

Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary¹, Basima Abdul HussinZaidan² and Nibras A. Al-marsomy³

^{1,2}Department of Chemistry- College of Education for Pure Sciences- Ibn -Al-Haitham University of Baghdad

Received 22 May 2016

Accepted 17 October 2016

Abstract

In this work the preparation and characterization of tetradentate ligand (H_2L). The ligand obtained from the reaction of benzidine with 2-benzoyl benzoic acid . The synthesized ligand(H_2L) was characterized by UV-Vis , FT-IR spectroscopy, 1H , 13 C-NMR spectra, melting point and (C.H.N). The mixed ligand complexes were synthesis from ligand(H_2L) was used as a primary ligand while 1,10-phenanthrolineligand (phen) was used as a secondary ligand with metal ion (M(II) : Cu(II),Co(II), Mn(II) ,Ni(II) and Hg(II)). All the complexes were characterized by UV-Vis, FT-IR spectroscopy methods, elemental analysis (A.A), melting point measurements, conductivity and magnetic susceptibility. These measurements showed tetrahadral geometry around (Mn and Ni) ions and square planer geometry around (Co, Cu and Hg) ions. The antibacterial activity of (H_2L) and [$M_2(phen)_2(L)$]Cl₂] complexes in molar ratio [2:2:1] [M:(phn):L] were studied by using (MIC) inhibition method.

Keywords: Characterization, Schiff bases, 2-benzoyl benzoic acid, binuclear complexes, Benzidine and Biological activity.

Vol: 13 No:3 , July 2017 21 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

تخليق، تشخيص وتقييم الفعالية البايولوجية للمعقدات المزيج الليكاند قاعدة شف مشتقة من Benzidine, 2-Benzoyl benzoic acid

رحاب كاظم الشمرى 1 و باسمة عبد الحسين زيدان 2 و ونبراس عبد الامير المرسومى 3

1.2 قسم الصناعات الكيميائية - معهد التكنولوجيا - جامعة بغداد قسم الكيمياء كلية التربية ابن الهيثم للعلوم الصرفة -جامعة بغداد

الخلاصة

في هذا العمل تم تحضير وتشخيص ليكاند رباعي السن (H2L) من خلال تفاعل benzidine مع Denzidine في هذا العمل تم تحضير وتشخيص ليكاند رباعي التفاعل باستخدام الإيثانول المطلق كمذيب وبطريقة التصعيد الحراري، تم تشخيص الليكاند المحضر باستخدام اطياف الاشعة تحت الحمراء واطياف الاشعة فوق البنفسجية وطيف الرنين النووي المغناطيسي للبروتون وللكاربون13 والتحليل الدقيق للعناصر ودرجة الانصهار حضرت معقدات خلائط الليكاند تم الستخدام الليكاند (H2L) كليكاند الولي بينما (Phenanthroline (phn) كليكاند ثانوي مع M(II) = (Co, Mn كليكاند ثانوي مع الموق الطيفية الطرق الطيفية (1,10-phenanthroline (phn) بالصيغة بنسبة مولية (2:2:1). جميع هذه المعقدات المحضرة شخصت بواسطة الطرق الطيفية (اطياف الاشعة تحت الحمراء و اطياف الاشعة فوق البنفسجية والتحليل الدقيق للعناصر وقياسات درجة الانصهار وقياسات التوصيلية والحساسية المغناطيسية. وتم أستنتاج الشكل الهندسي رباعي السطوح حول الايونات الفلزية (H2L)و (Au) ومربع مستوي حول الايونات الفلزية (Cu and Hg) بنسبة مولية (2:2:1)[[M:(phen):(L)]باستخدام طريقة التثبيط.

الكلمات المفتاحية: تشخيص ، قواعد شف ،benzoyl benzoic acid،معقدات ثنائية النواة ،Benzidine والفعالية البايولوجية

Introduction

The compounds have (-HC=N-) azomethine group are called Schiff bases, which were product by condensation of carbonyl compounds with primary amines [1]. They are also known as imines or anils and their metal chelates can be used in coloring dying processes, catalysis [2], analytical applications, biological systems and the spectroscopic studies[3]. A

Vol: 13 No:3 , July 2017 22 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

