



## Synthesis, Characterization and Antibacterial Study of Selected Metal Complexes Derived from Modified of PVA

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### Abstract

A new ligands(modifier polymers) L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, L<sub>4</sub> and L<sub>5</sub> were prepared according to method [8] by reaction of polyvinyl alcohol(PVA) with (acid chloride)[1]a or [2,3]a,b in dimethyl formamide. The Ligands were characterized by (FT-IR), (UV- Vis) and (<sup>1</sup>H-NMR) spectra some of them. Synthesis some transition metals complexes of these ligands and described via (FT-IR, UV-Vis) spectra, [Thermo gravimetric analysis (TGA), Differential Scanning Calorimetry (DSC)], (SEM) and antibacterial activity was screened thought two types of bacteria. The octahedral geometrical was suggested for Co<sup>+2</sup>, square Planer geometrical was suggested for Ni<sup>+2</sup> and tetrahedral geometrical was suggested for Cd<sup>+2</sup>

**Keywords:** PVA; Metal complexes; Antibacterial.

### Introduction

Polyvinyl alcohol is a polymer with extraordinary properties like water solubility, biocompatibility, biodegradability, non-carcinogenity and non-toxicity that have the ability to form hydrogels by physical or chemical methods [1-3]. Its fields of applicability were widely broadened during the later years caused by the evolution of medicine [4].

A polymer-metal complex is a coordinate complex among a ligand functional group anchor to a polymer matrix and a metal ion in which the metal ion is tied to the polymeric ligand by a coordination bond [5]. Polymeric materials with the capability to create complexes with metal ions are very common, originating from both synthetic and natural sources.

Recent progress made in design and synthesis of novel coordination polymers has brought a variety of polymeric materials that exhibit the structural diversities and attractive properties which can be further utilized in various fields, like catalysis , sewage treatment , optics, luminescence and sensor technology or polymer drug grafts [6].

The synthesis of a polymer-metal complex can take place by the synthesis of a macromolecular ligand followed by the binding of the metal salts which involves different processes, such as complexation, coordination, ion exchange and electrostatic attraction or by the incorporation of a metal by polymerization of a suitable metal containing monomer[5]. With repetition functional groups, biopolymers are excellent chelating and complexing materials for vast variety of applications, especially in medicine and pharmaceutical industry[7].

### Experimental

#### Materials

The chemicals used in this work were all off reagent grade by BDH, Merck and Fluka.

#### Instrumentation

FT-IR was registered on SHIMADZU-FT-IR-8400 spectrometer. <sup>1</sup>H-NMR a spectrum was registered on Bruker 500 MHz at Central lab, Tahrn University (Iran). A UV/vis spectrum was on record on UV/vis Varian UV-Cary-100 spectrophotometer and (TGA-DSC) analyses were carried out use LINSEIS (STA TT-1000) instrument.

## Preparation of Ligands [L<sub>1</sub>- L<sub>5</sub>] [8]

(1mol.) of PVA and (1mol.) of compounds [1] <sub>a</sub>, or [2, 3] <sub>a, b</sub> were placed in 20 ml DMF. Mixture was frequent shaking for (3hr.) then reflux for (2 hr.) produce was poured into H<sub>2</sub>O, wash with a little NaHCO<sub>3</sub>, washed with H<sub>2</sub>O, then C<sub>2</sub>H<sub>5</sub>OH. The product purification by dimethylsulfoxide and reprecipitating from C<sub>2</sub>H<sub>5</sub>OH.

## Synthesis of Metal Complexes [9]

(0.6 g/1mmole) of ligands were blended with (0.2g/1mmole) of metal chloride (CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O, CdCl<sub>2</sub>.H<sub>2</sub>O) dissolved in 20 ml. of dimethylsulfoxide, stirred and heated in water bath at 60°C for (12 h.). Then cooled, then washed with C<sub>2</sub>H<sub>5</sub>OH and dried at 60°C in vacuum.

## Biological Activity

### Antibacterial Activity

Some of synthesized ligands and complexes had impact for antibacterial activities versus (*Escherichia coli* and *Bacillus cereus*) using cup-plate agar diffusion way [10]. Standard drug were used as a Pencilin (50 µg/ml).

## Results and Discussion

The compounds (ligands) L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, L<sub>4</sub> and L<sub>5</sub> were set by FT-IR spectra. FT-IR of ligand [L<sub>1</sub>], Fig.(1) clarify the being of a big peak at (3375) cm<sup>-1</sup> this is regarding to stretch of hydroxyl from the intermolecular and intermolecular hydrogen bonds, peaks at (2908) cm<sup>-1</sup>, (2941) cm<sup>-1</sup> respectively caused by symmetric and asymmetric stretching vibrational of (C-H) from alkyl groups[11], appear the demise of absorption at (1761)cm<sup>-1</sup> result of (C=O-Cl), apparited of band at

(1728) cm<sup>-1</sup> due to (C=O) of ester[12] and appearance of absorption bands at (C=O) of cyclic imide at (1710-1778) cm<sup>-1</sup>. The <sup>1</sup>H-NMR spectrum of [L<sub>1</sub>], Figure(2), (DMSO-d<sub>6</sub>) displays[13,14] the following signals: many signals at δ (8.30-8.32) ppm for aromatic protons, triplet peak at (4.32-4.77) ppm for proton of (N-CH) group, doublet peak at δ(3.99) ppm for proton CH<sub>2</sub> in (CH<sub>2</sub>-OH), singlet peak at δ(3.45) ppm for proton (OH) group, triplet peak at δ (3.05) ppm for (CH-CH<sub>2</sub>)group and doublet peak at δ(1.54) ppm for proton (CH<sub>2</sub>-CH) group.

FT-IR of complex [L<sub>1</sub>+Co] [15], Fig.(3) the stretching vibration of u(OH) shifted lower frequency at (3223) cm<sup>-1</sup>, stretching vibration of carbonyl of ester in the range (1728)cm<sup>-1</sup> shifted to lower frequency at (1716) cm<sup>-1</sup> denoted the potential of coordination of ligand through the oxygen atom at the (C=O), band at (3481) cm<sup>-1</sup> may be refer to u (O-H) water molecules, band at (945) cm<sup>-1</sup> refer to coordinates water (aqua) [16] and u(M-O) at (420)cm<sup>-1</sup>. Table (1) shows FT-IR spectra of all the prepared complexes were compared with the free ligands (L<sub>1</sub>- L<sub>5</sub>).

FT-IR of prepared complexes display broad band at (3210– 3394) cm<sup>-1</sup>, attributed to u (hydroxyl) group in starting material and the band at (3325- 3558) cm<sup>-1</sup>, that attributed to (O-H) water molecules, bands at(923-948) cm<sup>-1</sup> referred to coordinates water (aqua) the stretching vibration of (carbonyl)ester in range (1728-1710)cm<sup>-1</sup> shifted to lower frequencies suggesting the possibility of the coordination of ligand through the oxygen atom at the (C=O) group and metal-oxygen was definite by the presence of stretching of (M-O) in range (420-482)cm<sup>-1</sup>.

