

Antimicrobial Studies of novel metal complexes of 3,5-dimethyl-1H-pyrazol-1-yl phenyl methanone and 1-benzoyl-3-methyl-1H-pyrazol-5(4H)-one

تحضير ودراسة الفعالية المضادة للجراثيم لمعقدات جديدة مشتقة من 3,5-ثنائي مثيل-1-هيدرو-بايروزول-1-يل فنيل ميثانون و 1-بنزويل-3-مثيل-1-هيدرو-بايروزول-5 (4هيدرو)-ون

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Abstract:

Chromium (III), cobalt (II), nickel (II), copper (II) and cadmium (II) complexes of 3,5-dimethyl-1H-pyrazol-1-yl phenyl methanone and 1-benzoyl-3-methyl-1H-pyrazol-5(4H)-one have been synthesized and characterized by elemental analysis, FT-IR, UV/visible spectra, and room temperature magnetic susceptibility. Cadmium complex is expected to have tetrahedral structure while the other complexes are expected to have octahedral structure. The free ligands and their metal complexes have been tested *in vitro* against a number of microorganisms (*Staphylococcus aureus*, *E.coli*, *Proteus vulgaris*, *Pseudomonas*, and *Klebsiella*) in order to assess their antimicrobial properties.

المستخلص

تم تحضير معقدات كلتيه لبعض العناصر الانتقالية [الكروم الثلاثي ، الكوبالت الثنائي ، النيكل الثنائي ، النحاس الثنائي ، والكاديوم الثنائي] للكاند 3,5-ثنائي مثيل-1-هيدرو-بايروزول-1-يل فنيل ميثانون و 1-بنزويل-3-مثيل-1-هيدرو-بايروزول-5 (4هيدرو)-ون . تم تشخيص المعقدات الصلبة بعد عزلها بالتحليل الدقيق للعناصر (C.H.N) ، وتحديد نسبة الفلز (M) في المعقدات ، طيف الأشعة تحت الحمراء F.T.I.R ، الأطياف الإلكترونية والخاصية المغناطيسية في درجة حرارة الغرفة . تم اقتراح الشكل الهندسي ثماني السطوح لجميع المعقدات ماعدا معقدات الكاديوم فتم اقتراح الشكل الهندسي رباعية السطوح . تم دراسة الفعالية المضادة للجراثيم لكل من الليكاندات ومعقداتها على خمسة أنواع من البكتريا هي *E. Staphylococcus aureus*, *E. Coli*, *Proteus Vulgaris*, *Pseudomonas*, and *Klebsiella* .

Introduction:

Some workers interested in synthesizing and studying the structural aspects of metal complexes containing sulfur and nitrogen donor ligands because of their increasing physiological importance and the active role played by certain metal ions coordinated

to them [1,2,3]. Various derivatives of 1, 3, 4-triazoles, thiadiazoles, and substituted pyrazoles have shown antitubercular [4], bacteriostatic [5], antibacterial [6] antifungal [7], anti-inflammatory [8] activities.

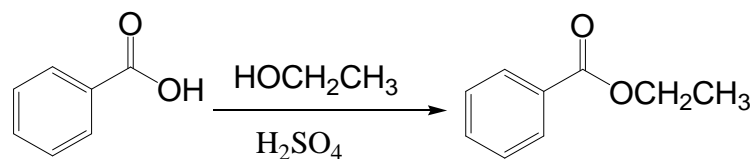
Most of the transition metal complexes are colored and their colors are different from the transition metal salts and the ligands, then this is an important indication to the occurrence of coordination [9]. Therefore the colored complexes show different characteristic absorption bands in their position, intensity or both when compared with the bands of the ligands and the metal salts and this is another indication for occurrence of coordination [10].

Materials and Method:

The chemicals used in this work were obtained from B.D.H. and they were all pure grade reagents. Flame atomic absorption of elemental analyzer, shimadzu AA-670 was used for metal determination. FT-IR spectra were recorded using shimadzu - 8000 spectrophotometer for the range 4000 – 200 cm^{-1} . Electronic spectra were recorded using shimadzu uv -visible spectrophotometer type 160A. Magnetic susceptibility was measured by BM6 using Gouy's balance.

