Structure, Attributive and Bacterial Effectiveness Studies for Complexes, Co(II), Hg(II), Ni(II), Cu(II) and Mn(II) with Ligand kind (N_2O_2)

Rehab K. Al- shemary
Faeza H. Ghanim
Dept. of Chemistry/ College of Education for Pure Science (Ibn -Al-Haitham)/
University of Baghdad

Received in:1/March/2016,Accepted in:28/June/2016

Abstract

Binuclear copper, nickel, cobalt, manganese and mercury complexes of the Schiff base H_2L ($C_{40}H_{28}N_2O_4$) obtained by condensation of 2-benzoyl benzoic acid with benzidine. The Schiff base and their complexes have been subjected to[FT-IR, elemental analysis ,UV-Vis, ^1H and ^{13}C NMR] spectral studies, molar conductivity, magnetic moment and HPLC measurements. All the complexes showed tetrahedral geometries with the general structure $[M_2(L)_2]$. Generality of the synthesized components offer antibacterial efficiency to *(Staphylococcu saureus*), (*Escherichia coli*),(*Bacillus subtilis*) and*(Pseudomonas aeruginosa).*

Keywords: Structure, Schiff bases, Attributive, 2-benzoyl benzoic acid and Bacterial effectiveness.

Introduction

The Ligand such as Schiff bases have a substantial part in a many of uses in biochemical and physicochemical[1] biochemical pertinent researches of metal complexes and given broad range of applications such as antipyretic[2],analgesic[3],anti-diabetic[4], anti-inflammatory[5],anti-cancer[6] anti-human immunodeficiency virus activity(HIV)] [7] and anti-bacterial [8]. Coordinating ligands including O and N giver atoms appear wide biological activity of special attention because of the set of ways in which they are bonded to metal ions [9]. It is well known that different Schiff base complexes have Tetra-chelating N,N,O,O-giver Schiff bases in their nickel(II) complex avail as substantial models for enzyme [10].Their binuclear homometallic copper (II),nickel(II) and cobalt(II) complexes avail as model compounds at the active groups of metalloenzymes [12]. Binuclear metal complexes find applications as active appliances for estimation and structure of outer kinds [13].Thus, functional and designing structural binuclear complexes keep a topic of continuous investigation. Tetradentate Schiff bases derived from benzoic acid with benzidine and its derivatives have been extensively explored; while Schiff bases obtained from 2-benzyl benzoic acid with benzidine and its derivatives has been searched very littler [14]. In this paper, we report the preparation, structural, spectral, and description of a new binuclear the copper (II), nickel(II), cobalt(II), mercury (II) and manganese(II)complex $[M(L)]_2$,derived from the $[H_2L]$ obtained by condensation of [2-benzoylbenzoic acid and benzidine] (Scheme1). Structure, attributive and bacterial effectiveness studies detect that five metal (II) ions select tetrahedral configurations.

Experimental

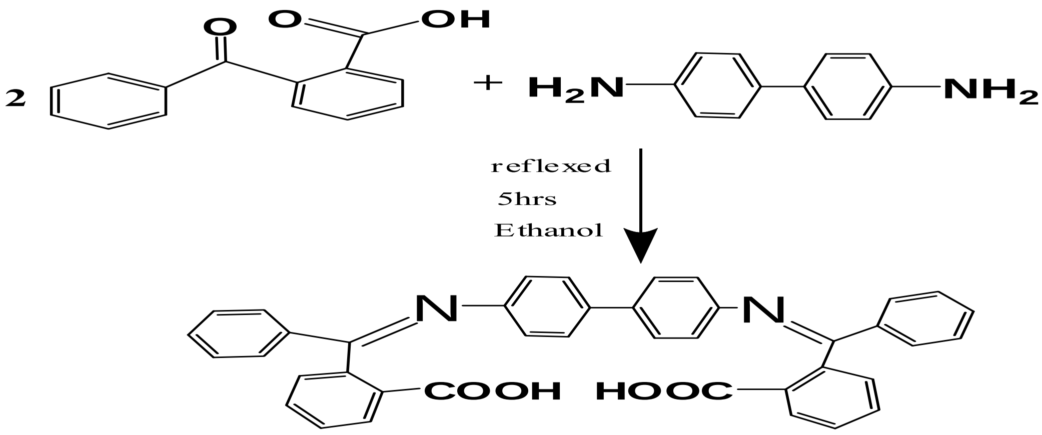
Materials: All chemicals and all metal (II) chlorides 2-benzoyl benzoic acid, solvents and benzidine used in this work were obtained from Merck products.