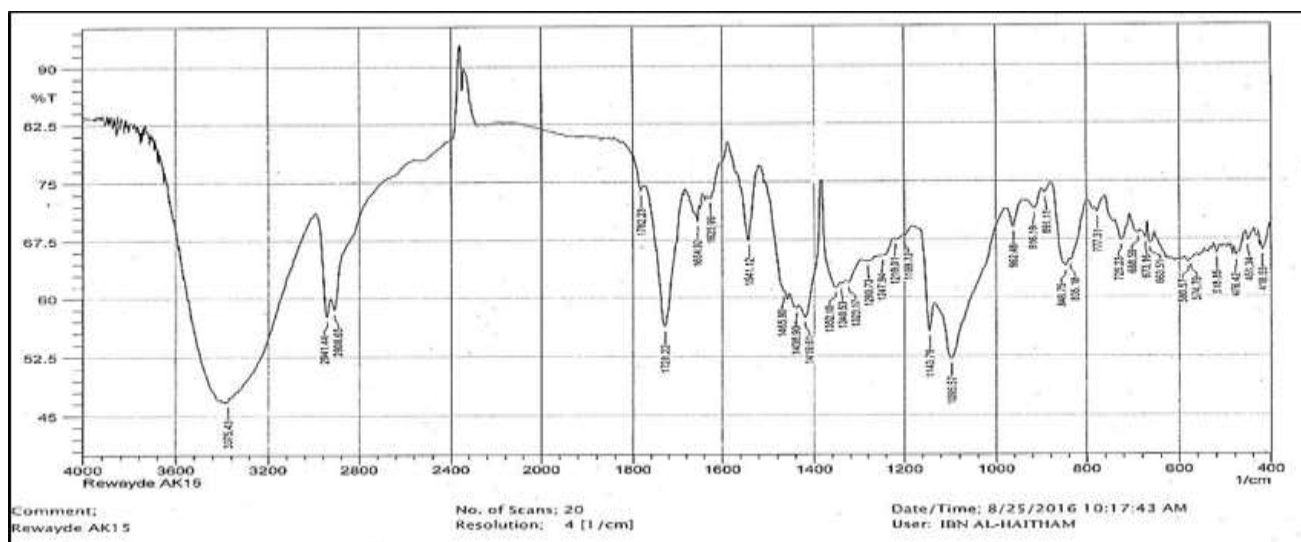


Fig1: Infrared spectrum of ligand [L<sub>1</sub>]

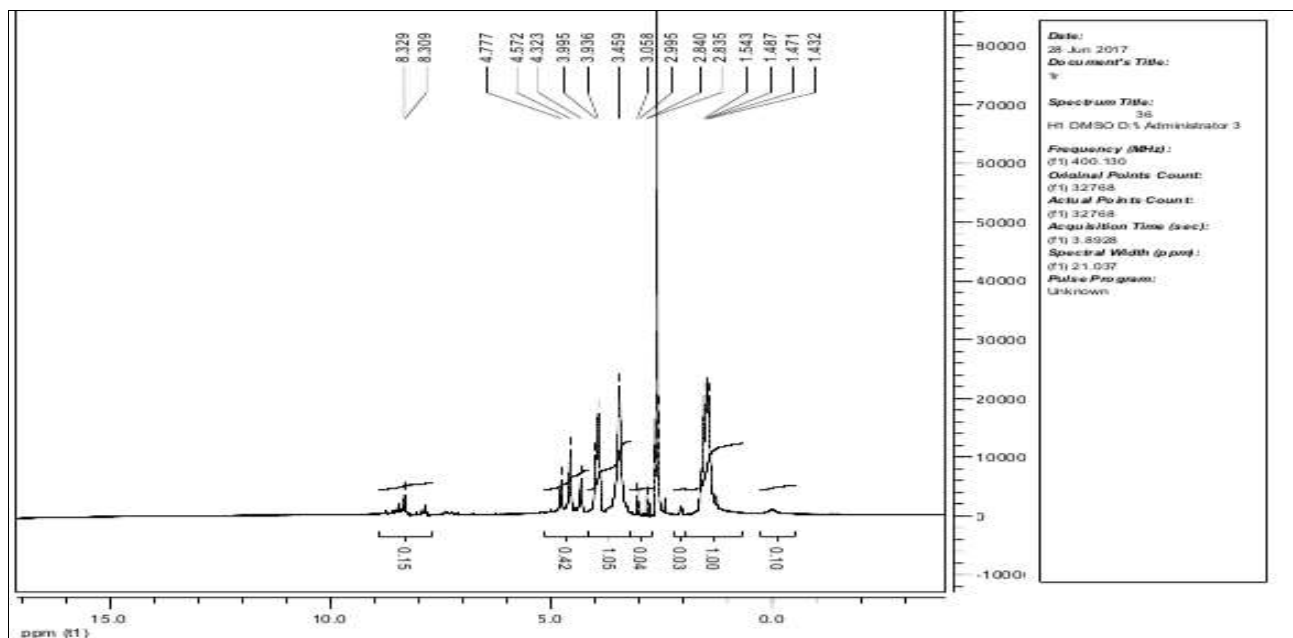


Fig.2: <sup>1</sup>H-NMR spectrum of [L<sub>1</sub>]

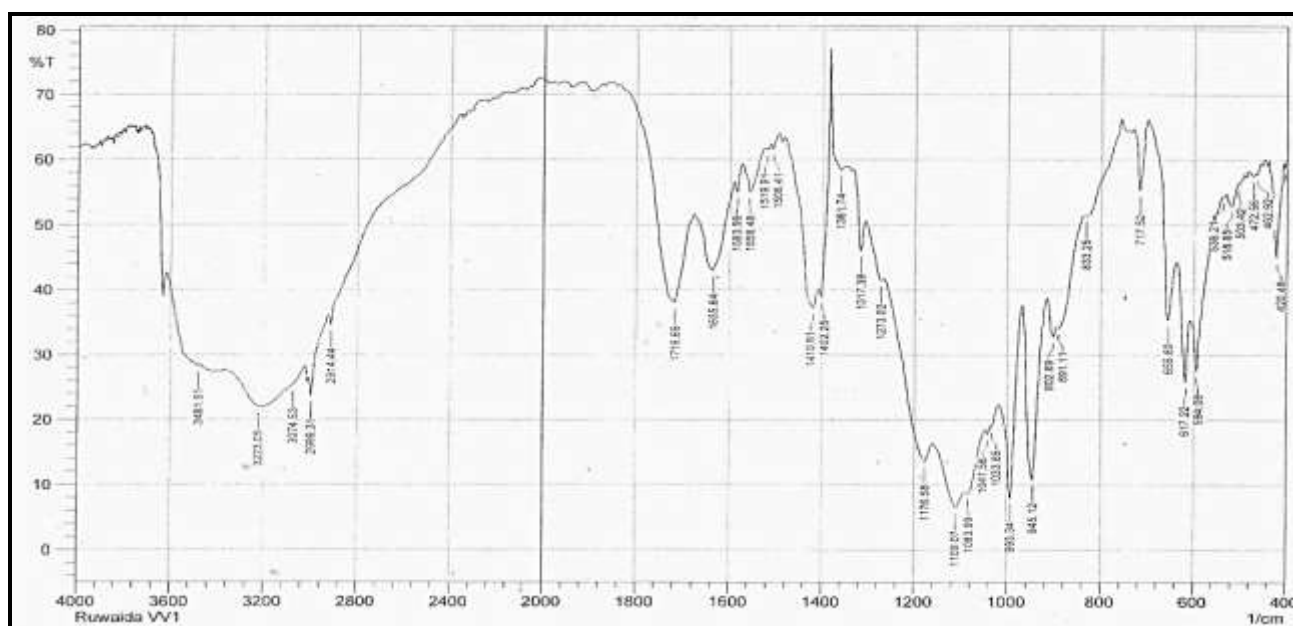


Figure3: FT-IR of complex [L<sub>1</sub>+Co]