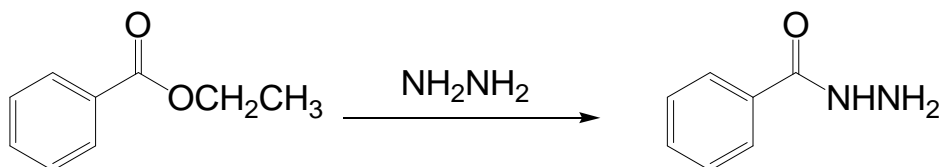
Synthesis of ethyl benzoate:

Treating (30 gm, 0.246 mole) of benzoic acid with (50 ml) absolute ethanol, and (2.5 ml) concentrated sulfuric acid and refluxing the mixture for 4 hrs., yielded the expected ester (ethyl benzoate) with 75% yield according to the following reaction:



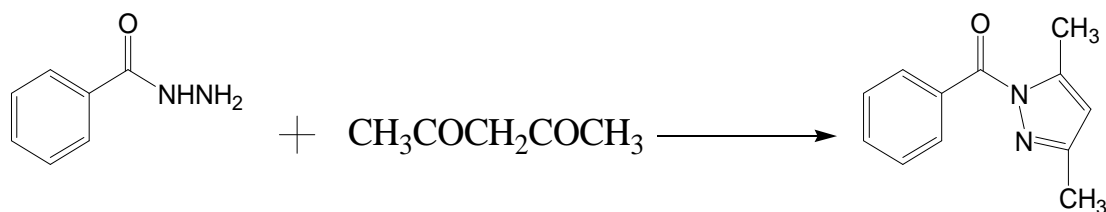
Synthesis of benzohydrazide [11]:

Benzohydrazide was synthesized by the addition of hydrazine mono hydrate (3.4 ml., 0.069 mole) to (10 ml, 0.069 mole) of ethyl benzoate with stirring, then the mixture was refluxed for 1 hr. Absolute ethanol (50 ml) was added and the mixture was refluxed again until a precipitate is separated out. After cooling, the product was filtered off and recrystallized from ethanol. m.p. 113-116°C, Yield 70%.



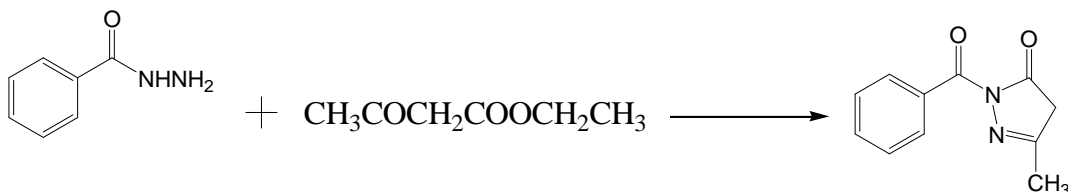
Synthesis of 3,5-dimethyl-1H-pyrazol-1-yl phenyl methanone:

Acetylacetone (0.002 mole, 0.2 g) was added to (0.002 mole) of benzohydrazide in (30 ml) ethanol and the mixture was refluxed for (7-8 hours), then left to cool. The solvent was evaporated and the oily product washed with ethanol, yield 45%.



Synthesis of 1-benzoyl-3-methyl-1H-pyrazol-5(4H)-one:

Ethylacetoacetate (0.002 mole, 0.26 g) was added to the mixture of 0.002 mole of benzohydrazide in (30ml) ethanol and the mixture was refluxed for (6-8 hours), then left to cool. The solvent was evaporated and the oily product washed with ethanol, yield 45%.



Synthesis of metal complexes:

3,5-dimethyl-1H-pyrazol-1-yl phenyl methanone and 1-benzoyl-3-methyl-1H-pyrazol-5(4H)-one metal complexes were obtained by refluxing the mixture of hydrated metal chlorides of Cr(III), Co(II), Ni(II), Cu(II) and Cd(II), (1 mmol) with (2 mmol) of the ligands in 50 ml ethanol at pH (8-9). The complexes were filtered, washed with water, ethanol and dried under vacuum (table 1). The results obtained from elemental analysis are in good agreement with the calculated values. The suggested molecular formula was also supported by spectral measurements as well as magnetic moments.

Study of biological activity for ligands (L₁ & L₂) and C₁-C₁₀ complexes:

The biological activity of the newly prepared ligands and their metal complexes were studied against selected types of bacteria which include gram positive bacteria (*Staphylococcus aureus*), and gram negative bacteria (*E. coli*, *Proteus vulgaris*, *Pseudomonas*, and *Klebsiella*) in agar diffusion method in which dimethyl formamide (DMF) was used as a solvent and as a control for the disc sensitivity test. This method involves the exposure of the zone of inhibition toward the diffusion of micro-organism on agar plate. The plates were incubated for (24 hrs), at 37C^o, the zone of inhibition for bacterial growth around the disc was observed.

