Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(9):4141-4148

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis, Characterization, Schiff Base Phenyl 2-(2-hydroxybenzylidenamino)benzoate and its complexes with La^{III}, Cr ^{III} and Pr ^{III}

Taghreed H. Al-Noor, Sajed. M. Lateef and Mazin H. Rhayma

Department of Chemistry, College of Education, Ibn Al-Haitham, University of Baghdad-Iraq

---

ABSTRACT

The aim of the work is the synthesis and characterization of the tridentate Schiff base (HL) containing (N and O) as donor atoms type (ONO). The ligand is: (HL) phenyl 2-(2-hydroxybenzylidenamino)benzoate . This ligand was prepared by the reaction of (phenyl 2-aminobenzoate) with salicylaldehyde under reflux in ethanol and few drops of glacial acetic acid which gave the ligand (HL). The prepared ligand was characterized by (FT IR,UV–Vis) spectroscopy, Elemental analysis of carbon, hydrogen and nitrogen (C.H.N.) and melting point. The ligand was reacted with some metal ions under reflux in ethanol with (1 metal :2 ligand)mole ratio which gave complexes of the general formula:

$[M(L)_2]Cl$, $M =$ Cr^{III} La^{III} *and* , Pr^{III}

Products were found to be solid crystalline complexes, which have been characterized through the following techniques: Molar conductivity .Spectroscopic Method [FTIR and UV-Vis], additional measurement magnetic suspeliblity, Chloride content and Program [Chem. office–CS. Chem.–3D pro 2006]was used. Our research also includes studying the bio–activity of the (ligand and$[La(L)_2]Cl$ *some compounds prepared against a kind of bacteria three of which were negative to gram dye (Proteus mirabilis, Klebsiella pneumonia, Escherichia coli), and one was positive to gram dye (Staphylococcus aureus). The* $[La(L)_2]Cl$ *showed inhibitive activity against some of bacteria under consideration. The magnetic moment coupled with the electronic spectra suggested an octahedral geometry for all the complexes .*

Key words: *Complexes , Schiff Base, phenyl2-(2-hydroxybenzylidenamino)* benzoate *and Antibacterial Activities*