Table 1: The characteristic infrared band for free ligand and its metal complexes

Comp.	$\nu$ (O-H) alcohol	$\nu$ (O-H) coordante	H <sub>2</sub> O coordante	$\nu$ (C-H) aliph.	$\nu$ (C=O) ester.	(C-O)	(C=C)	$\nu$ (M-O)
L <sub>1</sub>	3375	-	-	2941-2908	1728	1143	1590	-
L <sub>1</sub> +Co	3223	3481	945	2999-2914	1716	-	1583	420
L <sub>1</sub> +Ni	3213	3412	923	2985-2908	1707	-	1589	420
L <sub>1</sub> +Cu	3251	3350	928	2987-2908	1720	-	1590	482
L <sub>2</sub>	3390	-	-	2939-2910	1710	1141	1579	-
L <sub>2</sub> +Cu	3315	3417	935	2943-2916	1702	-	1588	482
L <sub>3</sub>	3387	-	-	2941-2910	1716	1140	1580	-
L <sub>3</sub> +Cu	3210	3325	941	2923-2916	1707	-	1597	480
L <sub>4</sub>	3394	-	-	2968-2910	1716	1141	1590	-
L <sub>4</sub> +Co	3381	3558	948	2922-2912	1710	-	1595	460
L <sub>5</sub>	3307	-	-	2943-2910	1716	1140	1585	-
L <sub>5</sub> +Cd	3269	3331	941	2916-2823	1707	-	1590	465
L <sub>5</sub> +Co	3212	3419	948	2949-2918	1706	-	1592	445

### Electronic Spectral Data for the Complex

The UV-Vis Spectra of the ligands exhibit absorption peaks around (314 -332) nm, assigned to  $\pi \rightarrow \pi$  [17]. Electronic Spectra of complexes with L<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup>, L<sup>4</sup> and L<sup>5</sup> exhibit peaks at around (236-328) nm, due to the (intra-ligand) and peaks around (426-506) nm are attributed to charge transfer (M→L) transition. Electronic spectra of Co(II) complexes for L<sup>1</sup>, L<sup>4</sup> and L<sup>5</sup> exhibited bands which can be attributed to  ${}^4T_{1g}(f) \rightarrow {}^4T_{1g}(p)v_3$ ,  ${}^4T_{1g}(f) \rightarrow {}^4A_{2g}(f)v_2$ ,  ${}^4T_{1g}(f) \rightarrow {}^4T_{1g}(p)v_3$ ,  ${}^4T_{1g}(f) \rightarrow {}^4T_{2g}(f)v_1$ ,  ${}^4T_{1g}(f) \rightarrow {}^4T_{1g}(p)$ ,  ${}^4T_{1g}(f) \rightarrow {}^4A_{2g}(f)$  and  ${}^4T_{1g}(f) \rightarrow {}^4T_{2g}(f)$

transition that is consistent with octahedral assignment . While the electronic spectra of the Ni (II) complex for L<sub>1</sub> exhibited band which can be attributed to  ${}^1A_{1g} \rightarrow {}^1B_{1g}$  transition that is consistent with square planer assignment. Electronic spectra of Cu (II) complexes for L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub> exhibited bands which can be attributed to  ${}^2T_2 \rightarrow {}^2E$  transition that is consistent with tetrahedral for L1 while band which can be attributed to  ${}^2B_{1g} \rightarrow {}^2E_g$  transition for L<sub>2</sub> and L<sub>3</sub> that are consistent with octahedral assignment. Finally the spectrum of the Cd (II) complex for L<sub>5</sub> exhibited band is assigned to (M→L) charge transfer [18].

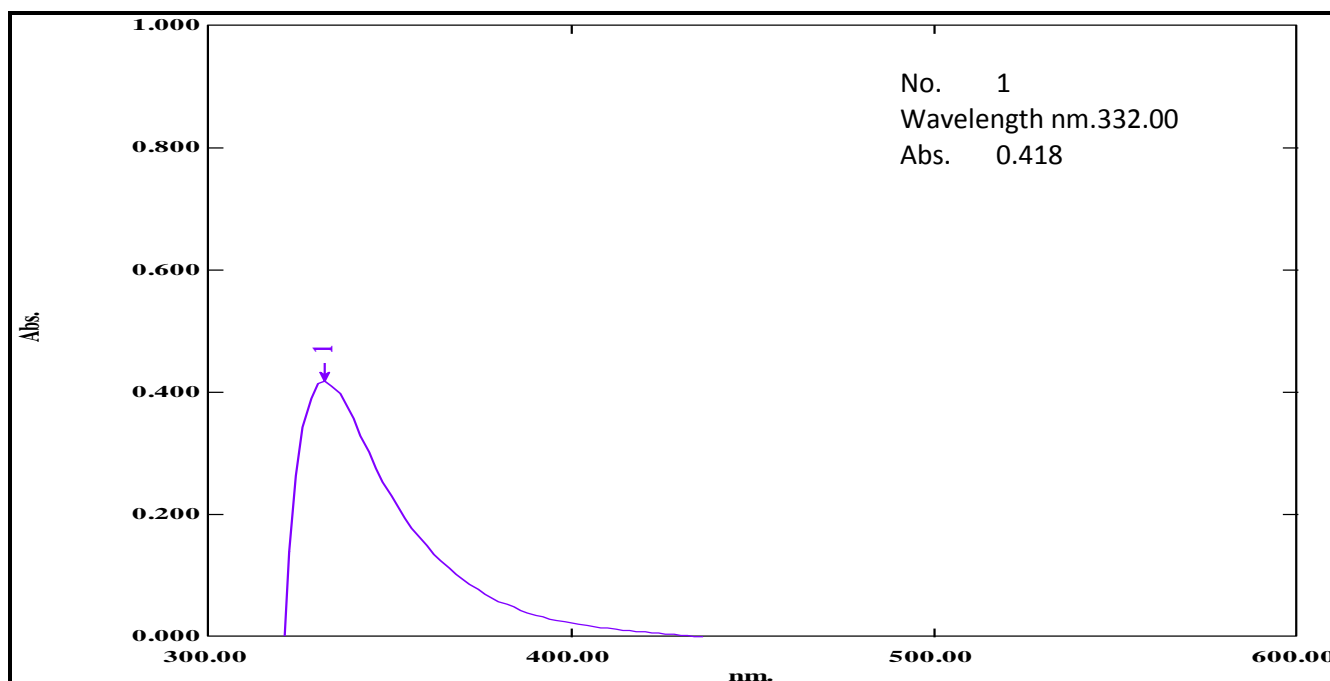


Fig.4: U.V spectrum of ligand [L<sub>5</sub>]

