1g \rightarrow {}^2B_2g$ | 212<br>242<br>365<br>507 | $[Cu_2(L)_2(H_2O)_4]$ |
| octahedral | Non-electrolyte | 4.23 | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$<br>C.T. | 207<br>242<br>287 | $[Zn_2(L)_2(H_2O)_4]$ |

C.T. :Charge Transfer

**Table (3): The biological activity of the compounds**

| Pseudomonase (G-) | Bacillus (G+) | compound |
|---|---|---|
| 20 | 20 | $[H_2L]$ |
| 5 | 21 | $[Co_2(L)_2(H_2O)_4]$ |
| 5 | 22 | $[Cu_2(L)_2(H_2O)_4]$ |
| 25 | 30 | $[Zn_2(L)_2(H_2O)_4]$ |
| 2 | 2 | control |

**Table (4): Results of elemental analysis and physical properties for the ligand and the synthesised complexes**

| $Cl^-$ content | Metal Found, (calculate) | m.p. | Color | Yield % | M.wt | compound |
|---|---|---|---|---|---|---|
| - | - | 240 Dec. | Red-brown | 74 | 418 | $[C_{26}H_{18}N_4O_2]$ |
| Nil | 11.9 (12.4) | Over 300 Dec. | brown | 86 | 1021.8 | $[Co_2^{II}C_{52}H_{32}N_8O_4(H_2O)_4]$ |
| Nil | 13.0 (13.2) | Over 300 Dec. | Dark brown | 45 | 1031 | $[Cu_2^{II}C_{52}H_{32}N_8O_4(H_2O)_4]$ |
| Nil | 13.2 (13.5) | Over 300 Dec. | brown | 86 | 1034.8 | $[Zn_2^{II}C_{52}H_{32}N_8O_4(H_2O)_4]$ |