Methods: ^{1}H-, ^{13}C- NMR spectra values of the compound of ligand were registered by DMSO-d_6 at [Bruker specrospin ultra shield magnets instrument 300 MHz]. (C, H, and N %) of the made compounds were loaded employing a[CHN Analyzer on Perkin Elmer].Compounds were measured by [FT-IR spectra] were registered on [Shimadzu FTIR–8400] Fourier Spectrophotometer. Magnetic sensitiveness measurements were got by Bruker BM_6 instrument. Conductivities were registered by Philips PW- Digital Conduct meter. for 10^{-3} M solutions of complexes. Melting points were studied by utilizing [start melting point Apparatus]

Preparation

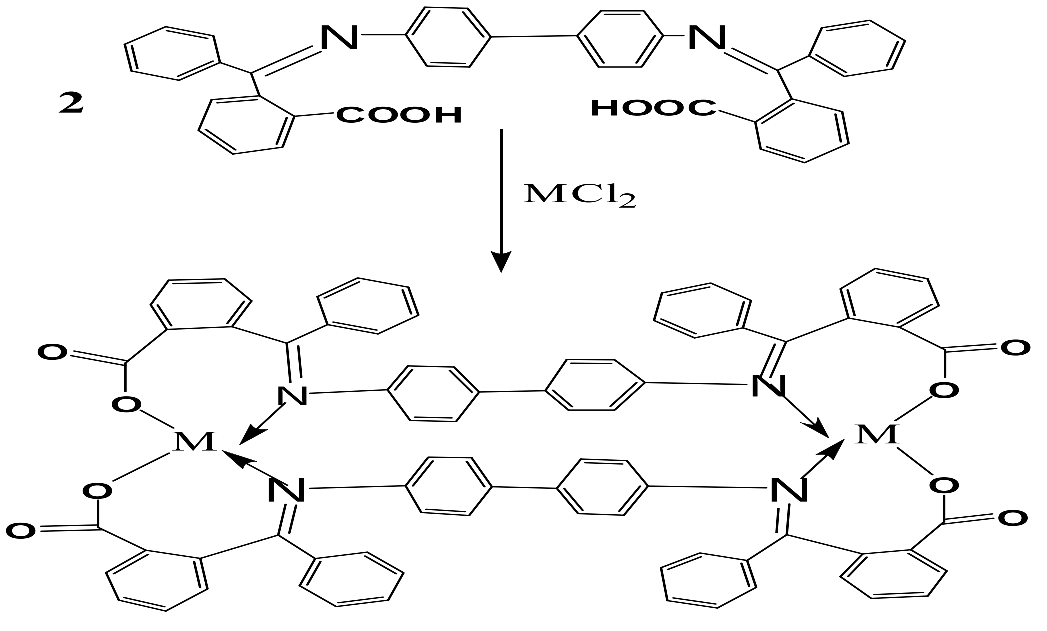
The Ligand

The compound was synthesized from the condensation (1mmol) benzidine with (2mmol) 2-benzoylbenzoic acid and (3) drops of glacial acetic acid in 25ml ethanol absolute (scheme 1). This reaction was refluxed at (75°C) during 5hrs on water bath. A yield isolated out on refrigeration, was filtered off. A product result was got then re-crystallized from a hot solution of [(1ml) distilled water, (3ml) methanol and (2ml) acetone]. This result was then submitted to chromatography “flash” as dry column by ethanol as eluent, yield (0.24g, 79%), m.p. (170)°.



Co(II), Mn(II),Cu(II),Hg(II) and Ni(II) Complexes.

All the complexes were synthesized employing the same synthetic path way characterized in literature by mixing of H_2L (0.6g ,1mmol) in(13mL) ethanol and [0.238 g $CoCl_2.6H_2O$, 0.175g $CuCl_2.2H_2O$, 0.271 g $HgCl_2$, 0.198 g $MnCl_2$ and 0.237 g $NiCl_2$] in [1 :1 molar proportion]. Then stirring for (30min.) at 55°C.The result instantly produced, filtered off and re-crystallized from (10mL) the hot solvent. Their pureness was proved utilizing (TLC) [thin layer chromatography] and (3:7, v/v) (ethanol / CH_2Cl_2) as eluent and were displayed, in any case, to consist (Rf0.55) of only one component, the complexes in yields (89-74%) (Table1).



M^{+2}=Co^{+2}, Ni^{+2},Cu^{+2},Mn^{+2}&Hg^{+2}

Study of Biological Efficiency

The antibacterial activity for these compounds was evaluated by using method similar with the traditional disc diffusion method [7 and 8], sterile 5 mm filter paper discs (What man, no.1) were soaked in this compound (Disc loaded with the DMSO and allowed until complete evaporation to be used. Then discs were placed onto the surface of the Muller Hinton agar plates at different areas on the surface of each plate, after a 24 hrs. culture of the pathogenic strains*(Staphylococcus usurers*),(*Escherichia coli*),(*Bacillus btilis*) and *(Pseudomonas aeruginosa)* were spreading with a antiseptic cotton wipe over the surface of Muller Hinton agar plates. The plates were incubated for 24 hrs at 37C^{o}. Products were fixed by registering the diameter in (mm) for a region of restraint on each plate.

Results and Discussion

The ^{1}HNMR spectrum in DMSO of [H_2L] offers in δ ppm the next signals at: (12.26) (s, 2H, COO$\underline{H}$) ; (6.84-8.44), (m, 6H,$C_6\underline{H_5}$) and 2.48 (s, 6H ,DMSO) ; [9, 10] (Fig.1). The ^{13}CNMR spectrum of (H_2L) appeared the signals at: (40.81, DMSO); (122.12~153.67), (s,DMSO) ;(159.09),(s,COO$\underline{H}$); and(161.12), (s, C=N) (Fig.2).