generally coordinates N atom of imines groups and O atoms of the deprotonated carboxylate groups in the Schiff base ligand[4]. In chemistry Schiff base ligands have considerable importance; chiefly they are possible capable of forming with metal ions stable complexes in the expansion of their complexes [5]. The oxygen donor organic compounds that large physiological importance through coordination them with metal ions which made the interested users are studied and synthesized structural aspects for some oxygen, sulphur and nitrogen donor atoms in ligands with metal ions[6]. Carboxylates complexes have observed significant attention due to their broad applications in numerous fields such as potential antineoplastic [7], PVC stabilizers[8], anti-tumour drugs[9], polymer catalysts[10], PS photo stabilizers[10]as well as ant tuberculosis agents[11]. Binuclear one of types Schiff bases has their powerful coordination capacities ,that meaningful perceive the nature of exchange interactions between metals existent in polymer and clusters [12],magnetochemistry[13], effective devices for recognition[14], assembly of external species magnetic resonance imaging contrast agent, rheumatoid drugs are materials, also find in medicine as chemotherapeutic agent anticancer drugs and reagents: as antibacterial, antifungal, antiviral [15]. Therefore, the topic of continuous investigation about structural, designing, functional and designing binuclear complexes [16]. The Schiff base complexes were derivative from nickel ions display obvious fungal activities, antibacterial activities, cytotoxic activity, against human pathogenic bacteria, herbicidal and anticancer applications [17]. Copper and Nickel complexes may be acted as therapeutic agents are well established and notable [18]. Preparation new binuclear complexes with tetradentate Schiff base ligand as a result of these big biological applications such as inhomogeneous [19] and heterogeneous [20] catalysis. They show excellent catalytic activity at rising temperature and moisture in various reactions [21].

Experimental

Materials: All chemicals benzidine, 2-benzoyl benzoic acid, and various metal (II) chlorides used were got from (Merck). The Methanol, DMSO, Ethanol, DMF and another solvents were used throughout the study were of high purity (sigma).

Vol: 13 No:3 , July 2017 23 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

Methods: Micro analytical data, ¹H- and ¹³C- NMR spectra of the ligand was recorded at Bruker specrospin ultra shield magnets 300 MHz instrument using tetramethyl silane (TMS) as an internal standard by using a solvent (DMSO-d₆) in Sharif University of technology in Iran. Products were examined by FT-IR spectra were obtained on Shimadzu FTIR–8400 Fourier Transform Infrared Spectrophotometer by KBr disc. Magnetic susceptibility instruments were obtained at room temperature on the solid state applying Faraday's Method using Bruker BM6 measurement at 298°K.Micro analysis (C, H, and N%) of the synthesized compounds was carried out in the central service laboratory, College of Education for pure science, Ibn Al-Haitham using a CHN Analyzer on Perkin Elmer 2400 series II. Melting points were measured by using (start melting point Apparatus) type Digimelt (MSRS). Conductivities were determined at 25°C for 10⁻³ M ethanolic solutions of complexes in using Philips PW- Digital Conductimeter. The chem. Office prog 3DX (2006) using to draw and suggest molecular structures of the compounds

Preparation

Preparation of the Schiff base Ligand

The ligand was prepared [6] from the reaction of (2mmol) 2-benzoylbenzoic acid, with benzidine (1mmol), in 25mlabsolute ethanol and (3-4) drops of (CH₃COOH) glacial acetic acid that refluxed at (70°C) in water bath for 4-5hrs. A product mass separated out on cooling, was filtered off. A yellow precipitate was obtained then rercystallized from a hot mixture of [(5ml) methanol, (2ml) distilled water and (5ml) acetone]. This product yield was almost quantitative (83%), melting point(187)°C and elemental microanalysis C.H.N were listed in Table(1). The reaction is shown in (scheme 1).

Scheme (1): Synthesis route for the preparation of ligand (H₂L)

Vol: 13 No:3 , July 2017 24 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



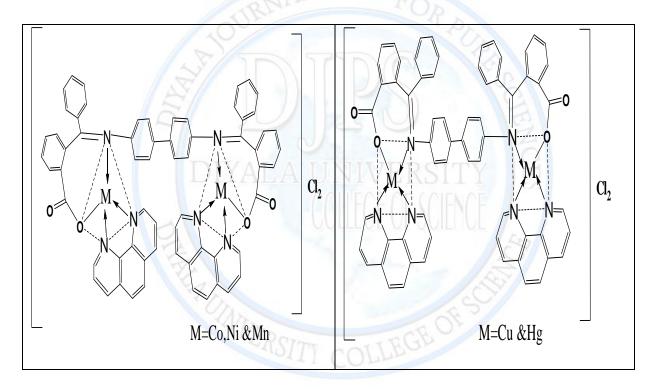
Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

Preparation of mixed complexes

An ethanol solution of the some metal salt such as ([NiCl₂.6H₂O], CoCl₂.6H₂O], [CuCl₂.2H₂O], [MnCl₂.4H₂O] and [HgCl₂] was added to an ethanol solution of potassium-,[2,2'-(biphenyl-4,4'-diylbis(azan-1-yl-1-ylidene))bis(phenylmethan-1-yl-1-

ylidene)dibenzoicacid](1mMol and 1,10-phenanthroline (2 mmol,0.36g) in(2:1:2) (Metal: ligand: (phen) molar ratio was carried out. After stirring for 1hr. with heating 55°C, resulting solids formed cooling at room temperature. The colored precipitates were filtered off, washed by hot ethanol and dried in vacuum.