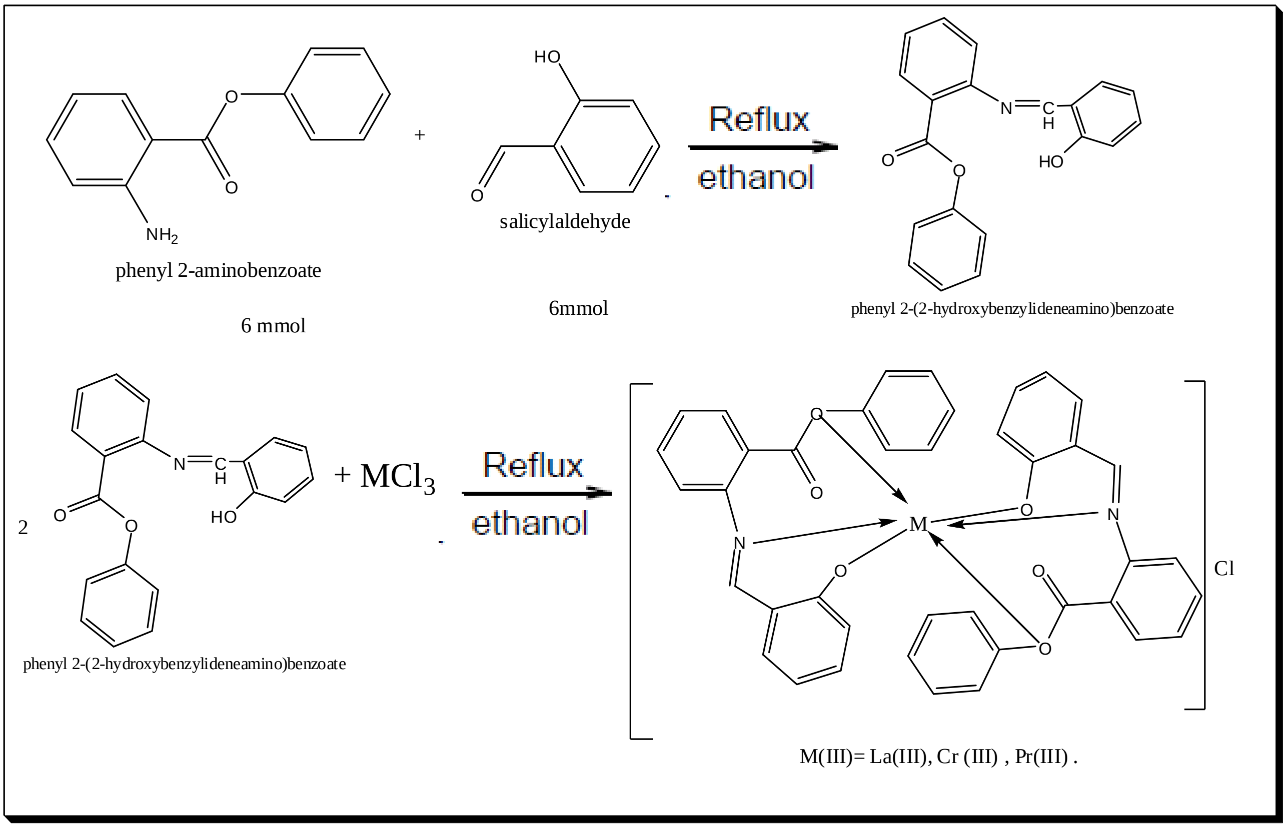
INTRODUCTION

Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions [1-2]. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species. Schiff base metal complexes were investigated for fungicidal, , bactericidal activities[3-5].Among the ligands the linear or cyclic Schiff bases obtained by the condensation of primary amines with carbonyl compounds and their metal complexes find a variety of applications including biological, clinical, analytical and industrial, in addition to their important role in catalysis and organic synthesis [6,7]. Schiff bases ligands and their metal complexes have a variety of applications in biological, clinical ,analytical and industrial fields [8, 9]. Among these, heterocyclic Schiff base ligands and their metal complexes do have significant interest because of their pharmacological properties [10]. Furthermore, the interaction of these complexes with DNA has gained much attention due to their possible applications as new therapeutic agents [9,10].

The Cr(III), Fe(III) and Co(III) complexes formed form tetradentate (ONNO) Schiff base ligands, 1,4-bis[3-(2-hydroxy-1-naphthaldimine)propyl] piperazine and 1,8-bis[3-(2-hydroxy-1-naphthaldimine)-pmenthane, show moderate antimicrobial activity [11] compared to standard antibiotics [12].

The antibacterial activity of the tridentate Schiff base, formed by condensation of 2-amino-3-carboxyethyl-4,5-dimethylthiophene with salicylaldehyde, was found to increase on chelation with transition metal ions [4].

This paper reports the synthesis and characterization of a new ligand derived from the reaction of Salicylaldehyde and 2-phenyl-amino benzoate and its complexes.



(Figure. 1)Schematic representation of synthesis of HL ligand and its complexes

EXPERIMENTAL SECTION

2.1. Chemical and Instrumentals

All chemicals used were of reagent grade (supplied by either Merck or Fluka , and used as supplied.

a - Metal salts ($CrCl_3$, and $LaCl_3$.Salicylaldehydes, 2-phenyl-amino benzoate ($C_{13}H_{11}NO_2$) , ethanol, methanol and dimethylforamaide , and KBr from (B.D.H).

Instrumentation

b - UV-Vis spectra were recorded on a (Shimadzu UV- 160A) Ultra Violet-Visible Spectrophotometer. IR- spectra were taken on a (Shimadzu, FTI R- 8400S) Fourier Transform Infrared Spectrophotometer (4000- 400) cm^{-1} with samples prepared as KBr discs.. Microelemental analysis (C.H.N) were performed in Al-Mustansiriyah university – college of science While metal contents of the complexes were determined by atomic absorption(A.A)technique using a Shimadzu AA 680G atomic absorption spectrophotometer.. Conductivities were measured for 10^{-3}M of complexes in ethanol at 25^{o}C using (Philips PW- Digital Conduct meter). Magnetic measurements were recorded on a Bruker BM6 instrument at 298°K following the Farady's method . In addition melting points were obtained using (Stuart Melting Point Apparatus). The proposed molecular structure of the complexes were drawing by using chem. office prog, 3DX (2006).