The conductance [non-electrolytic nature] specified of the complexes specified [11].The magnetic sensitivity for these complexes (Table 5) in ethanolic which has been adduced for utmost *tetrahedral* arrangement [12].

The UV- Vis spectra in (10^{-3} M) ethanolic solution of the ligand offered fundamentally two absorptions at 289 and 343 nm were spotted to the middle energy $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition Figure (5) [13 and 14]. The UV-Vis spectrum of Mn(II) complex displayed absorptions at (297 and 365 nm) were regarded to L.F and C.T transitions respectively, and other absorptions at 487 and 584 nm were regarded to$\{^6A_1 \rightarrow {}^4A_{1(G)}$ and $^6A_1 \rightarrow {}^4E_{(G)}\}$, separately [15]. The UV-Vis spectrum of Co(II) complex offered absorptions at 292 and 347 nm due to L.F and C.T transitions, other peak at 621 nm regarded to electronic transition type $\{^4A_{2(F)} \rightarrow {}^4T_{1(P)}\}$ .The spectrum of Ni (II) complex displayed absorptions at 284 and 346 nm result to L.F and C.T transition respectively. The peaks at 419 nm and 702 nm were result to (d-d) electronic transition types [16] $\{^3T_1 \rightarrow {}^3T_1$ and $^3T_1 \rightarrow {}^3A_2\}$ Figure (6). The spectrum of Cu(II) complex showed peaks at 290 and 340 nm result to L.F and C.T transitions respectively, then other peak at 509 nm was described to electronic transition type[17] $^2T_2 \rightarrow {}^2E$.The spectrum of complex displayed absorptions at 310 and 388 nm result to C.T transitions. The non-attendance of peaks in the Vis-area specified no (d-d) transitions showed *tetrahedral* geometry Table 5 [18].

The IR-spectrum of the ligand displayed frequency at 3441 cm^{-1}, which was described to υ (OH) group [19]. This frequency was lost in the spectra of these complexes [20]. A considerable shift in the in position intensity to lower wave number was noticed in all the complexes with metal ion for the strong frequency in the (H_2L)spectrum, which shows at 1681 cm^{-1} described to υ(C=N) group[21].An important change in position to lower wave number and in the intensity was noticed with metal ion on complexation for the strong frequency in the ligand (H_2L) spectrum at 1535 cm^{-1}, which appears due to $\upsilon_{as}(COO^-)$ [22].The band at 1367 cm^{-1} in the spectrum of the ligand (H_2L), which was described to the $\upsilon_s(COO^-)$. These frequencies moved to lower or higher vibrations at (1496 -1525cm^{-1}) and (1367-1404cm^{-1}) for all the complexes, $\Delta\upsilon$=(92-132) cm^{-1} [23].

The occurrence of new bands in the range (484-571)cm^{-1} are temporarily designated to (Metal-Ligand) υ(M-O) and υ(M-N) frequencies [24], giving to the data gained, a tetrahedral arrangement has been temporarily given these complexes.

The antimicrobial efficiencies of the compounds have been examined versus chosen kind of microorganism; the region of suppression of bacterial evolution on the plate. DMSO (which was used as a solvent and Controller) was a good solvent to prepare 1ppm of each tested sample Figure (7) [25 and 26]. Table (6).

References

1. Usharani, M.;Akila, E.; Ramachanran, S.; Velraj, G. and Rajavel, R. ;(2013)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), 640- 647.

2. Lionel, S.; Pierre, T.; Eric R., Shinpei M., Takehiko Y.and Michel E.;(2006) Synthesis, structure and magnetic behaviour of dinuclear uranium(IV)complexes with a ‘calixsalophen’ type macrocycle , New Journal of Chemistry , 7,331,5-17

3. Kara, H.; Elerman, Y.; and Elmali A.; (2003) Synthesis, Crystal Structure and Spectroscopic Properties of a Dinuclear Nickel(II) Complex Bridged by an Alkoxide and a μ-Pyrazolate Ligand, *Z. Naturforsch A Journal of Biosciences* . 58, 955 – 958

4. Tudor, R.;Simona,P.; Veronica L., Carmen, C.and Raluca C.;(2006)Copper (II) Complexes with Ligands Derived from 4-Amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one: Synthesis and Biological Activity, *Molecules*, 11, 904-914

5. Ali, H. K. and Islama, A.; (2013)Spectrophotometric Study of Complexation Between Some Salen Type Schiff Bases and Dimethyltin(IV) Dichloride, *Chem Sci Trans.*, 2(1),17-24.

6. Cusumano, M. A.; Messina, M.; Nicolo, F; Pietro, M., Rotondo, A. and Rotondo,E.;(2009)NMR Study of L-Shaped Quinoxaline Platinum(II) Complexes-Crystal Structure of] Pt(DMeDPQ) (bipy)]$(PF6)_2$,*Eur.J. Inorg. Chem.,* 4710-4717.
7. Kaymakcioglu, B. K. and Rollas, S;(2002)“Synthesis, Characterization and Evalution of Antibacterial Activity of Some Hydrazones”, *Farmaco*,57,595-599.