Results and Discussion:

Table (1) shows the physical data for the ligands (L₁ & L₂) and their metal complexes.

Table (1): Micro-elemental analysis for the ligands (L₁&L₂) and their metal complexes

Compound	Melting Point C? /color	Elemental analysis (calc.)			
		C%	H%	N%	M%
L ₁ : C ₁₂ H ₁₂ N ₂ O	Oily	-	-	-	-
L ₂ : C ₁₁ H ₁₀ N ₂ O ₂	Oily	65.01 (65.35)	5.32 (4.95)	13.93 (13.86)	-
C ₁ : [Cr (L ₁) ₂ Cl ₂]Cl	291-292/ dark green	51.1 (51.6)	4.2 (4.3)	10.3 (10.0)	10.1 (9.3)
C ₂ : [Co (L ₁) ₂ Cl ₂]	Over 300/ violet	53.8 (54.3)	4.6 (4.5)	11.2 (10.6)	11.9 (11.1)
C ₃ : [Ni (L ₁) ₂ Cl ₂]	275-279/ dark green	54.7 (54.4)	4.3 (4.5)	10.4 (10.6)	11.8 (11.1)
C ₄ : [Cu (L ₁) ₂ Cl ₂]	253-255/ light green	53.5 (53.9)	4.7 (4.5)	10.8 (10.5)	12.7 (11.9)
C ₅ : [Cd (L ₂) ₂ Cl ₂]	290-293/ white	50.1 (49.4)	3.9 (4.1)	9.9 (9.6)	20.1 (19.3)
C ₆ : [Cr (L ₂) ₂ Cl ₂]Cl	oily / dark green	-	-	-	-
C ₇ : [Co (L ₂) ₂ Cl ₂]	260-263/ blue	50.43 (49.46)	4.04 (3.77)	11.46 (10.49)	11.22 (11.03)
C ₈ : [Ni (L ₂) ₂ Cl ₂]	288-291/ green	50.26 (49.48)	4.42 (3.77)	11.67 (10.49)	11.84 (10.99)
C ₉ : [Cu (L ₂) ₂ Cl ₂]	241-245/ green	50.11 (49.04)	4.12 (3.74)	11.00 (10.40)	12.01 (11.79)
C ₁₀ : [Cd (L ₂) ₂ Cl ₂]	295-298/ white	-	-	-	-

Infrared Spectroscopy:**The ligand L₁:**

- C=O stretching vibration:** The band at 1720 cm⁻¹ of the ligand due to C=O stretching shifted to ≈ 1690 – 1700 cm⁻¹ on complexation.
- C=N stretching vibration:** The band at 1583 cm⁻¹ in the spectrum of the ligand due to symmetrical ν(C=N) stretching shifted to ≈ 1579 cm⁻¹ or to ≈ 1590 cm⁻¹ on complexation.

The ligand L₂:

- C=O stretching vibration:** The band at 1710 cm⁻¹ of the ligand due to C=O stretching shifted to ≈ 1680 - 1700 cm⁻¹ on complexation.
- C=N stretching vibration:** The band at 1625 cm⁻¹ in the spectrum of the ligand due to symmetrical ν(C=N) stretching shifted to ≈ 1600 cm⁻¹ on complexation, while the band at 1610 cm⁻¹ shifted to the lower frequency 1587 cm⁻¹ in the complex.

The low frequency bands of complexes:

New bands which appeared at low frequencies in the spectra of the synthesized complexes were probably due to (metal–nitrogen) and (metal–oxygen) bond vibrational frequencies. The facts are further supported by newly formed low frequency bands;

- The bands at (450–460) cm⁻¹ have been assigned to ν (M–N) [12,13].
- The bands (425 – 440) cm⁻¹ have been assigned to ν (M–O) [14-16].

The above evidences are indications of complex formation. The IR bands are shown in table (2).