2.2.Preparation of Schiff Base*:*

The Schiff base was Prepared by standard method (Figure. 1), In a round bottom flask .The Schiff base phenyl2-(2-form Salicylaldehyde and 2phenyl-amino benzoate was prepared by adding $25cm^3$ of Salicylaldehyde ethanolic solution (0.73gm; 6m mol) to the same volume of ethanolic solution of 2 phenyl-amino benzoate (1.28 gm; 6m mol). The resulting solution was evaporated under vacuum ^{o} C). 65The mixture was stirred for 3hrs at () to remove the solvent.

The Product was collected by filtration, washed several times with ethanol and recrystallized from hot ethanol and air dried . The melting point of the product found to be (170 ^{o}C) The color of the product is orange. yield 94.14 %. Anal. Calcd for ligand(HL) C = 33.03%, H = 5.19%, N = 10.27%; Found: C = 33.23%, H = 5.34%, N = 10.21%.

2.3.General Method for Preparation of the Complexes:

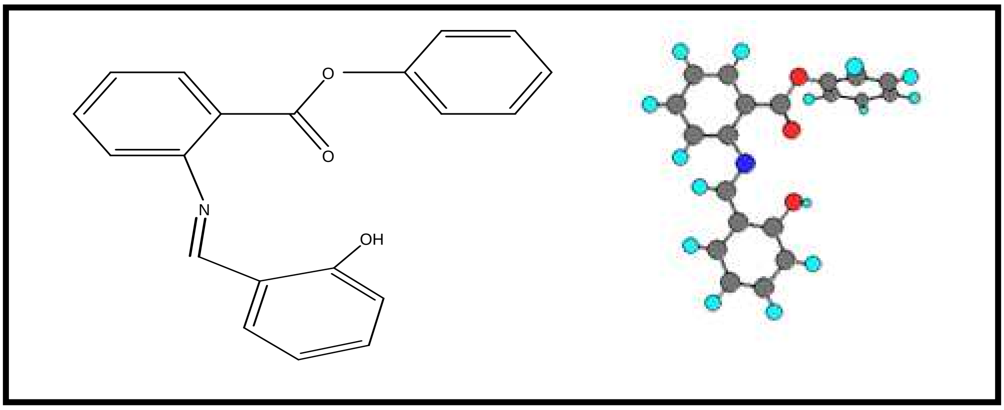
All complexes were prepared by dissolving (0.634gm; 2mmole) of phenyl2-(2-hydroxybenzylidenamino)benzoate(HL) in (30ml)ethanol. The solution was added gradually with stirring to(20ml) solution of the respective metal (II) chloride (1mmole). The mixture was stirred for(2-3)hrs at 65^{o} C).The resulting solution was evaporated under vacuum to remove the solvent. the colored complexes separated out in each case. The Product was filtered, washed several times with ethanol and recrystallized from hot ethanol and air dried at room temperature .

2.4. Antimicrobial activities

Antimicrobial activities of the ligand and the complex $[La (L)_2]Cl$ have been carried out against the pathogenic bacteria like Escherichia coli, Bacillus subtilis, Staphylococcus aureus, and Pseudomonas aeruginosa, using nutrient agar medium by disc diffusion method [8] . The test solution were prepared in DMSO and soaked in filter paper of 5 mm diameter and 1mm thickness. These discs were placed on the already seeded plates and incubated at 37 ^{o}C for 24 h. The diameters (mm) of the inhibition zone around each disc were measured after 24 hours. [12-13].

RESULTS AND DISCUSSION

The phenyl2-(2-hydroxybenzylidenamino)benzoate(HL)(Figure. 2)*was*_prepared by reacting equimolar amounts of Salicylaldehyde and 2phenyl-amino benzoate in ethanol. The complexes were prepared by direct reaction of the ligand (HL) with the metal (II) chlorides in ethanol.



(Figure. 2) Chemical structure of phenyl 2-(2-hydroxybenzylidenamino)benzoate (HL)

3.1.Characterization of Schiff bases and metal complexes:

The Schiff base ligands and their complexes were characterized by using, FT-IR, UV-Vis spectroscopy , magnetic susceptibility and conductance measurements. And elemental analysis for Schiff base only.

3.2. Physical properties of the prepared complexes*:*

Table (1) shows the physical data for the prepared complexes which show different melting points, All the complexes are colored, non-hygroscopic and thermally stable solids indicating a strong metal-ligand bond. The complexes are insoluble in water and benzene but soluble in common organic solvents such as ethanol, ethyl alcohol, acetone, chloroform ,DMF and DMSO. and atomic Absorption measurements (Table-1)) C l (٪ Chloride content for all complexes gave approximated values for theoretical values.