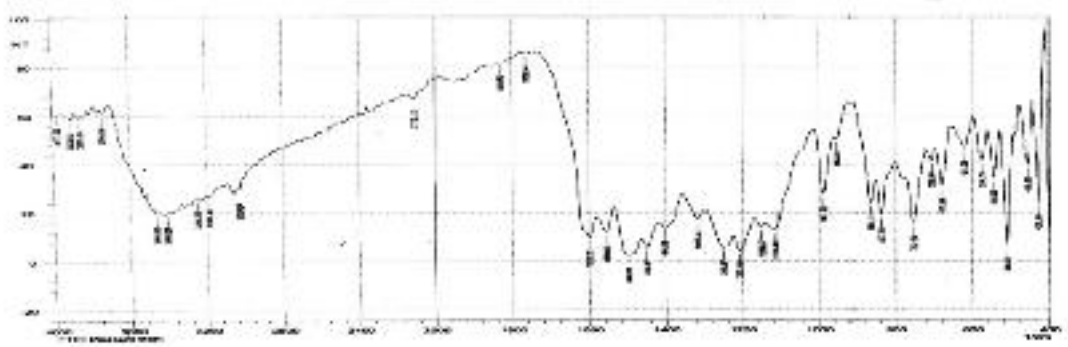


**Fig. (1): The I.R Spectrum of Ligand [$H_2L$]**

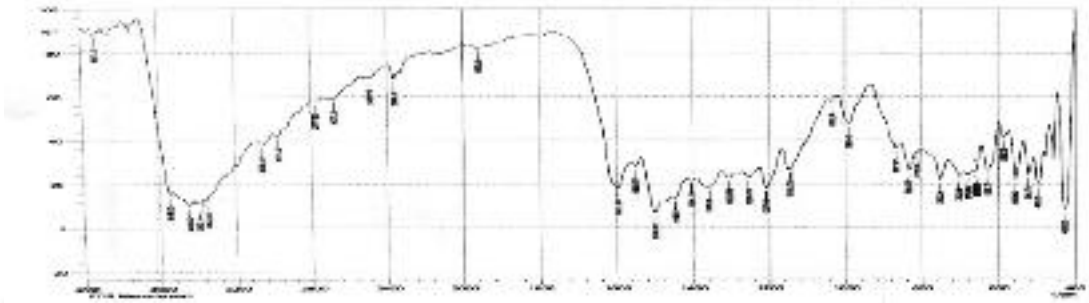


**Fig. (2): The I.R Spectrum of complex (1)**

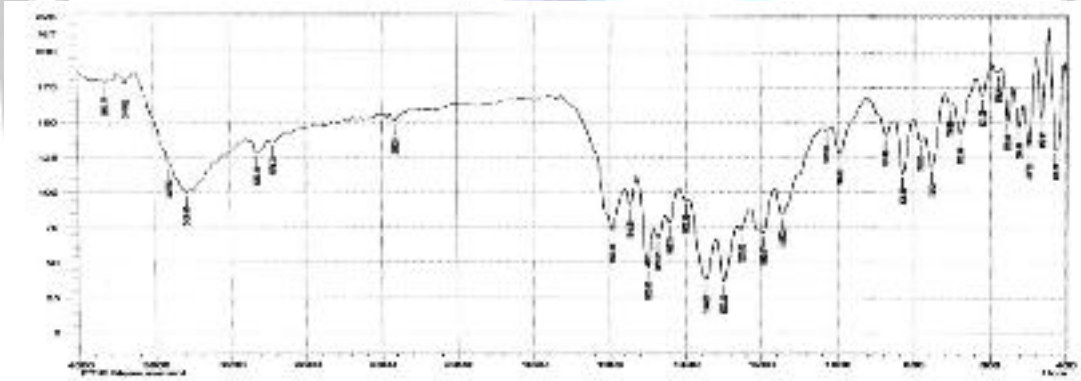


**Fig. (3): The I.R Spectrum of complex (2)**

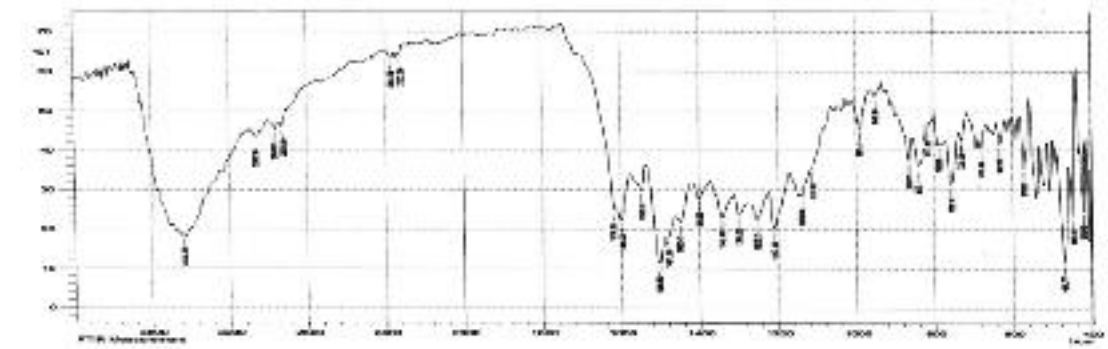


**Fig.(4): The I.R Spectrum of complex (3)**

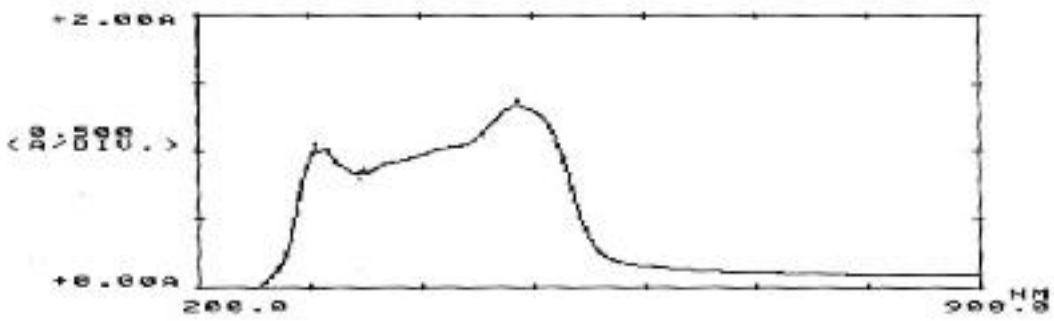


Fig. (5): The U.V.-Vis. Spectrum of ligend ($H_2L$)