8. Loncle, C; Brunel, J. M.; Vidal, N.; Dherbomez, M. and Letourneux, Y; (2004)“Synthesis and Antifungal Activity of Cholesterol-Hydrazone Derivatives” *Eur. J. Med. Chem.*, 39, 1067-1071.
9. Canpolat, E. and Kaya, M.; (2004) Studies on mononuclear chelates derived from substituted Schiff-base ligands (part2) synthesis and characterization of a new 5-bromosalicyliden paminoacetophenone oxime and its complexes with Co(II), Ni(II), Cu(II) and Zn(II) ,*J. Coord.Chem.* 7,123.
10. Chakravarty,A.R.; Nreddy,A.P.; Santra, B.K. and Thomas, A.M.; Copper Complexes as Chemical Nucleases, 2002; J. Indian. Chem. Sci., 114, 319-401 .
11. Patole, S. D; Padhye, S. and Ratledge, C.; (2006) “Schiff Base Conjugates of P-Aminosalicylic Acid as Antimycobacterial Agents”,*Bioorg. Med. Chem. Lett*, 16, 1514-1517.

12. Lever, A.B.P.;(1968) Crystal Field Spectra, Inorganic Electronic Specroscopy, first ed .*Elsevier.*, Amsterdam, 249.

13. Natesan, M. and Rajavel Dr. R. (2011),Binuclear Copper (II), Ninckel(II) and oxovanadium (IV) Schiff Base ComplexesBearingN_2O_2 Donors And Their DNA Cileavage And Antibacterial Activity *International Journal Of Pharmacy & Technology*, 2(4), 1133-1157.

14. Shyamapada, S.; Ravish, S. and Tayur, R. N. A;(2014)Dinuclear Cadmium(II)Schiff Base Thiocyanato Complex: Crystal Structure and Fluorescence *Acta Chim. Slov*, *61,* 59-66

15. Hirayama N, Takeuchi I, Honjo T, Kubono K and Kokusen H; (1997)Ion-pairextraction system for the mutual separation of lanthanides using divalent quadridentate schiff bases *Anal. Chem.*, 69, 4814-4818.

16. .Jasim, Sh. S. ;(2012) Synthesis, Characterization of New Schiff Base and Some Metal Complexes Derived from Glyoxylic acid and O-Phenylenediamine, Ibn-AL-Haitham, *J. for Pure and Appl. Sci.*, 25,264-275.

17. Tajmir, R. ;(1991) Coordination chemistry of Vitamin C. part (II). Interaction of L-Ascorbic Acid with Zn(II), Cd(II), Hg(II), and Mn(II) Ions in the solid state and in Aqueous Solution, *Int. J. Inorg. Biochem*, 42, 47-55

18. Geeta,B.and Ravinder, V.; (2011) Synthesis, Characterization and Biological evaluation of mononuclear Co(II) ,Ni(II) and Pd(II) Complexes, with New N_2O_2Schiff base ligand, *Chem., pharm. Bull.*, 95 (2), 166-171.

19. Tajmir, R. ;(1991) Coordination chemistry of Vitamin C. part (II). Interaction of L-Ascorbic Acid With Zn(II), Cd(II), Hg(II), and Mn(II) Ions in The Solid State and in Aqueous Solution, *Int. J. Inorg. Biochem*, 42, 47-55.

20. Arif, M.; Qurashi, M. M. R. and Shad, M. A.;(2001) Metal- Based Antibacterial Agents; Synthesis, Characterization and in Vitro Biological Evaluation of Cefixime- Derived Schiff Bases and Their Complexes With Zn (II), Cu (II), Ni (II) and Co (II), *J. Coord. Chem.* 64, (11), 1914-1930.

21. Choi, K. Y.; Jeon, Y. M.; Lee, K. C.;Ryu ,H.,Suh M.; Park, H. S.; Kim, M. J. and Song,Y. H.;(2004) Preparation and Characterization of a Bidentate Carboxylate Bridged Dinuclear Cadimium (II) Complex With Bis(2-Pyridyl Methyl) Amino-3-Propionic Acid*, J.Chem. Cryst.*, 34 (9), 591-596.

22. Hankare, P.P.; Patil, R.K.; Chavan, S.S.; Jagtap, A.H. and Battase, P.S.;(2001) Synthesis , Characterization and Biological Studies of Bivalent Metal Complexes of Schiff Bases Derived from Aminothiazole and Substituted Azosalicyl aldehyde. *Ind. J.Chem.*, 40A:1326–1329.

23. Mahalakshmi,N; and Rajavel R.;(2011)Synthesis, Spectroscopic Characterization, DNA Cleavage And Antimicrobial Activity Of Binuclear Copper(II), Nickel(II) And Oxovanadium (IV) Schiff Base Complexes, *Asian J. of Biochemical and Pharmaceutical Research* ,2 (1), 526-543

24. Rajavel, R.;Vedanayaki, S.; Sandhanamalar, D. and Jayaseelan, P.;(2011), Synthesis, Spectroscopic and Antimicrobial Studies of Binuclear Transition Metal Complexes with Tetradentate Schiff Base, *Research J. of Pharma., Bio. and Chem.Sci.*,3(2), 994-1001.