3.3. Molar Conductance (Λm):

The observed molar conductance (Table 1) values measured in ethanol in 10^{-3}M solution lie in the (30.4-36.2) Ω^{-1} cm^{2} mol^{-1} range, indicted that the complexes are electrolytes 1:1 nature.[14]

3.4. Fourier transform infrared spectra:

Infrared spectral data have been reported by research groups working on the synthesis of Schiff bases their metal complexes. The characteristic bands in Schiff base are used to determine the binding modes found in the system are (C=N), υ (O-H), υ (M-O), υ (M-N).

A summary of characteristics IR bands is shown in Table 2 (Figure. 3). Generally, the band that are in the 1640 cm^{-1} are assigned to the existence of ν(HC=N-) group of the azomethine. for ligand and complexes are in the range of 1620-1625 cm^{-1}.This band gets shifted to lower frequency in the complexes, indicating the coordination through azomethine nitrogen to metal atom. [15-16] υ(C=O) in the1659 cm^{-1} are assigned to ligand and and its complexes' . υ (O-H) in the 3039cm^{-1} are assigned to ligand and 3232-3549 cm^{-1} are assigned to complexes. Metal oxygen and metal nitrogen are found to be in the range of (420-466)$cm^{-1}$and (513-524)cm^{-1}.The complexes show band at (590-520) and (470-489) cm^{-1} rang, due to the υ (M-O) and υ (M-N) vibrations respectively. [17-19]

3.5. Electronic spectra and magnetic moment:

The UV-Vis spectra data for of the free ligands (HL) and three complexes are listed in (Table-3). The UV-Vis spectrum of the ligand (HL) (Figure. 4) shows three peaks at 235 nm (42553 cm^{-1}), 299 nm(33445 cm^{-1}) and 358 nm (28169 cm^{-1})assigned to $(\pi - \pi^*)$, $(n - \pi^*)$, and, $(n - \pi^*)$ electronic transitions respectively).[18].The absorption peaks in the region(223-283)and (345-349)nm for all complexes assigned to ligand field (LF),and charge transfer (CT) respectively).[20 -23], while the peaks in the region (808-872) nm which assigned to 4f-4f or 4f-5d transition for [Pr(L)$_2$] Cl and[La (L)$_2$] Cl respectively. [20] .The visible absorption spectra of lanthanide compounds is generally dominated by *f-f* transitions. Because the f orbitals are well shielded from the surroundings and are not involved in the bonding, the *f-f* transitions are very sharp and essentially insensitive to the coordination environment. [21 -23]

The electronic spectrum of Cr(III) shows two intense bands, characterized in the descending order of frequency to represent the transitions 4A2 → 4T1(F) and 4A2 → 4T2(F) . respectively.

The magnetic moments of the complexes shown in Table (3) were calculated from the measured magnetic susceptibilities after employing diamagnetic corrections and revealed their diamagnetic nature as expected for La(III) with 4f ^{0} configuration.The magnetic moment shows the Cr(III) ion to be (3.34BM) with d^3 (T_2g^3 eg) configuration in a distorted octahedral environment. The magnetic moment shows the Pr(III) ion to be (3.3BM). [21 -23]

3.6. Antibacterial Activities:

Antibacterial activity of ligand and [La(L)$_2$] Cl complex, are recorded in Table 4. (Figure. 5) It has been observed that the metal complex have a high activity than ligand against same organisms under the identical experimental condition.

It is evident from the above data that the antibacterial activity significantly increased on coordination. This enhancement in the activity may be rationalized on the basis of their structures mainly possessing an additional azomethine bond. It has been suggested that the ligand with nitrogen and oxygen donor systems inhibit enzyme activity. Coordination reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor groups within the chelate ring system..[24- 25]

Table (1) The physical properties of the complexes

Chemical Formula L =$C_{20}H_{14}NO_3$	**Formula Weight g·mol^1**	**Color**	**Melting Point (°C)**	**Λm Ω^{-1} cm^2 mol^{-1}**	**Metal % Theory**	**Metal% Exp**	**Cl % Exp (Theory)**
[Cr(L)$_2$] Cl	720.11	green	166	32.8	**7.22**	**8.32**	6.97 (4.92)
[La (L)$_2$] Cl	807.02	Pale green	160	36.2	17.21	17.**8**2	3.78 (4.39)
[pr(L)$_2$] Cl	809.02	White yellow	166	30.4	17.42	1**8.2**2	3.65 (4.38)