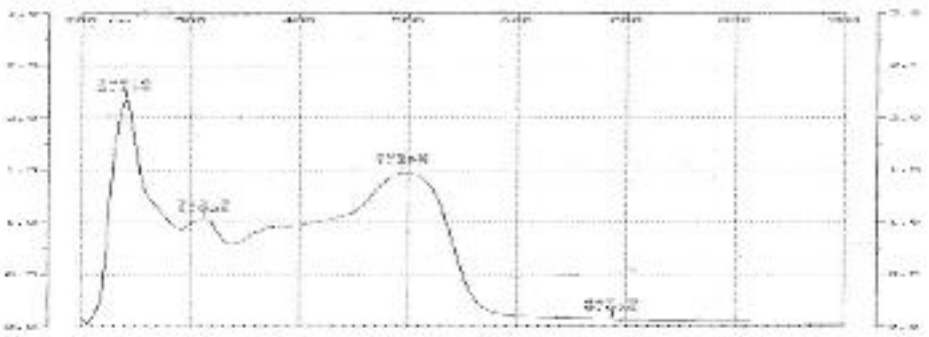


Fig.(6): The U.V.-Vis. Spectrum of complex (1)

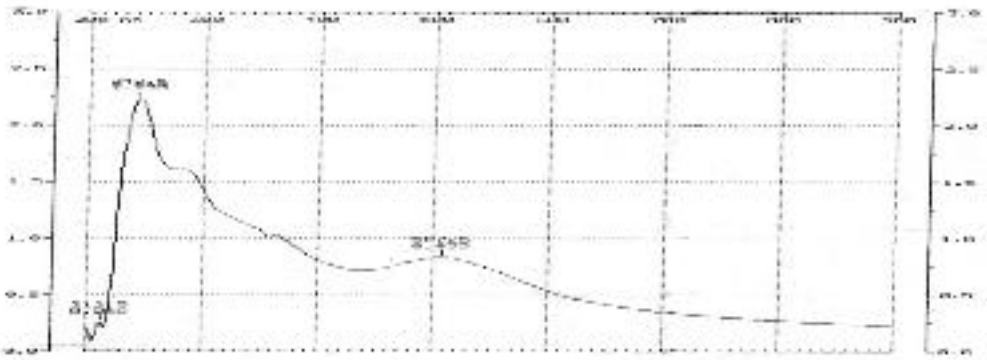


Fig.(7): The U.V.-Vis. Spectrum of complex (2)

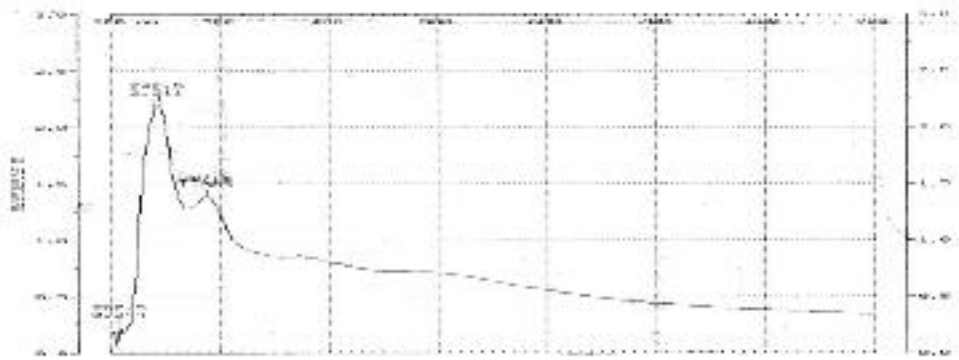


Fig.(8): The U.V.-Vis. Spectrum of complex (3)