Study of antibacterial Efficiency

The *in vitro* antibacterial activity of ligand $[H_2L]$ and its complexes type, $[M_2 \text{ (phen)}_2(L)]$ [M = Co(II),Mn(II), Ni(II), Cu(II) and Hg(II)], were tested using the bacterial cultures of: (Staphylococcus aurous), (Escherichia coli), (Bacillus subtilis) and (Pseudomonas aeroginosa), resistant by the disc diffusion method then using minimum inhibition concentration (MIC) that mean the (minimum inhibitory concentration) of the ligand and

Vol: 13 No:3 , July 2017 25 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

complexes was measured. The disk poured in ethanol was used as the control. Test compounds, which can restrain the apparent growth at 37°C after 24 h incubation. The sensitivity was determined on the foundation of diameter of zone of inhibition against Gramnegative and Gram-positive strains of bacteria. Results were indicated by recording the diameter (mm) for a zone of inhibition around each disc on the plate.

Results and Discussion

The preparation procedure of the ligand[2,2'-(biphenyl-4,4'-diylbis(azan-1-yl-1-ylidene)) bis(phenyl methan-1-yl-1-ylidene) di benzoic acid] are offered in scheme(1). All the isolated compound are insoluble in water but soluble in DMF, methanol, ethanol, DMSO and acetone. The Schiff base H_2L was prepared by the condensation reaction of benzidine and 2-benzoylbenzoic acid in one step according to (Scheme1). Then mixed complexes - ligand with1, 10-phenanthroline were prepared in this work .The 1 HNMR spectrum of the ligand (Fig.1) in (DMSO-d₆) exhibits the following signals in δ ppm at: (2.479, singlet, 6H for DMSO protons); the rang at (6.83-8.42) for 6 benzene ring protons and (12.35), singlet, 2H,-COOH group) [9, 10]. The 13 CNMR spectrum of ligand (H₂L) in DMSO-d₆ solution (Fig.2) showed the signals at:(40.80 for DMSO);(122.10~153.64 to 6 benzene rings. The peak observed at 159.07for C=O carbonyl group; and the signal at 161.10 for the C=N imine group

Electronic Spectra of ligands

The UV-Visible of (H₂L) and its mixed ligand- complexes recorded in Table (5). The solution of (H₂L) in 10^{-3} M (ethanol) exhibited two peaks, Figure (5) at (289nm) (34602cm⁻¹) (ϵ_{max} = 1980 molar⁻¹ .cm⁻¹) and (343nm) (29154cm⁻¹) (ϵ_{max} = 532 molar⁻¹.cm⁻¹) due to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transition respectively [13]. The electronic spectrum of 1,10-phenanthroline, (Fig.4) display high intense absorption peaks at (202 nm) (49504 cm⁻¹) (ϵ_{max} = 789 molar⁻¹ .cm⁻¹) and (228nm) (43859 cm⁻¹) (ϵ_{max} = 1992 molar⁻¹ .cm⁻¹) due to ($\pi \rightarrow \pi^*$) and another peak at (264nm) (37878cm⁻¹) (ϵ_{max} =134molar⁻¹.cm⁻¹) which assigned to ($n \rightarrow \pi^*$) transition respectively, the data recorded in Table(5).

Vol: 13 No:3 , July 2017 26 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

The Electronic Spectra of complexes

- [Mn₂(phen)₂(L)]Cl₂ d⁵: the pale complex of Mn^(II) shows bands at (299 nm) (33444 cm⁻¹) (ϵ_{max} = 1264 molar⁻¹ .cm⁻¹) and (383nm) (27855 cm⁻¹) (ϵ_{max} = 2514 molar⁻¹ .cm⁻¹) due to ligand field and charge transfer .Another bands at (372 nm) (26881 cm⁻¹) (ϵ_{max} = 875 molar⁻¹ .cm⁻¹) and (383 nm) (26109 cm⁻¹) (ϵ_{max} = 934 molar⁻¹ .cm⁻¹)which are caused by the electronic transfer ${}^{6}A_{1} \rightarrow {}^{4}E_{(D)}$ and ${}^{6}A_{1} \rightarrow {}^{4}T_{2(D)}$ respectively[15].

-[Cu₂(phen)₂(L)]Cl₂ d⁹:the spectrum of the pale brown complex gave three bands at (287 nm) (34843 cm⁻¹) (ϵ_{max} = 1824molar⁻¹ .cm⁻¹) and(340 nm) (29411 cm⁻¹) (ϵ_{max} = 1521 molar⁻¹ .cm⁻¹) assigned to ligand field .Another bands at (668 nm) (14970 cm⁻¹) (ϵ_{max} = 134 molar⁻¹ .cm⁻¹) and (846 nm) (11820 cm⁻¹) (ϵ_{max} = 57molar⁻¹ .cm⁻¹) assigned to charge transfer[17].

-[Co₂(phen)₂(L)]Cl₂d⁷:the spectrum of the pale brown complex gave four bands at (357 nm) (28011 cm⁻¹) (ϵ_{max} = 2176 molar⁻¹ .cm⁻¹) assigned to charge transfer. Another bands at (372 nm) (26881 cm⁻¹) (ϵ_{max} = 962 molar⁻¹ .cm⁻¹),(621 nm) (16103 cm⁻¹) (ϵ_{max} = 18 molar⁻¹ .cm⁻¹) and (745nm) (13422 cm⁻¹) (ϵ_{max} = 34 molar⁻¹ .cm⁻¹)attributed to⁴A_{2(F)} \rightarrow ⁴T_{1(P)}, ⁴A_{2(F)} \rightarrow ⁴T_{1(F)} and ⁴A_{2(F)} \rightarrow ⁴T_{2(F)} transitions respectively[16].