25. Ruaa M. Al-Juburi ;(2012) Synthesis and Characterization of Some Heterocyclic Compounds (Oxazepine, Tetrazole) Derived from Schiff Bases, *J. of Al-Nahrain University* 15(4), 60-67.

26. Maccari, R; Ottana, R. and Vigorita, MG;(2005)"In Vitro Advanced Antimyco- bacterial Screeninig of Isoniazid-Related Hydrazones, Hydrazides and cyanoboranes: Part 14", *Bioorg. Med. Chem . Lett.*, 15, 2509-2513.

Table (1) Physical properties of the ligand and its complexes.

Compounds	Formula	Molecular Weight	Colour	Wight g, Yeild%	M.P.	%Elemental Analysis Found % (Calculated)			
						C	H	N	M
H_2L	$C_{40}H_{28}N_2O_4$	600.66	yellow	0.24g, 85%	187	79.76 (79.98)	4.78 (4.70)	4.43 (4.66)	-
$[Co(L)]_2$	$C_{80}H_{52}Co_2N_4O_8$	1315.16	Brown	0.31g, 77%	220	72.98 (73.06)	4.09 (3.99)	4.42 (4.26)	9.08 (8.96)
$[Ni(L)]_2$	$C_{80}H_{52}N_4Ni_2O_8$	1314.68	Brown	0.31g, 72%	254	72.87 (73.09)	3.67 (3.99)	4.09 (4.26)	8.78 (8.93)
$[Cu(L)]_2$	$C_{80}H_{52}Cu_2N_4O_8$	1324.38	Deep brown	0.23g, 75%	228	72.57 (72.55)	3.52 (3.96)	3.14 (4.23)	3.75 (4.23)
$[Mn(L)]_2$	$C_{80}H_{52}Mn_2N_4O_8$	1307.17	Brown	0.31g, 64%	245	73.12 (73.51)	3.89 (4.01)	4.33 (4.29)	8.32 (8.41)
$[Hg(L)]_2$	$C_{80}H_{52}Hg_2N_4O_8$	1598.47	Off-White	0.31g, 68%	241	59.5 (60.11)	3.64 (3.28)	6.89 (3.51)	25.45 (25.10)

DMSO	**C=$\underline{C_6H}_5$(aromatic protons)**	**-COO$\underline{H}$ (carboxylate proton)**
2.49	6.84-8.44.	12.26

Table (3) ^{13}C-NMR Chemical transfers for (H_2L)

DMSO	**C=$\underline{C}_6$H 5(aromatic carbons)**	**$\underline{C}$OOH(carboxylate carbon)**	**$\underline{C}$=N-(imine carbon)**
40.81	122.11~153.67	159.09	161.12

Table (4) The major hesitations of the compounds (cm^{-1}).

Compounds	υ(OH)	υ(C=N)	$υ_{as}(COO^-)$	$υ_s(COO^-)$	$Δυ_{as(COO^-)}$.- $Δυ_{s(COO^-)}$	υ(M-N)	υ(M-O)
Ligand(L)	3441	1683	-	-	-	-	-
$[Mn_2(L)_2]$	-	1645	1499	1424	99	571	472
$[Co_2(L)_2]$	-	1651	1502	1389	119	541	469
$[Ni_2(L)_2]$	-	1662	1509	1372	137	484	440
$[Cu_2(L)_2]$	-	1637	1507	1366	141	519	483
$[Hg_2(L)_2]$	-	1660	1510	1378	132	557	445

Table (5) Conductance measurements magnetic susceptibility and UV-Vis data

Compounds	(B.M) $μ_{eff}$	$Λ_m(S.cm^2.mol^{-1})$ (10^{-3}M) in ethanol	(nm)$λ_{max}$	ABS	(cm^{-1}) Wave number	$L.mol^{-1}.cm^{-1}$ $€_{max}$	functions	Geometry
Ligand	-	-	288 342	1.981 0.531	34722 29239	1981 531	n→π* π→π*	-
$[Mn_2(L)_2]$	5.64	16	297 365 487 584	2.026 2.127 0.510 0.112	33670 27397 20533 17123	2026 2127 510 112	L.F C.T $^6A_1→^4A_{1(G)}$ $^6A_1→^4E_{(G)}$	Tetrahedral
$[Co_2(L)_2]$	4.35	15	292 347 621	2.069 2.145 0.032	34246 28818 16103	2069 2145 32	L.F C.T $^4A_2→^4T_{1(P)}$	Tetrahedral
$[Ni_2(L)_2]$	3.80	12	284 346 419 702	2.016 1.971 1.215 0.016	35211 28901 23866 14245	2016 1971 1215 16	L.F C.T $^3T_2→^3T_1$ $^3T_1→^3A_2$	Tetrahedral
$[Cu_2(L)_2]$	2.2	17	290 340 509	0.056 1.521 0.402	34482 29411 19646	56 1521 402	L.F C.T $^2E→^2B_2$	Tetrahedral
$[Hg_2(L)_2]$	Dia.	11	310 388	1.820 0.623	32258 25773	1820 623	C.T C.T	Tetrahedral