Table (2)FT-IR spectral data of the Ligand and its Complexes

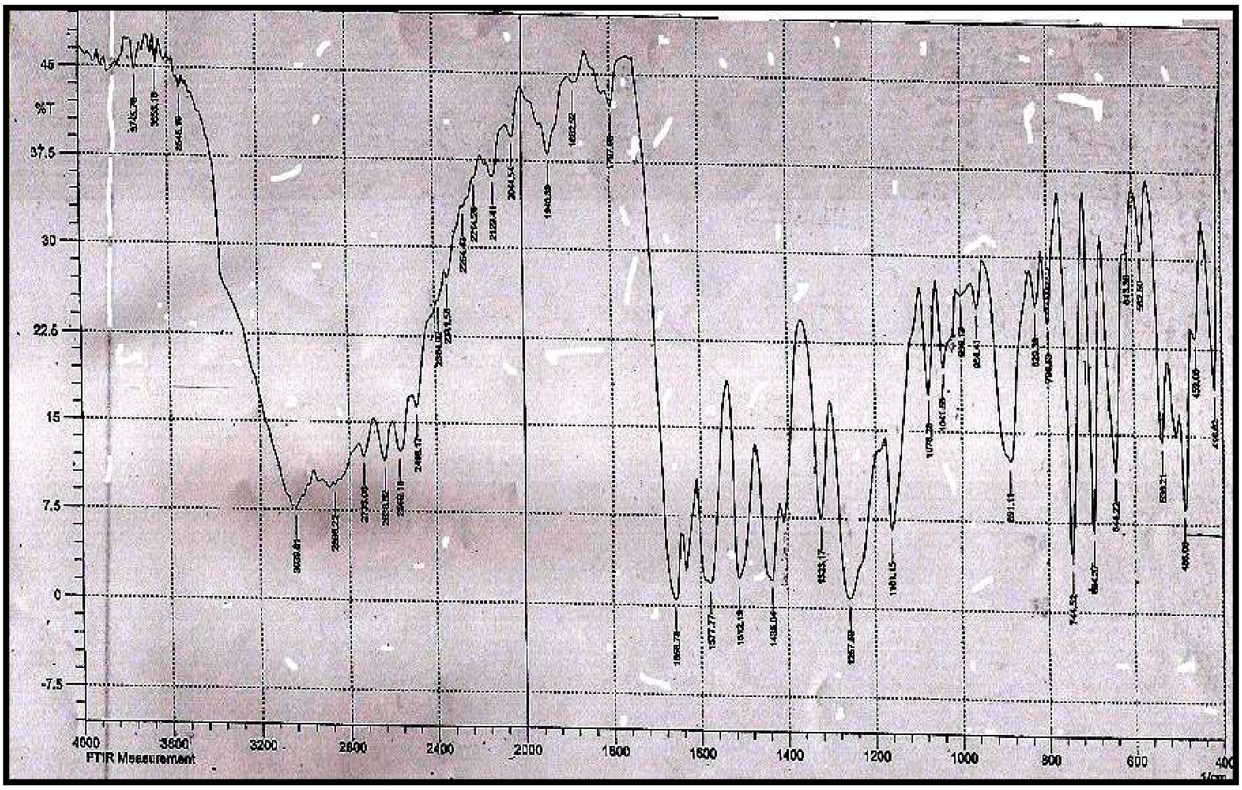
Compounds	**υ (O-H)**	**υ (C=O)**	**υ (C-O-C) asy. , sy.**	**υ(C=N)**	**υ (C-O)**	**δ (C-O)**	**υ (M-O)**	**υ (M-N)**	**Additional bunds**
[HL]	3039 (b)	1659 (m)	1257 (s) 1161 (m)	1640 (w)	1240 (w)	826 (w)	-	-	υ(C=C)aroma. 1527,1512,1435. υ(C-H) aroma. 3039 υ(C-H)imin. 2735, d(Co_2)644 υ(C-N) 1041 r(Co_2) 536 b(C-OH)486
$[Cr(L)_2]$ Cl	3452 (b)	1659 (m)	1261 (Vs) 1161 (m)	1620 (w)	1130 (w)	829 (w)	443 (w)	509 (w)	υ(C=C)aroma. 1577,1508,1435. υ(C-H) aroma. 3043 υ(C-H)imin. 2760 υ(C-N) 1041 d(Co_2)644 r(Co_2) 536
$La(L)_2]$ Cl	3402 (b)	1659 (s)	1261 (Vs) 1161 (m)	1618 (w)	1140 (w)	825 (w)	435 (w)	508 (w)	υ(C=C)aroma. 1569,1512,1435. υ(C-H) aroma. 3093 υ(C-H)imin. 2735, υ(C-N) 1041 d(Co_2)644 r(Co_2) 536