-[Ni₂(phen)₂(L)]Cl₂d⁸:the spectrum of thegreen complex gave four bands at (284 nm) (35211 cm⁻¹) (ϵ_{max} = 1752molar⁻¹.cm⁻¹) and (366 nm) (27322cm⁻¹) (ϵ_{max} = 987 molar⁻¹.cm⁻¹) assigned to ligand field and charge transfer. Also the third band at (801 nm) (12484cm⁻¹) (ϵ_{max} = 15 molar⁻¹.cm⁻¹) attributed to³A₂ \rightarrow ³T _{1(P)} transition[18].

-[**Hg₂(phen**)₂(**L**)]Cl₂ d¹⁰:the spectrum of thebrowncomplex gave two bands at (292 nm) (34246 cm⁻¹) (ϵ_{max} = 2145molar⁻¹ .cm⁻¹) and (317 nm) (31545 cm⁻¹) (ϵ_{max} = 1356 molar⁻¹ .cm⁻¹) are assigned to ligand field. Another band at (389 nm) (25706cm⁻¹) (ϵ_{max} = 1174 molar⁻¹ .cm⁻¹) is assigned to charge transfer [19]. All transition with their assignments is summarized in Table (3). According to spectral data as well as those obtained from elemental analyses, the chemical structure of the complexes can be suggested as tetrahedral for [**M₂(phen**)₂ (**L**)]Cl₂,where M⁺²=(Mn, Co and Ni),(Fig.7) while copper and mercury complexes

Vol: 13 No:3 , July 2017 27 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

$[Cu_2(phen)_2(L)]Cl_2$ and $[Hg_2(phen)_2(L)]Cl_2$ have square planer

The molar conductance of all complexes in ethanol was found which indicates the [1:2] electrolytesbehavior of these complexes. The μ_{eff} value of Mn, Co, Ni and Cu complexes are in the range (4.52, 3.43, 3.92, and 1.69) B.M. respectively, the physical properties of the ligand (H₂L) with their mixed complexes are shown in Table (5).

The infrared spectrum

The infrared spectrum of the [2,2'-(biphenyl-4,4'-diylbis(azan-1-yl-1-ylidene))bis (phenyl methan-1-yl-1-ylidene)dibenzoic acid ligand was appeared abroad band at (3446cm⁻¹), which was indicated to carboxyl-OH group[10]. The v(O-H) band is absent in the IR spectrum of the complexes indicated that the carboxyl OH protons were lost upon complexation [11]. The bond in the Schiff base ligand spectrum was obtained at (1681cm^{-1}) assigned to the v(C=N)band of the Schiff base ligand is shifted slightly to lower frequency in rang (1671-1651 cm⁻¹ 1)due to amine linkage was shifted towards lower frequency in all the complexes. Also in the spectrum of appeared of the 1,10-phenanthroline the band(1620) due to v(C=N) in range (1617-1614cm⁻¹), indicating that the 1,10-phenanthroline were coordinated to the metal atoms through azomethine nitrogen. Further proof of the coordination to N was provided by the show of the bands (M-N) in the range (573 -491cm⁻¹) of the spectra of the complexes [20]. Further confirmation comes from the absence of (C=O) bending peak for COOH group in mixed complexes [13]. While appeared the band due tov_{sym}COO-in range (1535-1496 cm⁻¹) and the band due to $v_{asym}COO^-$ in range(1404-1367cm⁻¹). The difference of the value between the asymmetric and symmetric stretching of COO frequencies ($\Delta v = v_{\text{sym}} \text{COO}^{-} - v_{\text{asym}} \text{COO}^{-}$)in range (168-92) of all complexes have been compared in order to predict the coordination mode of metal ions with 1,10-phenanthroline as shown in Table (4). The Δv values, for each prepared complexes, indicates the tetradentate coordination of the carboxylate group [22].

In vitro antibacterial activity:

The inhibition zones (mm) of ligand and its complexes against Gram-negative and Gram-positive strains of bacteria are shown in Table 6. The higher antimicrobial activity of the metal complexes as compared to Schiff base ligand may be explained in terms of chelation which makes metal complexes to act as more powerful and potent antimicrobial agents, thus

Vol: 13 No:3 , July 2017 28 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

inhibiting the growth of the microorganisms [23]. further, the polarity of the metal ion decreases with coordination at most due to the positive charge within the chelate ring system the partial sharing with the donor groups that rises the lipophilic nature of the central metal atom, which prefer its permeation more expeditiously through the lipid layer of the bacteria. This work is very important in the possibility that the ligand and mixed ligand complexes might be more effective against bacteria for which a thorough investigation about the structure activity relationship, regarding toxicity, and in their antibacterial affects which would be useful in designing more potent biological agents for therapeutic use if desired.