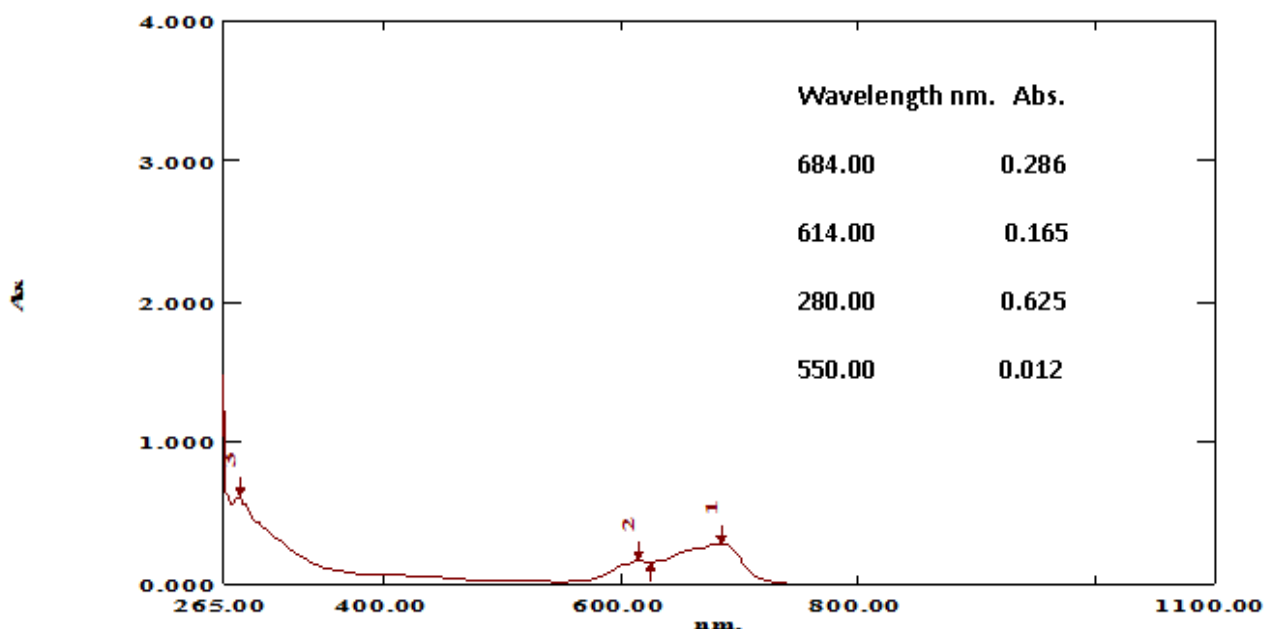


Fig.5: U.V spectrum of complex [L<sub>5</sub>+Co]

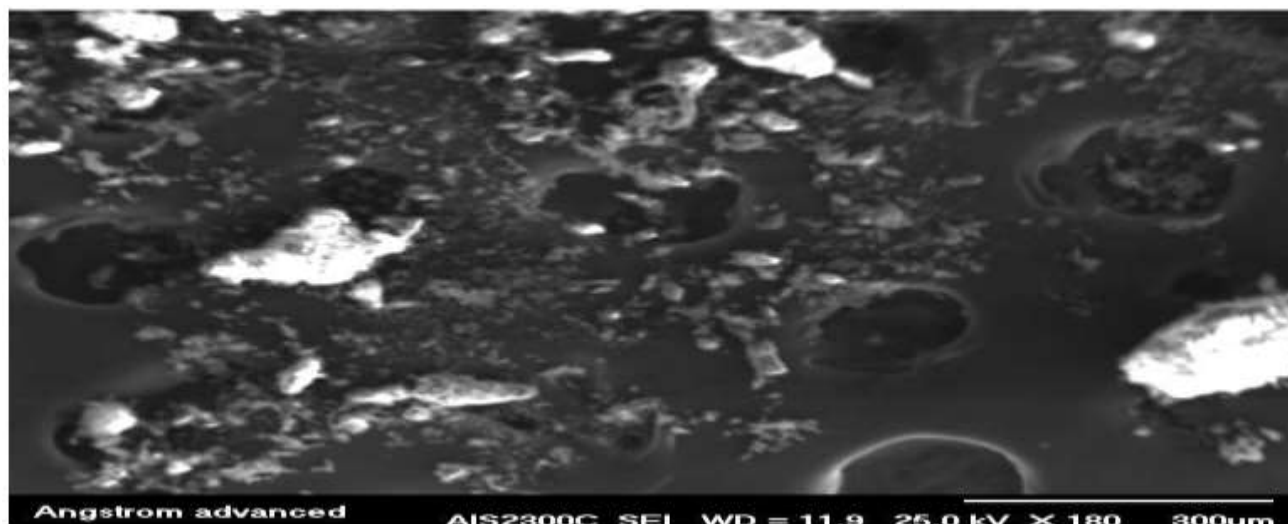
**Table 2: Electronic spectral data of some ligands and their complexes:**

Comp.	Suggests structure	$\lambda(\text{nm})$	$\nu \text{ cm}^{-1}$	Assignment	
L <sub>1</sub>		328	30488	$\pi \rightarrow \pi^*$	
L <sub>1</sub> +Co	Octahedral	310	32258	Intra-ligand	
		619	16155	${}^4\text{T}_{1g}(\text{f}) \rightarrow {}^4\text{T}_{1g}(\text{p})\nu_3$	
		684	14620	${}^4\text{T}_{1g}(\text{f}) \rightarrow {}^4\text{A}_{2g}(\text{f})\nu_2$	
L <sub>1</sub> +Cu	Tetrahedral	236	42393	Intra-ligand	
		315	31746	Intra-ligand	
		428	23364	ML→CT	
		884	11312	${}^2\text{T}_2 \rightarrow {}^2\text{E}$	
L <sub>1</sub> +Ni	Square planer	274	36496	Intra-ligand	
		316	31646	Intra-ligand	
		442	22624	${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$	
L <sub>2</sub>		332	30120	$\pi \rightarrow \pi^*$	
L <sub>2</sub> +Cu	Octahedral	302	33113	Intra-ligand	
		428	23364	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	
L <sub>3</sub>		320	31250	$\pi \rightarrow \pi^*$	
L <sub>3</sub> +Cu	Octahedral	296	33784	Intra-ligand	
		436	22936	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	
L <sub>4</sub>		314	31847	$\pi \rightarrow \pi^*$	
L <sub>4</sub> +Co	Octahedral	263	38023	Intra-ligand	
		426	23474	ML→CT	
		528	18939	${}^4\text{T}_{1g}(\text{f}) \rightarrow {}^4\text{T}_{1g}(\text{p})\nu_3$	
		864	11574	${}^4\text{T}_{1g}(\text{f}) \rightarrow {}^4\text{T}_{2g}(\text{f})\nu_1$	
L <sub>5</sub>		332	30120	$n \rightarrow \pi^*$	
L <sub>5</sub> + Cd	Tetrahedral	328	30488	Intra-ligand	
		506	19763	ML→CT	
L <sub>5</sub> +Co	Octahedral	280	35714	Intra-ligand	
		550	18182	${}^4\text{T}_{1g}(\text{f}) \rightarrow {}^4\text{T}_{1g}(\text{p})$	
		614	16287	${}^4\text{T}_{1g}(\text{f}) \rightarrow {}^4\text{A}_{2g}(\text{f})$	
		SEM was applied for proceed surface morphology analysis on the samples that producing images of a sample by scanning it with a focused beam of electrons			
		684	14620	${}^4\text{T}_{1g}(\text{f}) \rightarrow {}^4\text{T}_{2g}(\text{f})$	