Table (3) Selected electronic bands, spectral parameters and magnetic moments of the ligand and its complexes

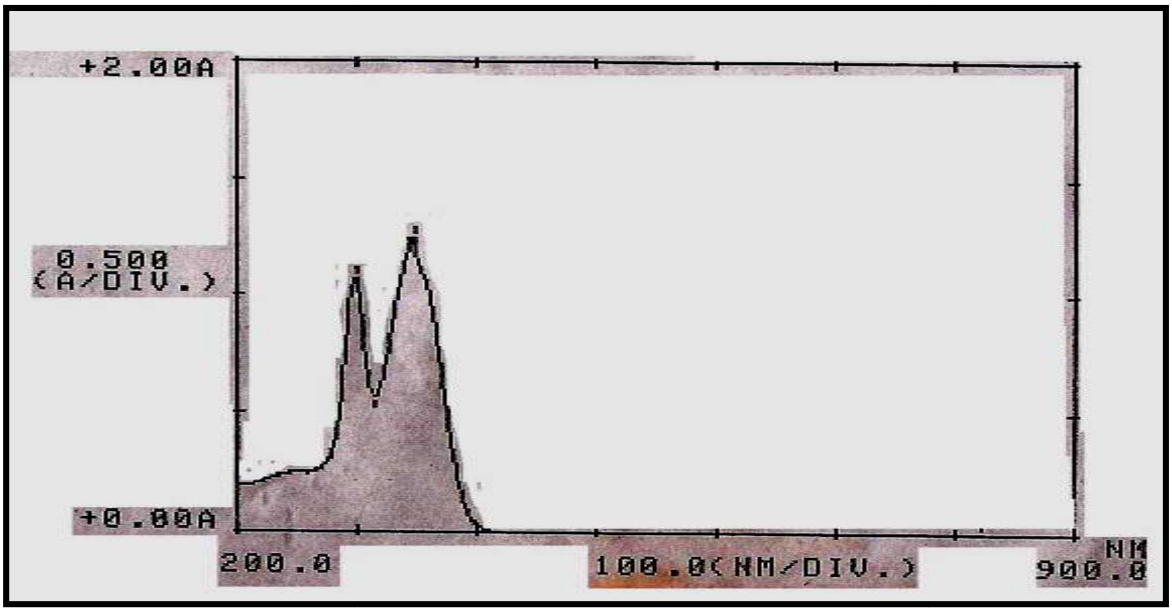
Compounds	**nm λ**	**υ^{-} $_{(Cm)}$ $^{-1}$**	**ξ_{max} L. mol^{-}.cm^{-1}**	**Assignment**	**μ_{eff} (BM)**
[HL]	235	42553	21	$\pi \rightarrow \pi^*$	-
	299	33445	1076	$\pi \rightarrow \pi^*$	
	358	28169	1244	$n \rightarrow \pi^*$	
$[Cr(L)_2]$ Cl	228	43860	1880	L-F	3.34
	283	35336	1669	L-F	
	349	28653	738	C-T	
	426	23474	5	$^4A_{2g} \rightarrow {}^4T_{1g(F)}$	
	895	11173	4	$^4A_{2g} \rightarrow {}^4T_{2g}$	
$[La(L)_2]$Cl	226	44248	1882	L-F	0.00 diamagnetic
	283	35336	2079	L-F	
	348	28736	1040	C-T	
	869	11507	4	f-f	
$[pr(L)_2]$ Cl	227	44053	1632	L-F	3.38
	286	34965	1364	L-F	
	349	28653	601	C-T	
	808	12376	20	4f-4f or 4f-5d	
	872	11468	19	4f-4f or 4f-5d	