Table (6) Diameter of area of suppression (mm)

Comp.	DMSO control	H_2L	$[Mn_2(L)_2]$	$[Co_2(L)_2]$	$[Ni_2(L)_2]$	$[Cu_2(L)_2]$	$Hg_2(L)_2]$
Escherichia. Coli	-	2	11	4	10	7	7
Staphylococcus aureus	1	6	7	7	5	9	3
Bacllus	1	3	6	1	3	8	5
pseudmonas	-	7	4	3	1	6	3

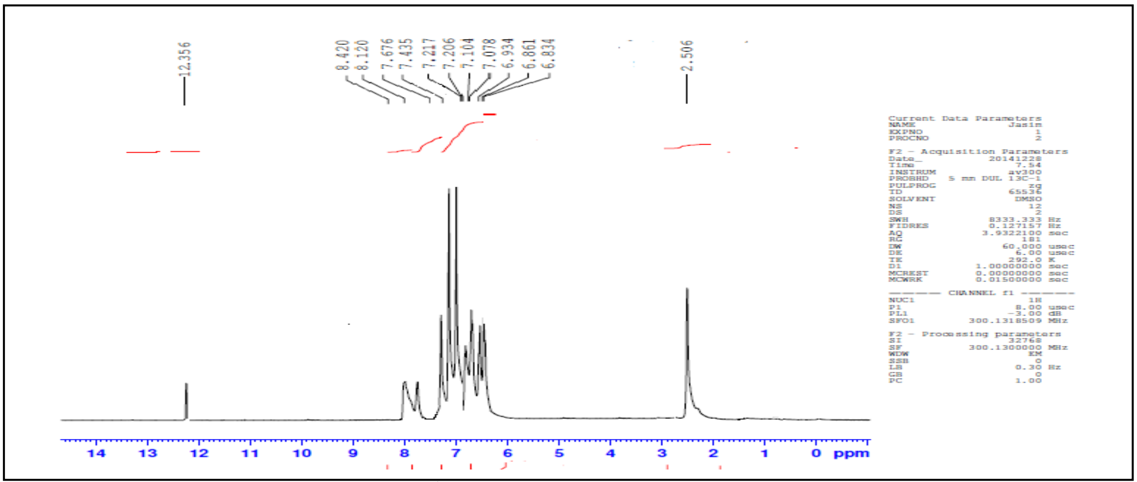


Figure (1) ^{1}HNMR spectrum of ligand.