Conclusion

A Schiff base ligand (H₂L) was derived from condensation of 2-benzoyl benzoic acid and benzidine was synthesized and characterized. The mixed complexes with Cu(II), Co(II), ,Mn (II), Ni(II) and Hg(II) ions was carried out. The bonding of the ligand in the mixed ligand complexes and the tetrahedral geometry around (Co, Mn and Ni) and square planergeometry around (Co, Cu and Hg) have been deduced on the basis of various spectroscopic techniques. The comparative *in vitro* antimicrobial results suggested that the metal complex shows a significant antimicrobial activity as compared to ligand (H₂L) and its Ni(II), Co(II),Mn(II), ,Cu(II) and Hg(II) complexes.

Table (1): Some physical properties of prepared lignad (H₂L) and its complexes

Compounds	formala	Molecular Weight	Colour	Yeild %	M.P.		%Elemental Analysis Found % (Calculated)		
•						С	Н	N	M
H ₂ L	C40H28N2O4	600.66	yellow	85	187	79.76 (79.98)	4.78 (4.70)	4.43 (4.66)	-
[Co ₂ (phen) ₂ (L)]Cl ₂	C64H42Cl2C02N6O4	1146.13	blue	60	240	70.86 (71.38)	4.09 (3.93)	7.54 (7.80)	9.08 (10.94)
[Ni ₂ (phen) ₂ (L)]Cl ₂	C ₆₄ H ₄₂ Cl ₂ N ₆ Ni ₂ O ₄	1147.35	Green	68	221	71.00 (71.41)	3.54 (3.93)	10.09 (10.91)	8.78 (8.93)
[Cu ₂ (phen) ₂ (L)]Cl ₂	C ₆₄ H ₄₂ Cl ₂ Cu ₂ N ₆ O ₄	1157.05	Pale- brown	70	235	70.51 (70.77)	3.23 (3.90)	4.13 (4.23)	11.54 (11.70)
[Mn ₂ (phen) ₂ (L)]Cl ₂	C64H42Cl2Mn2N6O4	1139.84	Pale- brown	66	264	71.10 (71.91)	3.63 (3.93)	7.47 (7.86)	10.08 (10.28)
[Hg2(phen)2(L)]Cl2	C ₆₄ H ₄₂ Cl ₂ Hg ₂ N ₆ O ₄	1431.14	Brown	61	258	59.11 (56.51)	2.87 (3.11)	5.89 (6.18)	29.17 (29.49)

Vol: 13 No:3 , July 2017 29 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

Table (2): 1H-NMR Chemical shifts for ligand(H₂L) (ppm in DMSO)

DMSO	C=C6 <u>H</u> 5(aromatic protons)	-COO <u>H</u> (carboxylate proton)
2.479	6.83-8.42	12.35

Table (3):¹³C-NMR Chemical shifts for ligand(H₂L) (ppm in DMSO)

DMSO	C=C6H 5(aromatic carbons)	COOH(carboxylate carbon)	C=N-(imine carbon)
40.80	122.10~153.64	159.07	161.10

Table (4):- The main frequencies of the ligand and it's complexes(cm⁻¹).

Compounds	v(OH)	υ(C=N)	vas(COO)	$v_s(COO)$	Δυcm ⁻¹	υ(M-N)
Ligand(H ₂ L)	3446 br.	1681 s.	1535 s.	1367 sh.	168	-
ligand	T>T>/ A	1620	-	-		-
$[Mn_2(phen)_2(L)]Cl_2$	DITE	1660 s. 1610 s.	1496 sh.	1404 sho.	92	573 w.
$[Co_2(phen)_2(L)]Cl_2$	-	1651 s. 1614 s.	1500 s.	1386 sho.	114	532 w.
[Ni ₂ (phen) ₂ (L)]Cl ₂	Y Y Y	1666 s. 1612 s.	1525 sho.	1394 sho.	131	491 w.
$[Cu_2(phen)_2(L)]Cl_2$	SAN,	1671sh. 1617 sh.	1496 s.	1388 m.	108	526 w.
$[Hg_2(phen)_2(L)]Cl_2$	-	1663 s. 1617 s.	1504 sh.	1379 s.	125	560 w.

s= strong, br=broad, w = weak, sh = sharp, s=symmetric, as=asymmetric, m = medium sho = shoulder,

Vol: 13 No:3 , July 2017 30 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