Table (4) Showed the inhibition circle diameter in millimeter for the bacteria after 24 hour incubation paid and 37°C for complexes

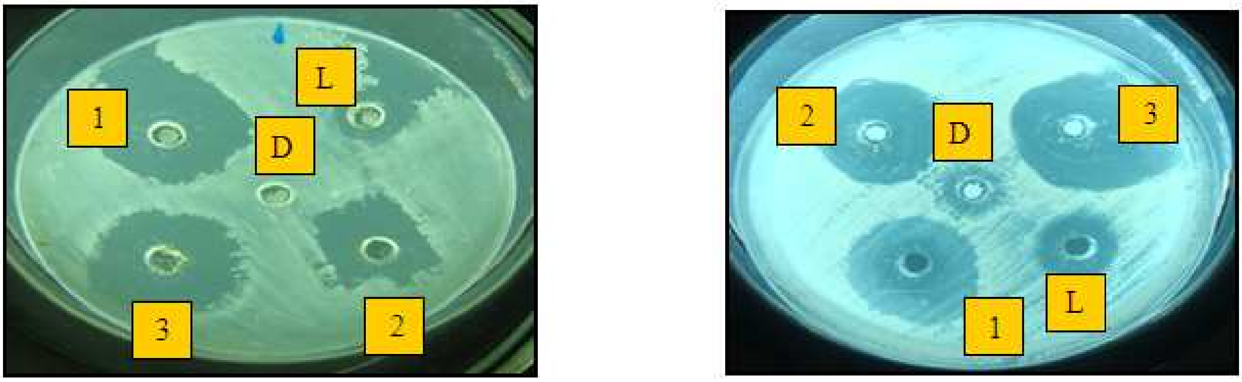
Compounds	***Escherichia coli***	***Proteus mirabilis***	***Klebsiella pneumonias***	***Staphylococcus aurens***
(DMF) Control	10	10	9	10
HL No (L)	11	12	11	12
$[Cr(L)_2]$ Cl No (1)	16	17	17	16
$[La(L)_2]$Cl No (2)	16	15	14	15
$[pr(L)_2]$ Cl No(3)	18	20	17	21



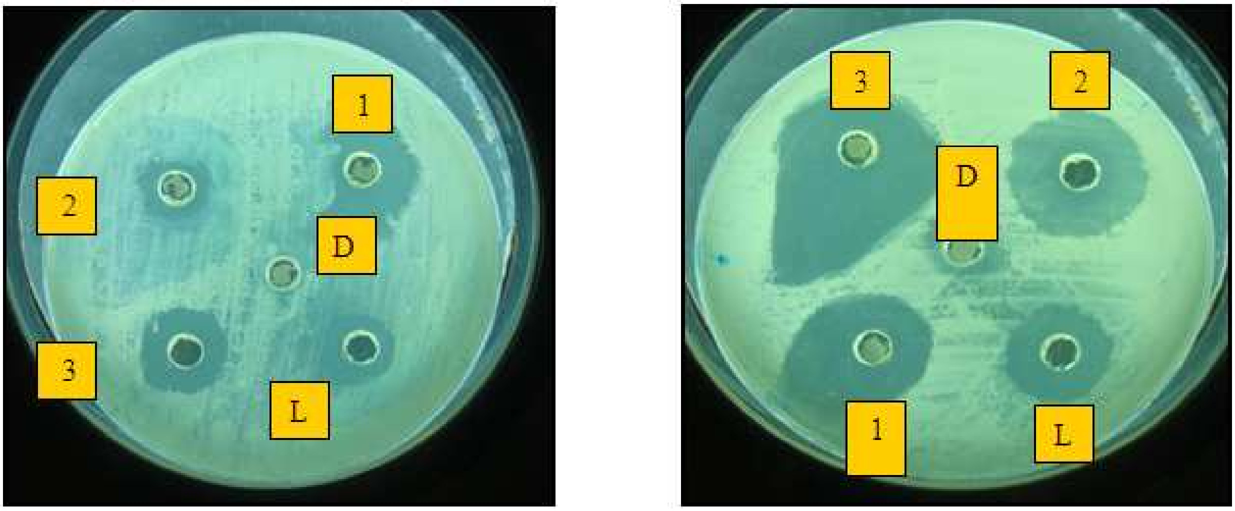
(Figure. 3) *The* (FTIR) Spectrum of phenyl2-(2-hydroxybenzylidenamino)benzoate(HL)