### Scanning electron microscope (SEM)

(SEM) was applied for proceed surface morphology analysis on the specimens that

producing images of sample by surveying it with a focused beam of electrons


**Fig.6: SEM of PVA**

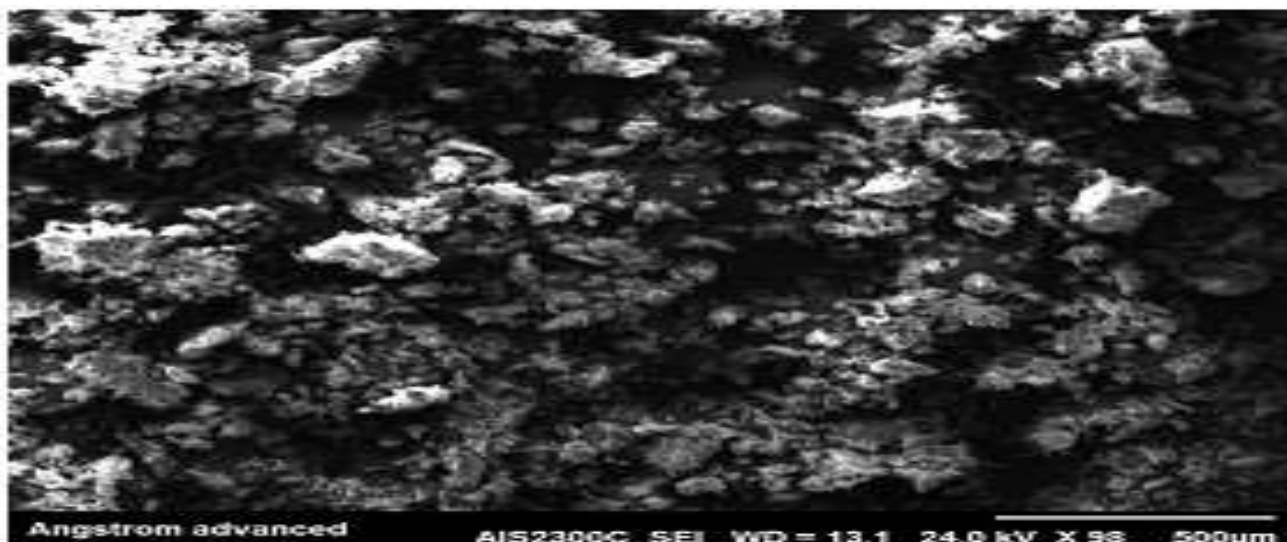


Fig.7: SEM of Ligand [L<sub>1</sub>]

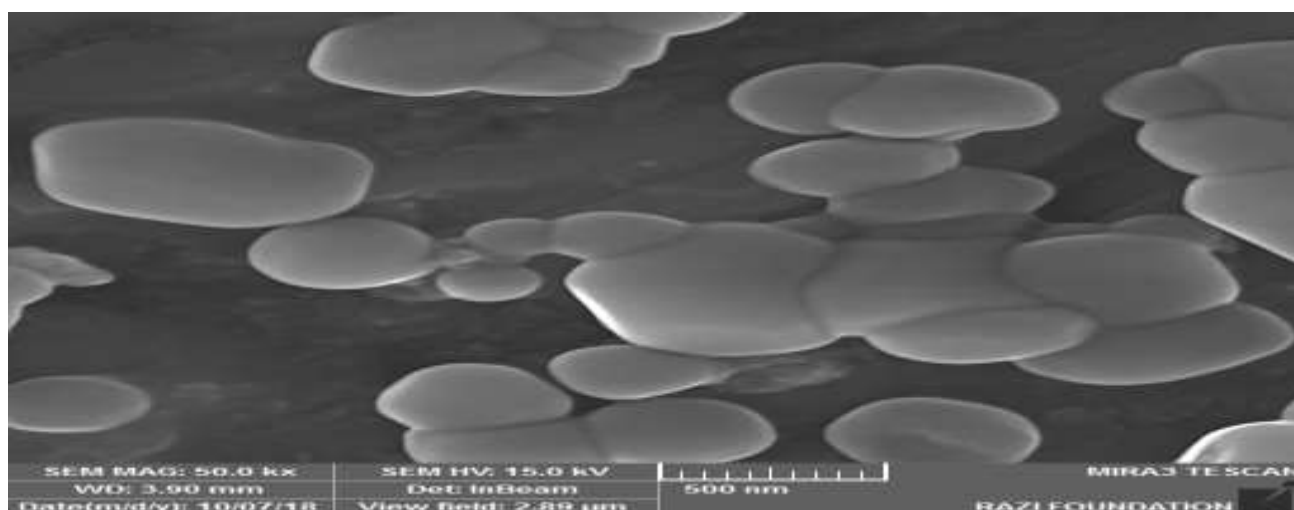


Fig. 8: SEM of complex [L<sub>1</sub> + Cu]

**Thermal Analysis [19]**

The thermo gravimetric (DSC/TG) curves of pure PVA and modifier PVA [ligand L<sub>1</sub> and

L<sub>3</sub>] and complexes were acquired at the heat rate of 10 °C. min<sup>-1</sup> under argon, was measuring in temperature (0-600) °C.

Table 3: DSC & TGA for PVA, some ligands and complexes

Compound	DSC				TGA			
	Tg/°C	Tc/°C	Tm/°C	Td/°C	Step	Ti/°C	Tf/°C	Wt.Los%
PVA	62	194	213.5	246	1	198	340.67	-48.139
					2	340.67	435.96	-14.071
					3	435.96	594.67	-22.372
[L <sub>1</sub> ]	74	120	155	182.6	1	130	347.73	-48.3032
					2	347.73	596.308	-39.9197
L <sub>1</sub> +Co	98	146	183	275.9	1	68	333.36	-22.655
					2	333.36	444.1	-7.0918
					3	444.1	595.13	-8.0829
[L <sub>3</sub> ]	79	100.3	192.7	236.1	1	180	361.56	-44.19
					2	361.56	594.03	-36.5193
L <sub>3</sub> +Cu	120	160	171.5	378.4	1	196	529.01	-64.1263
					2	529.01	590.63	-3.6596