Table (2): The most diagnostic FTIR bands of ligands and their metal complexes

Comp.	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\text{C}=\text{O}$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
L ₁	1625	1050	1720	-	-
C ₁	1605	1005	1702	450 s	425 s
C ₂	1604	1005	1701	455 s	440 s
C ₃	1600	1045	1691	450 s	435 s
C ₄	1599	1035	1696	460 s	425 s
C ₅	1599	1015	1694	450 s	420 s
L ₂	1625	1055	1710	-	-
C ₆	1593	1043	1685	444 s	437 s
C ₇	1600	1035	1705	450 s	441 s
C ₈	1598	1035	1681	445 s	431 s
C ₉	1587	1030	1699	445 s	433 s
C ₁₀	1601	1025	1700	460 s	425 s

UV/visible spectra:

The ultraviolet spectra of the two synthesized ligands in DMF showed two absorption bands, the position of the first band at 220 nm which represents the ($\pi - \pi^*$) transition while the position of the second band (which has higher intensity than the first band due to conjugated system) appeared at ~ 290 nm which represents the ($n - \pi^*$) transition. Generally, the bands of the newly synthesized complexes are either shifted to shorter or longer wavelengths than that of ligands, but the high intensity bands is an indication for complex formation [17-19].

Complexes. The peaks are classified into two distinct groups: those that belong to ligand transitions appeared in the UV region while d-d transitions appeared in the visible region; these transitions are assigned in relevance to the structures of complexes.

Table (3): Electronic spectral data, magnetic moments, and suggested geometries for the ligand L₁ and its complexes.

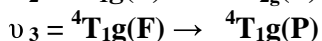
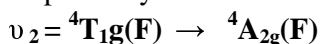
Compound	Absorption Bands (cm ⁻¹)	Assigned transition	Magnetic moment (B.M.)
L ₁	44444	$\pi \longrightarrow \pi^*$	-
	35088	$n \longrightarrow \pi^*$	
C ₁	15267	${}^4A_{2g}(\text{F}) \longrightarrow {}^4T_{2g}(\text{F})$	5.15
	20202	${}^4A_{2g}(\text{F}) \longrightarrow {}^4T_{1g}(\text{F})$	
	32595	${}^4A_{2g}(\text{F}) \longrightarrow {}^4T_{1g}(\text{P})$	
C ₂	7185 (calc.)	${}^4T_{1g}(\text{F}) \longrightarrow {}^4T_{2g}(\text{F})$	4.64
	13513	${}^4T_{1g}(\text{F}) \longrightarrow {}^4A_{2g}(\text{F})$	
	18691	${}^4T_{1g}(\text{F}) \longrightarrow {}^4T_{1g}(\text{P})$	
C ₃	11691 (calc.)	${}^3A_{2g} \longrightarrow {}^3T_{2g}(\text{F})$	1.61
	18618	${}^3A_{2g} \longrightarrow {}^3T_{1g}(\text{F})$	
	29974	${}^3A_{2g} \longrightarrow {}^3T_{1g}(\text{P})$	
C ₄	24691	$n \longrightarrow \pi^*$	1.47
	16260	${}^2E_g \longrightarrow {}^2T_{2g}$	
C ₅	32258	$n \longrightarrow \pi^*$	-

L₁ complexes:**Chromium-complex (C₁):**

At room temperature the magnetic susceptibility measurement after diamagnetic corrections yielded a magnetic moment of 5.15 BM which is close to that expected for an octahedral Cr (III) complexes [17]. The Uv-visible spectrum of the dark green solution of chromium the Cr(III) complex recorded in DMF showed three bands with the absorbance maxima at 15267 cm^{-1} , 20202 cm^{-1} and 32595 cm^{-1} which were considered as ν_1 , ν_2 , and ν_3 absorption bands respectively (table 3).

Cobalt-complex (C₂):

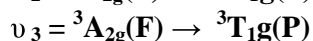
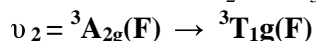
The magnetic susceptibility measurement after diamagnetic corrections yielded a magnetic moment of 4.64BM which is close to that expected for an octahedral Co (II) complexes [18,19]. The electronic absorption spectrum showed two absorption bands (as shown in table (3) at $(13513\text{ and }18691)\text{ cm}^{-1}$ which is considered as ν_2 and ν_3 respectively. These transitions may be assigned as:



Experimental ν_2 and ν_3 values have been employed to calculate the position of ν_1 [${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$] band from Lever tables [20,21]. Also these tables have been used to calculate the ligand field parameters, 10 Dq and B which were found to be 7185 and 898 cm^{-1} respectively. The calculated 10 Dq value which is the ν_1 transition is found to be in the near infrared region which is out of the range of our absorption apparatus. The calculated B value (898 cm^{-1}) for the complex is lower than the respective B_0 value of (971 cm^{-1}) for the free cobalt ion, indicating the presence of covalent bonding between the metal ion and the ligand. The β value which is the ratio of (B_{complex} / B_0) shows a value of 0.925 , and this reduction in the B_0 value indicates that ligand non-bonding orbitals have been used to delocalize the metal d-electrons i.e, increasing back donation from cobalt to the ligand.