*(*Figure. 4) The (UV-Vis) Spectrum of Phenyl 2-(2-hydroxy benzylidene amino)-6-amino benzoate(HL)



Klebsiella pneumonia(- to gram dye) *Proteus mirabilis*(- to gram dye)



Escherichia coli(- to gram dye) *Staphylococcus aureus*(+ to gram dye)

(Figure. 5) shows the antimicrobial activity of chemical compounds (ligands,complex ,1,2,3) appear the inhibition zones against some pathogenic bacteria

REFERENCES

[1] A M Shallaby, M Mustafa and Moussa, *J.Spectrochim Acta*, **1989**,40A, 999 **1989**.
[2] M, K Mustafa ,Ibrahim M and Moussa, *J*, *Trans Met Chem*., **1984** , 9, 243.
[3] D S, Rao, M C Ganorkar, C S ,Reddy and John V *J, Curr Sci*., **1980** , 49, 511.
[4] V.P. Daniel, B. Murukan, B.S. Kumari, K. Mohanan. *J, Spectrochimica Acta* ,**2008**, *Part A*, 70 .403–410
[5] B K Rai, Choudhary, P Rana S and P Sahi, *Oriental J Chem*., **2007** , 23(1), 291-296.
[6] A ,Budakoti, M .Abid and A. Azam, *Eur. J. Med. Chem*. **2006**, 41(1), 63
[7] V X Jin, S I Tan and J D Ranford, *Inorg. Chim. Acta,* **2005**., 358(3), 677.
[8] S. Kumar, D.N. Dhar, P.N. Saxena, a review. *J. Sci. Ind. Res*,**2009**, 68 (3), 181–187.
[9] K.C.Gupta, A.K Sutar, Catalytic activities of Schiff base transition metal complexes. *Coord. Chem. Rev*. **2008**, 52 (12–14), 1420–1450.
[10] P. Budhani, S.A. Iqbal,, S.M. Bhattacharya, *J. Saudi Chem*. Soc,**2010**, 14, 281–285.
[11] E. Keskioglu, A.B. Gunduzalp, S. Cete, F. Hamurcu, B. Erk. *Spectrochimica Acta*, **2008**,Part A, 70, 634–640.
[12] H. Katircioglu,Y. Beyatl, B.Aslim, Z.Yuksekdag, T.Atici. **2006** *Internet Journal of Microbiology*, 2(2).
[13] J.Awetz ,Melnick and A . Delbrgs,“ Medical Microbiology “2st Edition McGraw Hil-USA (**2007**).
[14] W.J.Geary, Coord. Chem. Rev., 7, 81-122.
[15] M. M.El-ajaily,; A. A.Maihub,; A. N. El-Tajouri, ,**2005**, *The Egyptian Science Magazine*; 2(4), pp 83-87.
[16] C. P. Prebhakaran and C. J. Patelc, *J. Inorg. Nucl. Chem*, **1969**, 31, 3316,.
[17] K, Nakamoto; “ Infrared spectra of Inorganic and coordination compounds ,**1996**, “4st Edition,; J. Wiely and Sons, New york,.
[18] K Sharma; R Singh; N Fahmi; RV Singh, *Spectrochim.* **2010**, *Acta A*, 75, 422.
[19] Y.Nishida., A.Niinuma., K. Abe., *Inorg. Chem. Commun*. **2009**, 12, 198–200.
[20] A.B.P. Lever.**“**Inorganic spectroscopy” Elsevier publishing company , **1984**, “2st Edition, London, New York.
[21] P.D Singh, N.K. Jha and L. K., Mishra , *J. Inorg. Nucl. Chem*, **1980**, 42 (2): 282.

[22] E. M. Stephens, S. Davis, M. F. Reid, and F. S. Richardson. *Inorg. Chem.* **1984**, 23: 4607–4611.
[23] D.W. Shriver, P.W. Atkins " Inorganic Chemistry", **2006**. "4st Edition, Freeman, New York.
[24] R ,Raja Sidambaram, J Jisha and NL Mary, *International Journal of Institutional Pharmacy and* Life Sciences 1(2): **2011**, September-October.
[25] Sarika Verma, Sarita Shrivastva and Poonam Rani, *Journal of Chemical and Pharmaceutical Research*, **2012**,4(1): 693-699