Table (5):- UV-Vis, magnetic susceptibility and conductance measurements data

Compounds	$\mu_{ m eff}({f B.M})$	A _m (S.cm ² .mol ⁻ 1)in ethanol(10 ⁻ 3M)	$\lambda_{ ext{max}}(ext{nm})$	ABS	Wave number (cm ⁻¹)	ϵ_{\max} L.mol ⁻¹ .cm ⁻¹	Assignments	Geometry
$egin{array}{c} H_2 \ L \end{array}$	-	-	289 343	1.980 0.532	34602 29154	1980 532	$ \begin{array}{c} n \rightarrow \pi^* \\ \pi \rightarrow \pi^* \end{array} $	-
ph			202	0.789	49504	789	$\pi \rightarrow \pi^*$	
1,10- phenanthroli ne	-	-	228	1.992	43859	1992	π→π*	-
hroli		1	264	1.345	37878	1345	n→π*`	
[Co ₂ (phen) ₂ (L)] Cl ₂	3.43	78	357 372 621 745	2.176 0.962 0.018 0.034	28011 26881 16103 13422	2176 962 18 34	$\begin{array}{c} C.T \\ ^{4}A_{2(F)} \longrightarrow ^{4} \\ T_{1(P)} \\ ^{4}A_{2(F)} \longrightarrow ^{4} \\ T_{1(F)} \\ ^{4}A_{2(F)} \longrightarrow ^{4} \\ T_{2(F)} \end{array}$	Tetrahedral
[Ni ₂ (phen) ₂ (L)]Cl ₂	3.92	80	284 366 801	1.824 0.987 0.015	35211 27322 12484	1824 987 15	$ \begin{array}{c} L.F \\ C.T \\ ^{3}A_{2} \rightarrow ^{3}T_{1} \\ (P) \end{array} $	Tetrahedral
$[Cu_2(phen)_2(L\\)]Cl_2$	1.69	79.4	287 340 668 846	1.752 1.521 0.134 0.057	34843 29411 14970 11820	1752 1521 134 57	L.F C.T ${}^{2}B_{1}g \rightarrow {}^{2}A$ ${}^{1}g$ ${}^{2}B_{1}g \rightarrow {}^{2}B$ ${}^{1}g$	Square planar
[Mn ₂ (phen) ₂ (L)]Cl ₂	4.52	81.6	299 359 372 383	1. 264 2.514 0.510 0.112	33444 27855 26881 26109	1264 2514 875 934	$\begin{array}{c c} & 1g \\ L.F \\ C.T \\ {}^6A_1 {\longrightarrow}^4E \\ & {}^{(D)} \\ {}^6A_1 {\longrightarrow}^4T_{2(} \\ & {}^{(D)} \end{array}$	Tetrahedral
$[Hg_2(phen) \atop {}_2(L)]Cl_2$	Dia	85.1	292 317 389	3. 145 1.356 1.174	34246 31545 25706	2145 1356 1174	L.F C.T C.T	Square planar

Vol: 13 No:3 , July 2017 31 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

Table (6): Diameter of zone of inhibition (mm)

Comp.	H_2L	$ \begin{array}{c} [Co_2(phen)_2(L)] \\ Cl_2 \end{array} $			$[Mn_2(phen)_2(L)]C \\ l_2$	$[Hg_2(phen)_2(L)] \\ Cl_2$
Escherichia. Coli	8	17	12	18	18	16
Staphylococcu s aureus	11	13	14	13	14	17
Bacllus	10	18	18	17	16	15
pseudmonas	13	16	16	14	15	16

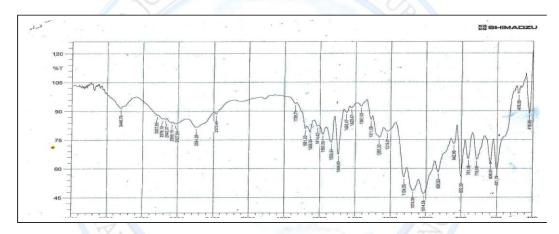


Fig.(1) The IR spectrum of ligand[H₂L]

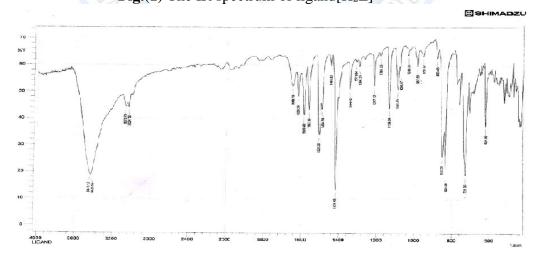


Fig.(2) The IR spectrum of 1,10-phenanthroline ligand.

Vol: 13 No:3 , July 2017 32 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

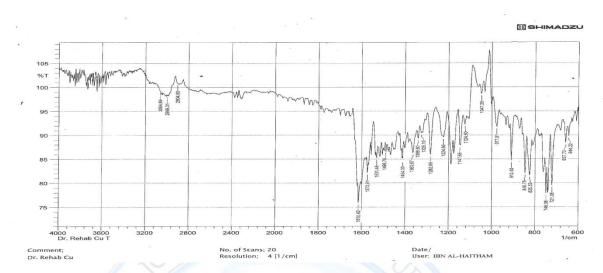
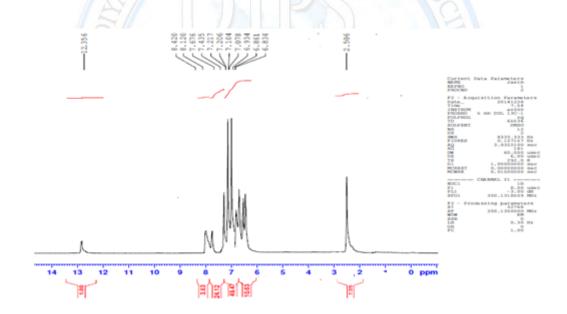