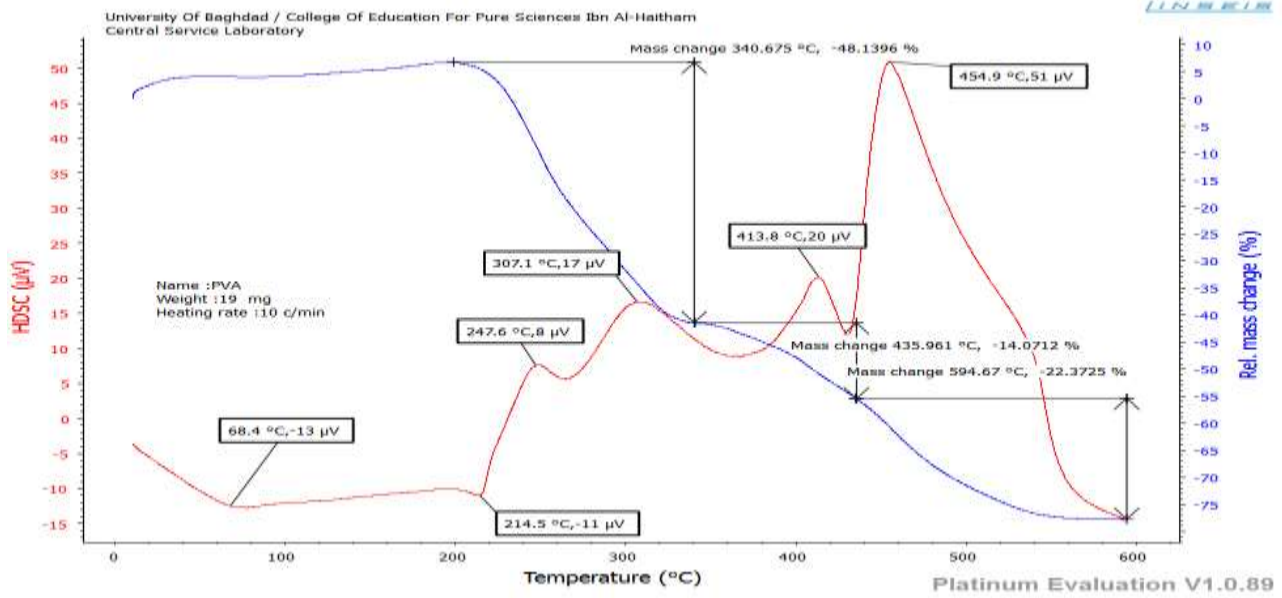


Figure 9: Thermal analysis of PVA

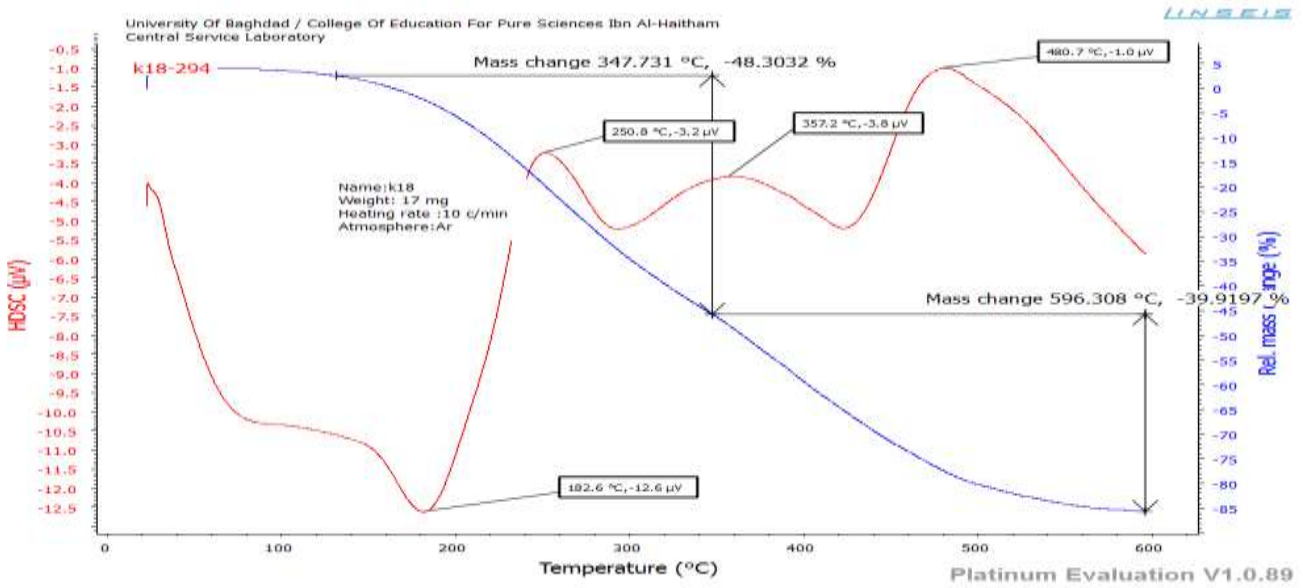


Fig.10: of [L1]

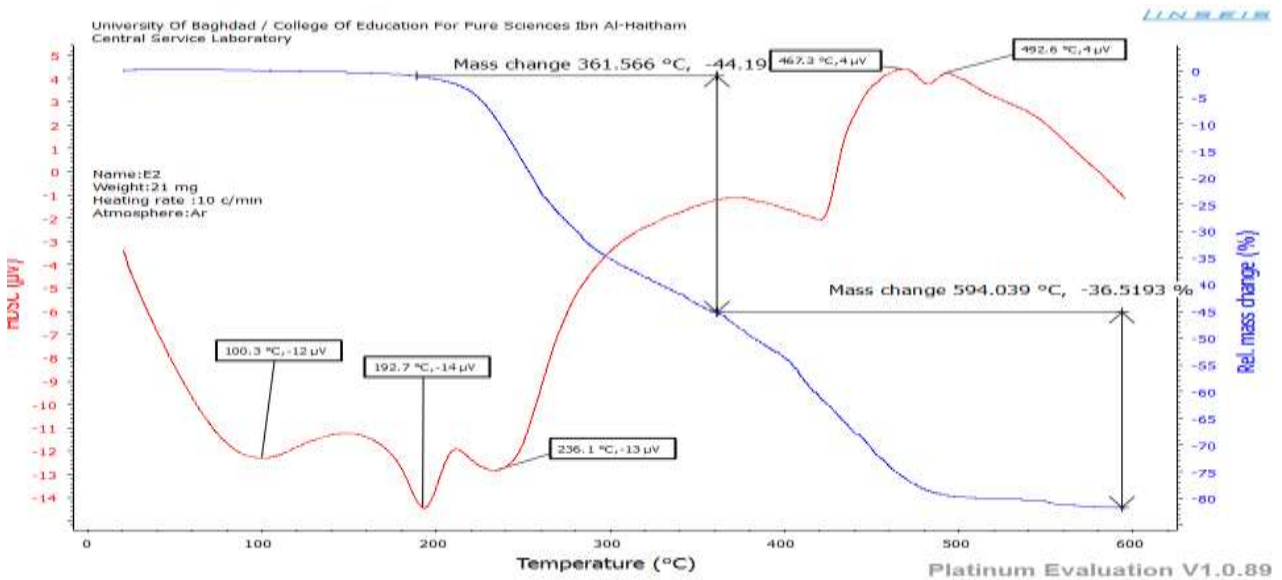


Fig.11: of [L3]

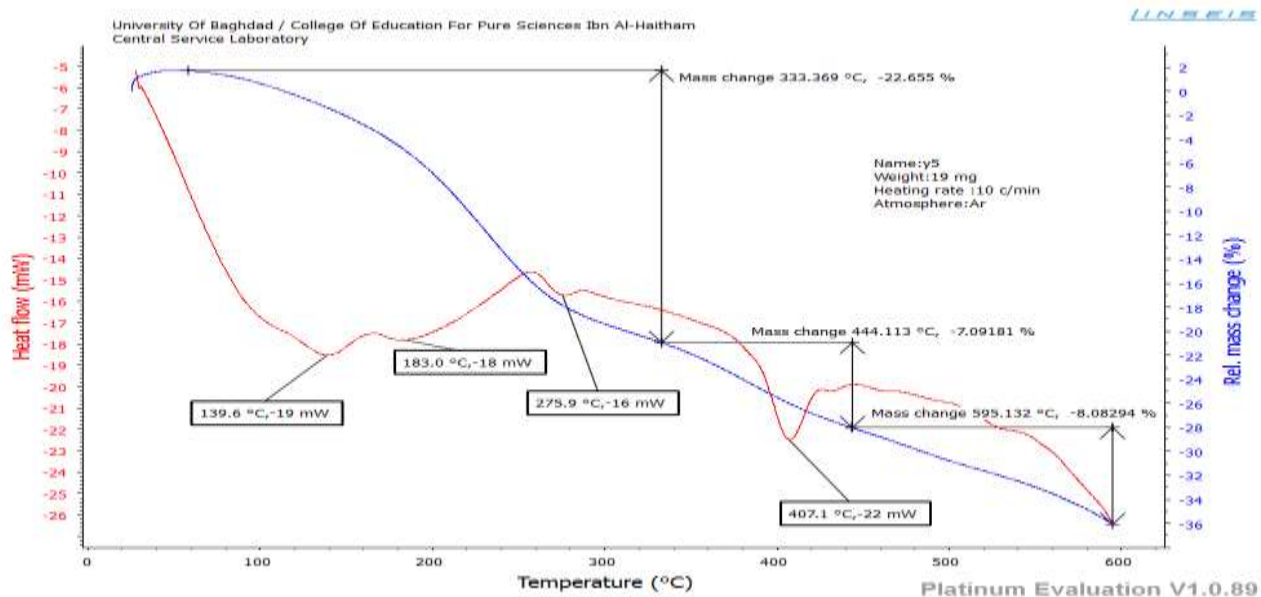


Fig. 12: of complex [L1 +Co]