Nickel-complex (C₃):

Nickel complex is paramagnetic with a room temperature magnetic moment of 1.61 B.M. which is consistent with an octahedral field. The electronic absorption spectrum showed two absorption bands as shown in table (3) at $(18618 \text{ \& } 29974)\text{ cm}^{-1}$ which are considered as ν_2 and ν_3 respectively. These transitions may be assigned as:



Experimental ν_2 and ν_3 values have been employed to calculate the position of ν_1 [${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$] band from Lever tables [20,21]. Also these tables have been used to calculate the ligand field parameters, 10 Dq and B which were found to be 11691 and 899.3 cm^{-1} respectively. The calculated 10 Dq value which is the ν_1 transition is found to be in the near infrared region which is out of the range of our absorption apparatus. The calculated B value (899.3 cm^{-1}) for the complex is lower than the respective B_0 value of (1041 cm^{-1}) for the free nickel ion, indicating the presence of covalent bonding between the metal ion and the ligand. The β value which is the ratio of (B_{complex} / B_0) shows a value of 0.86 , and this reduction in the B_0 value indicates that ligand non-bonding orbitals have been used to delocalize the metal d-electrons i.e, increasing back donation from nickel to the ligand. On the basis of spectral bands, an octahedral geometry is therefore proposed for the Ni (II) complex. The values of

ligand field parameters reflect that the M–L bond is quite strong, which in turn suggests sufficient overlapping of the metal orbitals with those of the ligand orbitals.

Copper-complex (C₄):

The complex has a room temperature magnetic moment of 1.47 B.M. which corresponds to octahedral structure for the Cu (II) ion [18,22]. The electronic absorption spectrum for Cu(II) complex shows two bands at 24691 and 16260 cm⁻¹ which were considered as (n→π*) and ²E_g → ²T_{2g} respectively.

Cadmium-complex (C₅):

The prepared white Cd(II) complex exhibited a band which appeared at 32258 cm⁻¹ which may be related to the ligand (n→π*) transition. The filled d- orbitals show no ligand field transitions and the magnetic moment measurement show that this complex is diamagnetic.

L₂ complexes:

Table (4) shows the electronic absorption peaks for the ligand (L₂) and its complexes. The interpretation and discussion for C₆, C₇, C₈, C₉, and C₁₀ complexes are the same as that for the previous mentioned complexes (C₁, C₂, C₃, C₄, and C₅) respectively and the data are listed in tables (2 , 4).

Table (4): Electronic spectral data, magnetic moments, and suggested geometries for the ligand L₂ and its complexes

compound	Absorption Bands	Assigned transition	Magnetic moment (B.M.)
L ₂	220 nm, 45454 cm ⁻¹	$\pi \rightarrow \pi^*$	-
	295 nm, 33898 cm ⁻¹	$n \rightarrow \pi^*$	
C ₆	230 nm, 43478 cm ⁻¹	$\pi \rightarrow \pi^*$	3.65
	615 nm, 16267 cm ⁻¹	⁴ A _{2g} (F) → ⁴ T _{2g} (F)	
	495 nm, 20202 cm ⁻¹	⁴ A _{2g} (F) → ⁴ T _{1g} (F)	
	313 nm, 31920 cm ⁻¹	⁴ A _{2g} (F) → ⁴ T _{1g} (P)	
C ₇	225 nm, 44444 cm ⁻¹	$\pi \rightarrow \pi^*$	4.7
	113 nm, 8813 cm ⁻¹ (calc.)	⁴ T _{1g} (F) → ⁴ T _{2g} (F)	
	615 nm, 16267 cm ⁻¹	⁴ T _{1g} (F) → ⁴ A _{2g} (F)	
	549 nm, 18202 cm ⁻¹	⁴ T _{1g} (F) → ⁴ T _{1g} (P)	
C ₈	215 nm, 46512 cm ⁻¹	$\pi \rightarrow \pi^*$	3.28
	899 nm, 11114 cm ⁻¹ (calc.)	³ A _{2g} → ³ T _{2g} (F)	
	555 nm, 18018 cm ⁻¹	³ A _{2g} → ³ T _{1g} (F)	
	335 nm, 29850 cm ⁻¹	³ A _{2g} → ³ T _{1g} (P)	
C ₉	215 nm, 46511 cm ⁻¹	$\pi \rightarrow \pi^*$	1.85
	675 nm, 14798 cm ⁻¹	$n \rightarrow \pi^*$	
	310 nm, 32268 cm ⁻¹	² E _g → ² T _{2g}	
C ₁₀	31995	$n \rightarrow \pi^*$	-