Fig.(2) The IR spectrum of [Cu₂(phen)₂(L)]Cl₂ complex



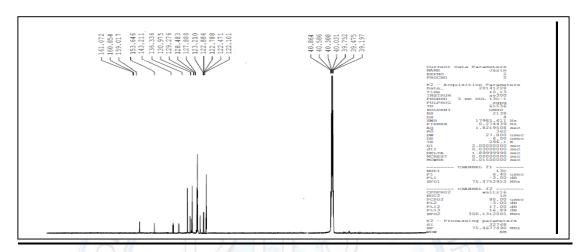
Fig(3): The¹H-NMR spectrum of the ligand (H₂L)

Vol: 13 No:3 , July 2017 33 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255

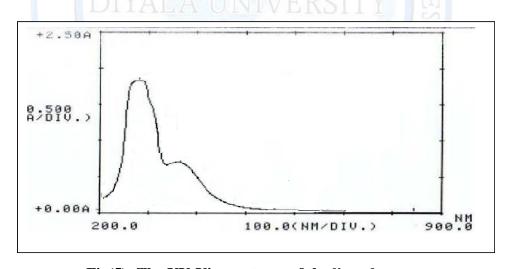


Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy



Fig(4): The¹³C-NMR spectrum of the ligand



Fig(5): The UV-Vis spectrum of the ligand

Vol: 13 No:3 , July 2017 34 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

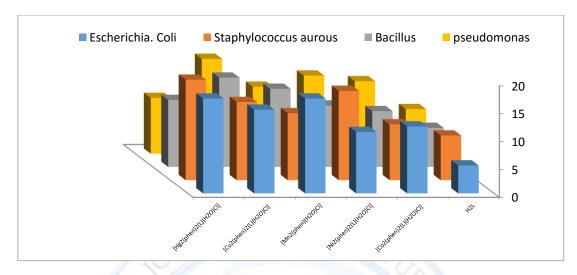


Fig.(6)Difference between the antimicrobial activity of ligand(H₂L) and metal complexes

References

- 1. ShitS., SankolliR., and GuruRowT. N., A Dinuclear Cadmium(II) Schiff Base Thiocyanato Complex: Crystal Structure and Fluorescence, ActaChim. Slov. 61:PP9-66, 2014.
- 2. MahalakshmiN. and RajavelR., Synthesis, Spectroscopic Characterization, DNA Cleavage And Antimicrobial Activity Of Binuclear Copper (II), Nickel (II) And Oxovanadium(IV) Schiff Base Complexes, Asian Journal of Biochemical and Pharmaceutical Research ,2 (1):PP.528-543, 2011.
- **3.** Rajavel R, Vedanayaki S, Sandhanamalar D, Jayaseelan P, Synthesis ,Spectroscopic and Antimicrobial studies of binuclear transition metal complexes with tetradentate Schiff base,Research J. of Pharma., Biological and Chem.Sci.,2011 2(3): PP 994-1001.
- **4.** MahalakshmiN. and RajavelDr.R.,Binulear Copper (II), Nickel(II) and Oxovanadium(IV) Schiff Base ComplexesBearing N2O2 Donors and Their DNA Cleavage AND Antibacterial Activity,International J. of Pharm. & Tech., 2, 4: PP1133-1157.
- **5.** Chandra S and Sangeetika J, EPR and electronicspectruml studies on copper (II) complexes of some N-O donor ligands 2004; J. Indian Chem. Soc, 81, 203-206.
- **6.** Usarani,M E. ,Akila, S. Ramachandan, VelrajG. and RajavelR.,Synthesis, Composition, Geometry and Antibacterial Assay of Binuclear Schiff Base Metal Complexes Derived

Vol: 13 No:3 , July 2017 35 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