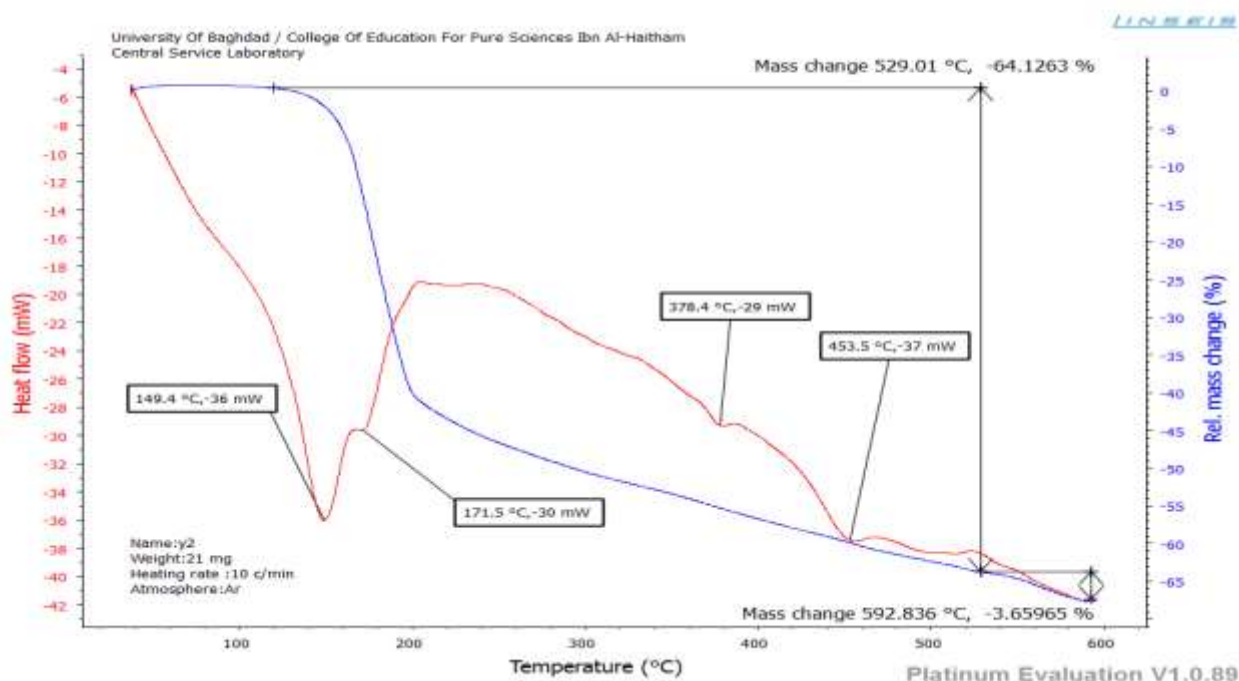


Figure 13: of complex [L3 +Cu]

### Antibacterial Activity

The ligands are biologically active and there are activity may emerge from (OH) groups that may play a significant role in antibacterial activity [20]. Results were evident that complexes exhibited significant antibacterial activity more than Penciline

activity and ligands , increasing in biological activity of metal chelates may be caused the impact of metal ion on the normal cell process. Results also showed that complex [L<sub>3</sub>+Cu] exhibited high antibacterial activity closed to penciline activity against *E .coli*. (-) and *Bacillus cereus* (+)

Table 4: The inhibition zone of some synthesized ligands and complexes

Comp.	<i>E .coli</i>	<i>Bacillus cereus</i>
Pencilin	16	22
L <sub>1</sub>	15	23
L <sub>3</sub>	15	16
L <sub>4</sub>	15	23
L <sub>5</sub>	10	21
L <sub>1</sub> +Ni	16	27
L <sub>3</sub> +Cu	20	30
L <sub>4</sub> +Co	13	26
L <sub>5</sub> +Cd	17	25