**Fig.( 9): Effect of the compounds towards the Bacillus**

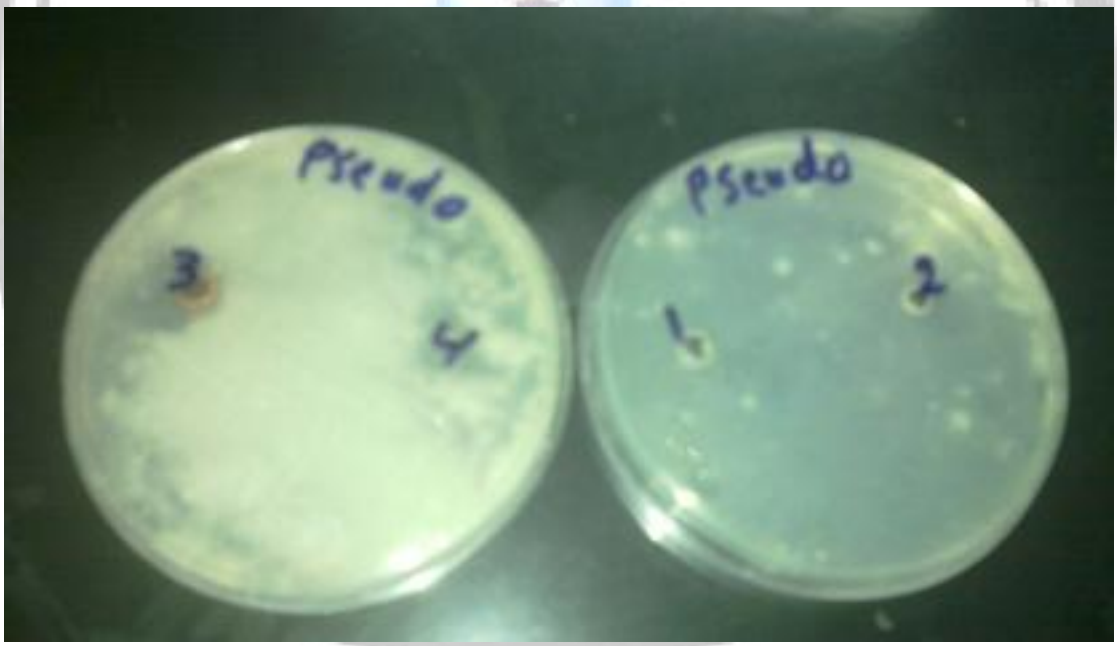



**Fig. (10): Effect of the compounds towards the**

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# تحضير وتشخيص و دراسة الفعالية البيولوجية

# لمعقدات ثنائية النواة بCo(II)، Cu(II)، Zn(II)مع الليكاند الجديد

# m-phenylendi(azo-2-naphthol) type $N_2O_2$

**ورود علي جعفر الساعدي**

**قسم الكيمياء كلية التربية ابن الهيثم جامعة بغداد**

**استلم البحث في :23 تشرين الثاني 2011 قبل البحث في :11 كانون الثاني 2012**

## الخلاصة

في هذا البحث تم إستعمال (m-phenylenediamine) و(2-naphthol) لتحضير الليكاند الرباعي السن [m-phenylenedi(azo-2-naphthol)][$H_2L$] من نوع ($N_2O_2$).

تم تصعيد الليكاند بإستعمال الايثانول مذيبا مع املاح الايونات [ Co(II) و Cu(II) مع Zn(II) ] بنسبة 22: بوجود تراي اثيل امين قاعدة لتكوين المعقدات الثنائيه النواة. شخصت المعقدات بالطرائق الطيفية (الاشعة تحت الحمراء والاشعة فوق البنفسجية-المرئية مع الامتصاص الذري) ،وقياسات محتوى الكلوريد، و التوصيلية الكهربائية مع درجة الانصهار. هذه الدراسات بينت ان الشكل الهندسي هو ثماني السطوح لمعقدات [ Co(II) و Cu(II) مع Zn(II) ] بالصيغة العامة [$M_2(L)_2(H_2O)_4$] أما قياسات الفعالية البيولوجية فأظهرت ان المعقدات فعالة تجاه نوعين من البكتريا Bacillus(G+) and Pseudomonase(G-)strains.

**الكلمات المفتاحية** : m-phenylenediamine , **azo, 2-naphthol**

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