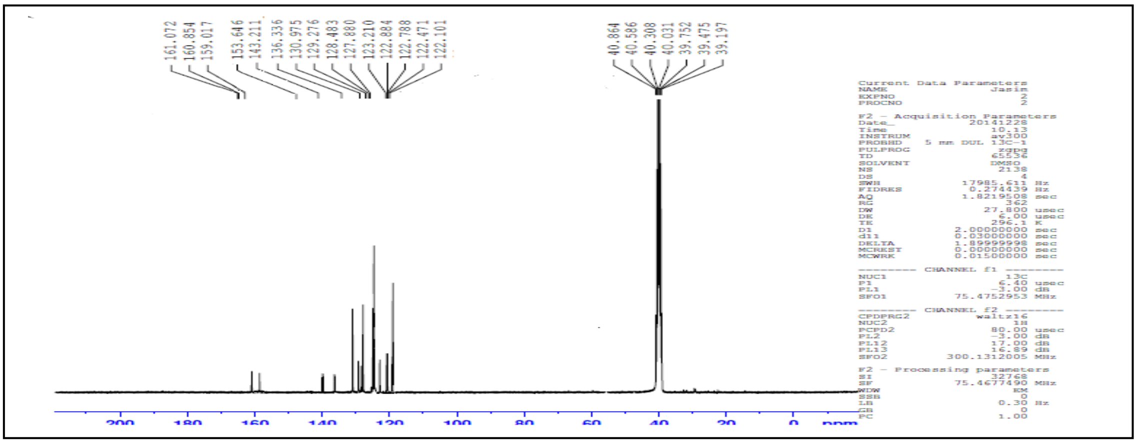


Figure (2) ^{13}CNMR spectrum of ligand

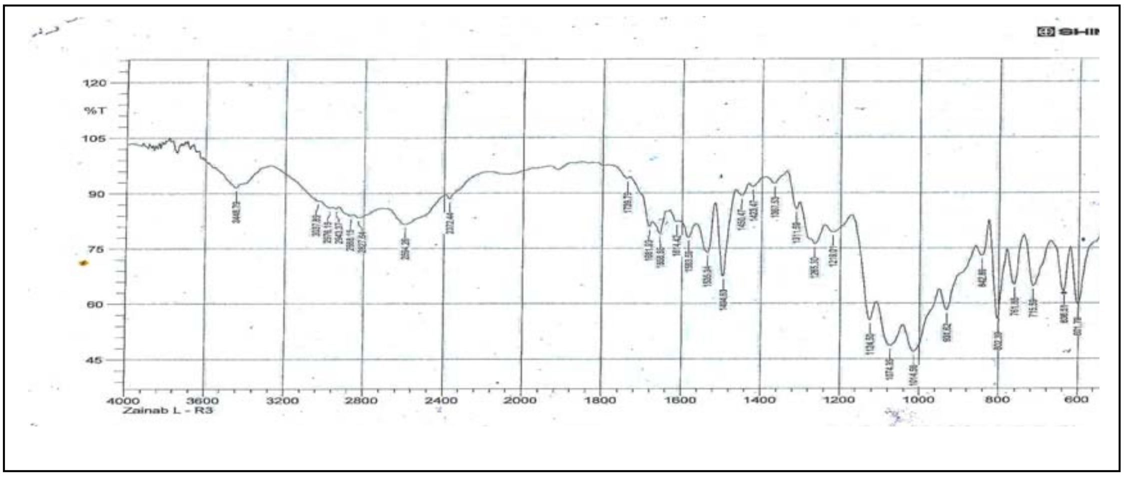


Figure (3) IR spectrum of ligand.

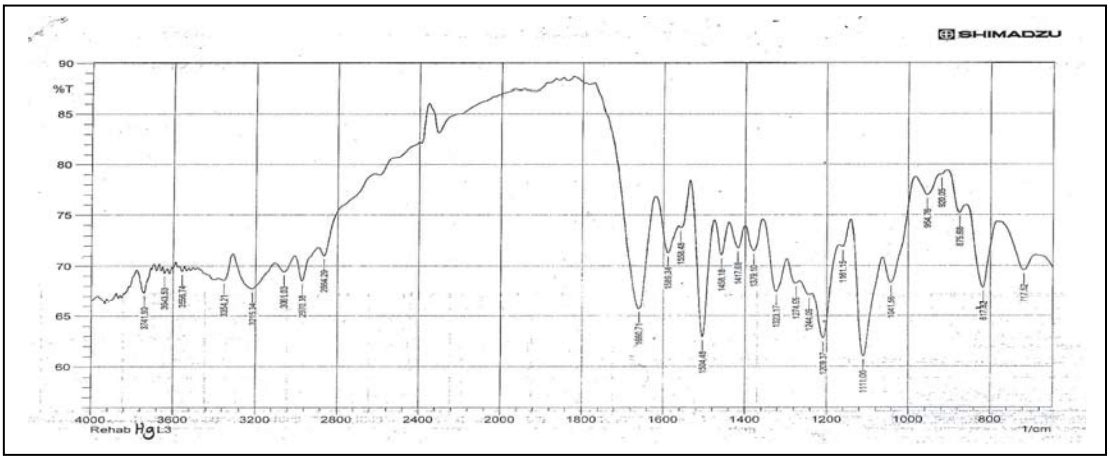


Figure (4) IR spectrum of Complex $[Hg_2(L)_2]$

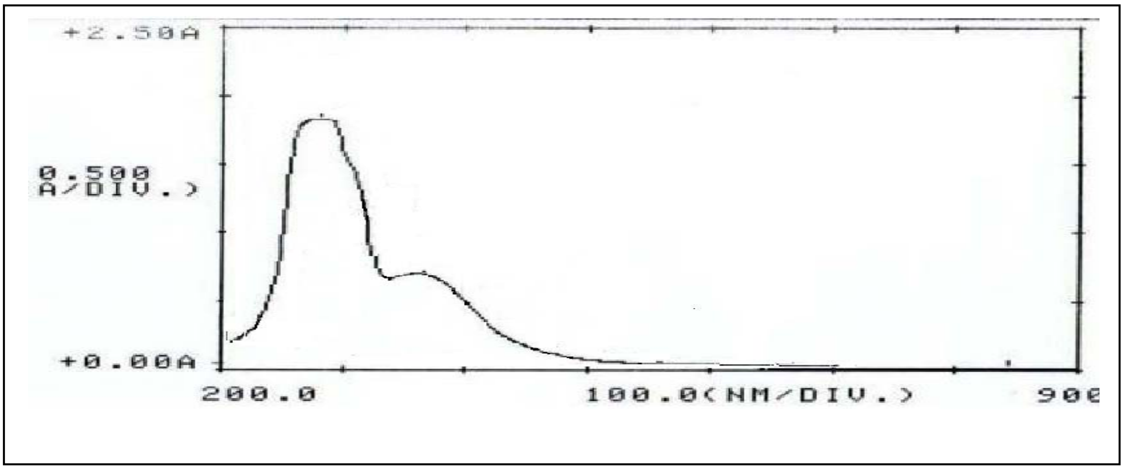


Figure (5) UV of (H_2L)