- FromBenzene-1,4-Dicarbldehde, 2-Hydroxy-Benzalaldehyde and Pyridine-2,6-Diamine,Intern. J.ofPharma. andPharma. Scienc., 5, 2:PP 639- 647, 2013.
- **7.** Asma N., Samreen S., Tabinda F., Humaira M. S. and Bushra M., Synthesis, characterization, biological evaluation and QSAR of some Schiff base esters: Promising new antitumor, antioxidant and antiinflammatory agents, Pak. J. Pharm. Sci., 26, 1, , PP.113-124,2013.
- **8.** Arulmurugan S., Helen P. K. and VenkatramanB.R.,Biological Activities of Schiff Base and its Complexes: a review,Rasayan Journal, 3, 3, 385-410, 2010.
- **9.** Sallam S. A.,Binuclear Copper(II), Nickel(II) and Cobalt(II) Complexes with N2O2 Chromophores of Glycylglycine Schiff-Bases of Acetylacetone, Benzoyl acetone and Thenoyl trifluoro acetone, Transition Metal Chemistry, 31, 1:PP 46-55,2006.
- **10.** Miquel C., Raul X., Antoni L., Miquel S., Juvencio R., Teodor P., Helen S. and Markus N., Dinuclear Copper(I) Complexes with Hexaaza Macrocyclic Dinucleating Ligands: Structure and Dynamic Properties Inorg. Chem., 42:PP4456-4468, 2003.
- **11.** Karbocek N., Karabocek S. and Kormali F., Mono-, Di- and Trinuclear Copper(II) Complexes of a Schiff Base Ligand,2-{(E)-[(6-{[(1E)-(2-hydroxy phenyl) methylene] amino}pyridin-2-yl)imino]-methyl}phenolTurk J Chem ,31:PP 271 277 , 2007.
- **12.** ALI H.and Kianfa .R. and Islam A. ,Spectrophotometric Study of Complexation Between SomeSalen Type Schiff Bases and Dimethyltin(IV) Dichloride, Chem. Sci. Trans., 2(S1), S17-S24, 2013.
- **13.** Maria DMC, Ribeiro da silva, Jorge MG, Ana LRS, Paula CFC, Bernd Schroder et al. Molecular Thermochemical Study of Ni(II), Cu(II) and Zn(II) Complexes with N,N-'bis(salicylaldehdo)ethylenediamine. J. Mol. Catal. A: Chem. 2004; 224, 207-212.
- **14.** Karaa H., Elermanb Y., and Elmalib A., Synthesis, Crystal Structure and Spectroscopic Properties of a Dinuclear Nickel(II) Complex Bridged by an Alkoxide and a μ-Pyrazolate Ligand, Verlag der Zeitschriftfu rNaturforschung, Tu bingen ,3,1000–0955 2003.
- **15.** Ruaa M. Al-Juburi Synthesis and Characterization of Some Heterocyclic Compounds (Oxazepine, Tetrazole) Derived from Schiff Bases, Journal of Al-Nahrain University, 15 (4), PP.60-67, 2012.

Vol: 13 No:3 , July 2017 36 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255



Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Schiff Base Derived from Benzidine and 2-Benzoyl benzoic acid

Rehab .K. Al- shemary, Basima Abdul HussinZaidan and Nibras A. Al-marsomy

- **16.** Selvana A. Y., Synthesis of substituted (oxazepine, Diazepine, tetrazde) via Schiff Bases for 2- AminobenzoThaizoleDerivatives, J. Baghdad for Sci., 10(3), PP: 637-647, 2013.
- **17.** A.A. Ahmed, S.A. BenGuzzi and A.O. Agoob, Synythesis and Characterization of Some N2O2-Schiff Bases and Their Metal Complexes, Rasayan J. Chem , 2,2, PP :271-275, 2009.
- **18.** Cocco M T, Congiu C, V. Onnis, M. C. Pusceddu, M. L. Schivo and A. De Logu, "Synthesisand antimycobacterial activity of some isonicotinoylhydrazones", Eur. J. Med. Chem., 1999, 1076-1071, 34.
- **19.** [19] Chohan ZH, Munawar A and Supuran CT, Transition metal ion complexes of Schiff's-bases synthesis 2001; characterization and antibacterial properties Metalbased drugs, 8: 137-143.
- **20.** Loncle C., Brunel J. M., Vidal N, Dherbomez M. and LetourneuxY, "Synthesis and antifungal activity of cholesterol-hydrazone derivatives" Eur. J. Med. Chem., 39, PP:1067-1071, 2004.
- **21.** CanpolatEand Kaya M,Studies on mononuclearchelates derived from substituted Schiffbase ligands (part2) synthesis and characterization of a new 5-bromosalicylidenpaminoacetophenoneoxime and itscomplexes with Co(II), Ni(II), Cu(II) and Zn(II) 2004; J. Coord.Chem. 123.
- **22.** Papakonstantinou-Garoufalias S, Pouli N, Marakos P and Chytyroglou-Ladas A, "Synthesisantimicrobial and antifungal activity of some new 3 substituted derivatives of 4-(2,4-dichlorophenyl)-5-adamantyl-1H-1,2,4-triazole", Farmaco, 57, PP:973-977, 2002.
- **23.** UsharaniM., Akila E.,Ramachanran, S.,Velraj G. and Rajavel R. Synthesis, Composition, Geometry And Antibacterial Assay of Binuclear Schiff Base Metal Complexes Derived From Benzene-1,4-Dicarbaldehyde Arbedehyde, 2-Hydroxy-Benzaldehyde And Pyridine-2,6-Diamine, Int. J. of Pharmacy and Pharmaceutical Sci.,5(2), PP:640-647,(2013).
- **24.** KaraH.,ElermanY. and Elmali A., Synthesis, Crystal Structure and Spectroscopic Properties of a Dinuclear Nickel(II) Complex Bridged by an Alkoxide and a μ-Pyrazolate Ligand, Z. NaturforschA Journal of Biosciences.,58, PP:955-958, 2003.

Vol: 13 No:3 , July 2017 37 P-ISSN: 2222-8373 DOI : http://dx.doi.org/10.24237/djps.1303.189C E-ISSN: 2518-9255