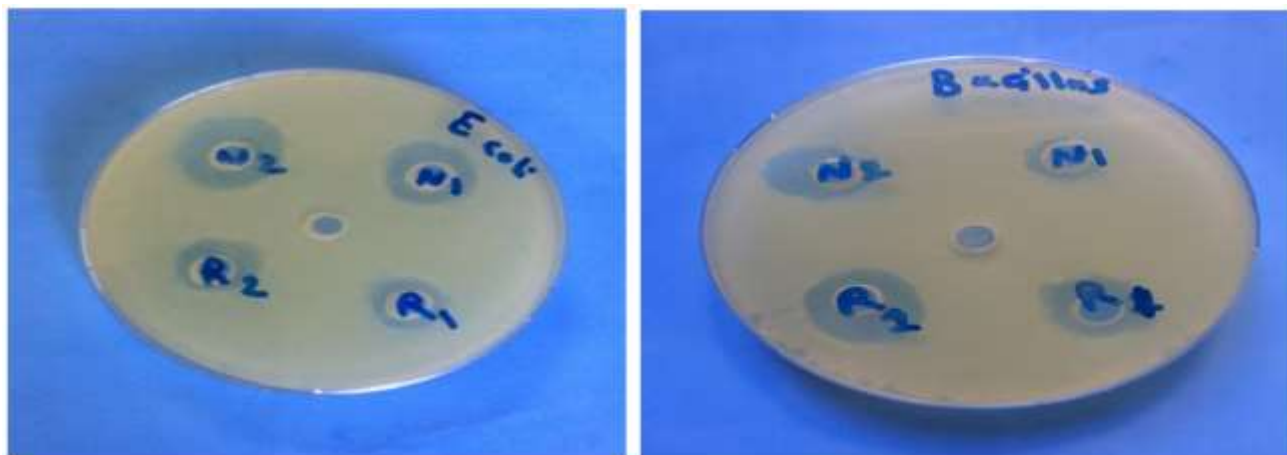


Fig.14: Antibacterial activities of Ligands

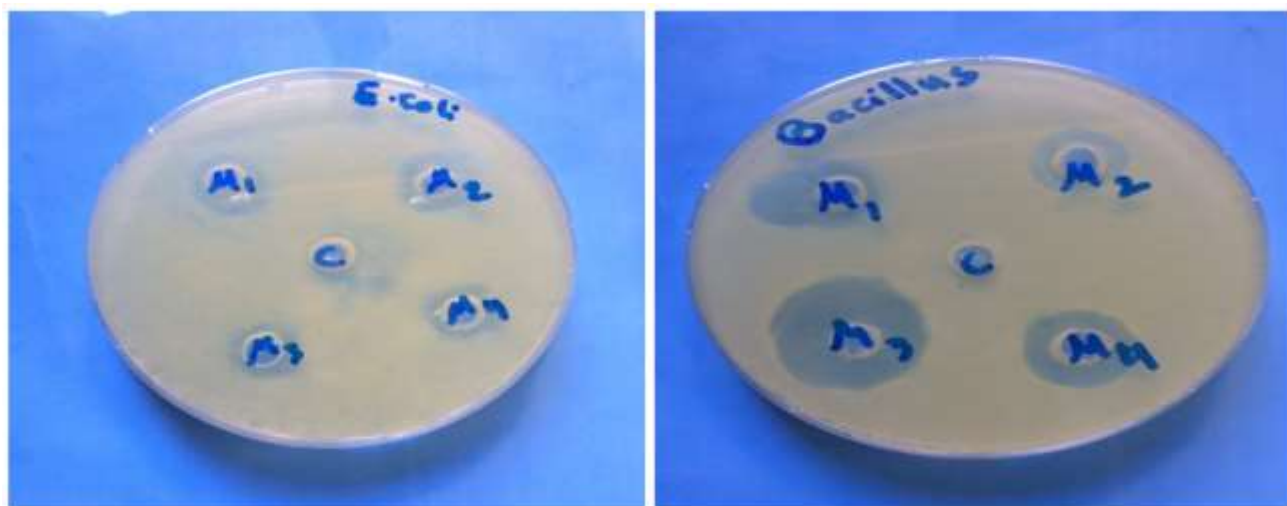
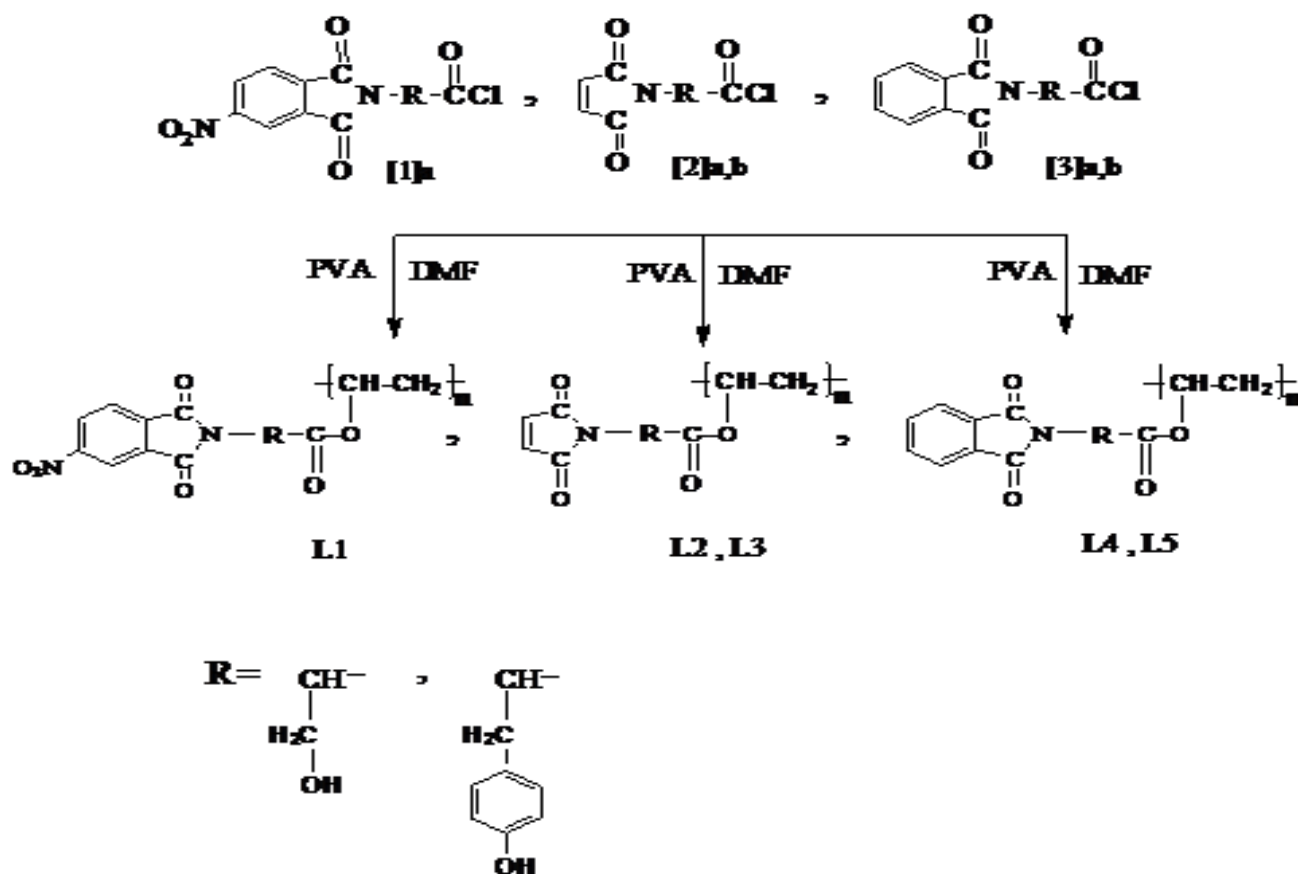


Fig.15: Antibacterial activities of complexes



Scheme1:

## References

1. C Vasile, AK Kulshreshtha (2003) Handbook of Polymer Blends and Composites, Rapra Technology. Ltd.: Shawbury, UK, 288-365.
2. B Ratner, AS Hoffman, FJ Schoen, JE Lemons (2004) Biomaterials science: An introduction to materials in medicine, Elsevier Academic Press, San Diego,.
3. CM Hassan, NA Peppas (2000) Adv. Polym. Sci., 153: 37-65.
4. Wafaa M Hosny\*, Perihan A Khalaf-Alaa (2013) Int. J. Electrochem. Sci., 8: 1520-1533.
5. Jeon C, Holl W (2004) Hydrometallurgy, 71: 421.
6. Silvia V, Stefania R, Violeta N, Marcel P, Jacques D (2010) POLIMERY 55: nr11-12.
7. Kang KS, Veeder GT, Mirrasoul PJ, Kaneko T, Cottrell J W (1982) Appl. Environ. Microb., 43 ,1086.
8. Ali H Samir, Ruwaidah S Saeed, Fadhel S Matty (2018) Oriental Journal of Chemistry, 34 (1): Pg. 286-294
9. TF Jian, J Zhoul, I Gao, Y Xing, X Li (2011) Iranian polymer Journal 20(2): 123-136.
10. A.L Barry (1977) The Antimicrobial Susceptibility Test: principle and practices,(Len and Febiger, Philadelphia, USA), Biol. Abstr., 180(64): 25183
11. H Awada, C Daneault (2015) Appl. Sci., 5: 840-850.
12. EG Crispim, JF Piai1, AR Fajardo, ERF Ramos, TU Nakamura, CV Nakamura, AF Rubira, EC Muniz (2012) Express Polymer Letters., 6(5): 383-395.
13. Roman Jantas, Zbigniew Draczyński, Lucyna Herczyńska, Dawid Stawski (2012) American Journal of Polymer Science, 2(5): 79-84.
14. Smith JG (2006) Organic Chemistry, 1st Ed, MC Graw Hill, New York 522.
15. Nakamoto K (1996) "Infrared spectra of inorganic and coordination compounds", 4th Ed., John wily and Sons, New York.
16. AS Al-Hamdani Abbas, AM Balkhi, A Falah, Shaker Sh A (2014) J. Chil. Chem. Soc., 59(4):2248-2259.
17. Silverstein RM (2005) Spectrometric identification of organic compounds.7th edn: Wiley, New York
18. Lever AB (1984) Inorganic Electronic Spectroscopy, 2nd edn. Elsevier, New York.
19. RM Horowitz, G Metzger (1963) Anal. Chem., 35: 1464.
20. N Sari, S Arslan, E Logoglu, I Sakiyan (2003) G.U. J. Sci., 16: 283-288