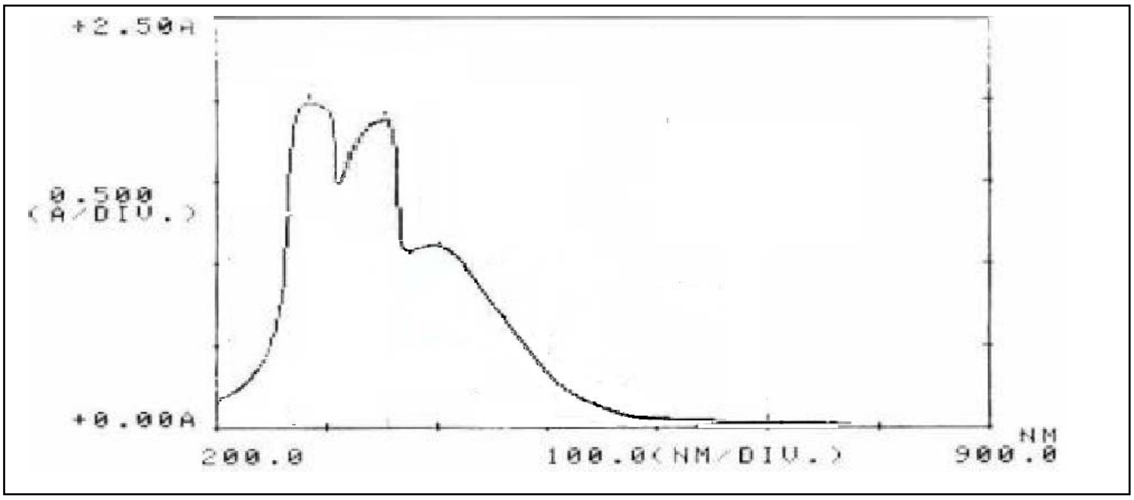


Figure (6) UV of $[Ni_2(L)_2]$

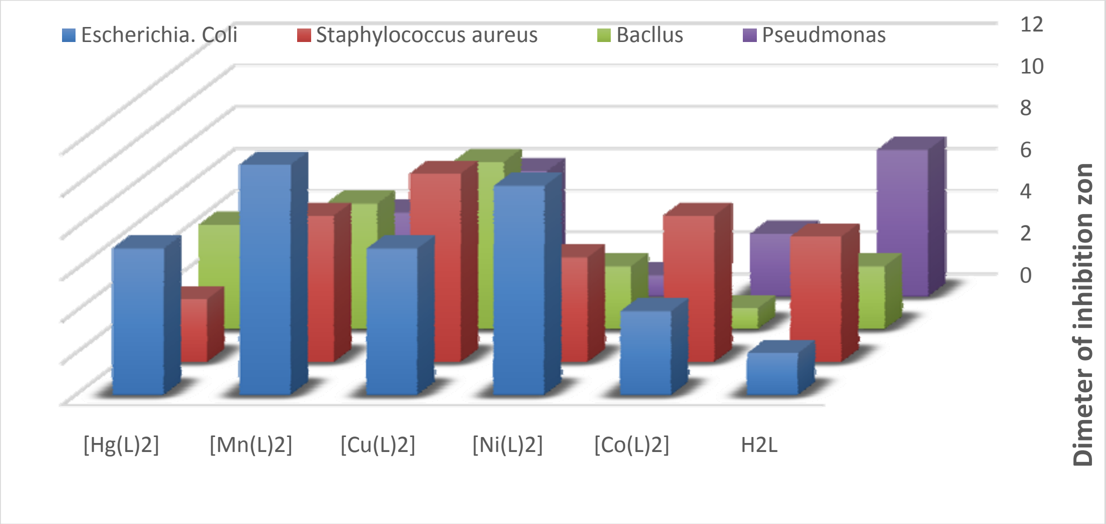


Figure (7) Difference between the antimicrobial activity of (H_2L)& metal complexes

توليف وتشخيص والنشاط الحيوي للثنائي النواة للمعقدات الكوبلت (II) والنحاس(II) ، النيكل(II) ، المنجنيز (II) والزئبق (II) مع ليكاند قاعدة شف من نوع N_2O_2

رحاب كاظم آلشمري
فائزة حسن غانم .
قسم الكيمياء/ كلية التربية للعلوم الصرفة (ابن الهيثم)/ جامعة بغداد

استلم في:1/اذار/2016، قبل في:28/حزيران/2016

الخلاصة

معقدات النحاس والنيكل والكوبالت والمنغنيز والزئبق الثنائي النواة مع قاعدة شيف H_2L ($C_{40}H_{28}N_2O_4$) التي حصلت عليها من تكثيف البنزينيدين مع 2-بنزويل حمض البنزويك. وقد تم تحليل العناصر لليكاند قاعدة شيف والمعقدات ، الدراسات الطيفية من خلال الاشعة تحت الحمراء والأشعة المرئية وفوق البنفسجية , الرنين النووي المغناطيسي وقياسات التوصيل المولي و العزم مغناطيسي والسائل اللوني عالي الأداء. وأظهرت جميع المعقدات هندستها رباعي السطوح مع الهيكل العام $[M_2(L)_2]$.معظم المركبات مستعدة لاظهار نشاط مضاد للجراثيم للبكتريا: (*Staphylococcus aureus*), (*Bacillus*),(*Escherichiacoli*)و(*Pesudomonas*).

الكلمات المفتاحية : تشخيص،قاعدة شف،2-بنزويل حمض البنزويك، البنزينيدين،معقدات ثنائية السن والفعالية البايولوجية