D- Biological Activity:

As a result from the study of antimicrobial activity for the prepared ligands and their metal complexes Fig. (1), the following points were concluded:

1. The results of antibacterial activity study for (L_1 , L_2) ligands indicated that the newly synthesised ligands exhibited antibacterial activity against the studied bacteria at low and high concentrations [23].
2. The study of antibacterial activity revealed that (L_1 , L_2) exhibited a greater activity against the studied bacteria *Pseudomonas eruginosa*.
3. Generally, the prepared complexes exhibited potent antibacterial activity toward *Pseudomonas* bacteria relative to the antibacterial activity of the complexes on other bacterial strand used in this study (*Staphylococcus aureus*, *E.coli*, *Proteus vulgaris*, and *Klebsiella*). Table (5,6,7,8,9).

Table (5): The effect of Staphylococcus aureus bacteria toward Ligands (L_1 & L_2) and their complexes (C_1 — C_{10})

Compound	Radius (mm)	Concentration mA
L_1	0.4,0.5,0.7,1.1, 1.3	5,10,15,20,25
C_1	0.3,0.4,0.6,1.0, 1.4	5,10,15,20,25
C_2	0.3,0.6,0.7,1.2, 1.4	5,10,15,20,25
C_3	0.3,0.4,0.8,1.1, 1.2	5,10,15,20,25
C_4	0.3,0.6,0.8,1.2,1.40	5,10,15,20,25
C_5	0.2,0.7,0.9,1.3,1.7	5,10,15,20,25
Amp.	0.3,0.8,1.4,2.0,2.5	5,10,15,20,25
L_2	0.2,0.4,0.7,1.0, 1.2	5,10,15,20,25
C_6	0.3,0.4,0.6,1.0, 1.2	5,10,15,20,25
C_7	0.3,0.6,0.9,1.1, 1.3	5,10,15,20,25
C_8	0.3,0.5,0.8,1.1, 1.5	5,10,15,20,25
C_9	0.2,0.6,0.1.1 ,1.2,1.7	5,10,15,20,25
C_{10}	0.2,0.7,1.0,1.3,1.8	5,10,15,20,25

Table (6): The effect of *E. Coli*, bacteria toward Ligands and their complexes (C_1 - C_{10})

Compound	Radius (mm)	Concentration mA
L_1	0.3,0.4,0.6,0.8,1.00	5,10,15,20,25
C_1	0.2, 0.3,0.7,0.1,1.2	5,10,15,20,25
C_2	0.0, 0.6,0.8,0.8,1.3	5,10,15,20,25
C_3	0.3,0.6,0.7,0.8,1.0	5,10,15,20,25
C_4	0.3,0.5,0.8,1.1,1.4	5,10,15,20,25
C_5	0.2,0.5,1.4,1.8,2.0	5,10,15,20,25
Amp.	0.2,0.8,1.3,1.9,2.3	5,10,15,20,25
L_2	0.3,0.6,0.8,1.0,1.3	5,10,15,20,25
C_6	, 0.4,0.7, 1.1,1.5 0.3	5,10,15,20,25
C_7	0.2, 0.5,0.8,1.0,2.2	5,10,15,20,25
C_8	0.3,0.4,0.7,0.9,1.2	5,10,15,20,25
C_9	0.3,0.3,0.8,1.1,1.4	5,10,15,20,25
C_{10}	0.2,0.7,1.2,1.8,2.4	5,10,15,20,25

Table (7): The effect of *Proteus Vulgaris*, bacteria toward Ligands and their complexes (C₁-C₁₀)

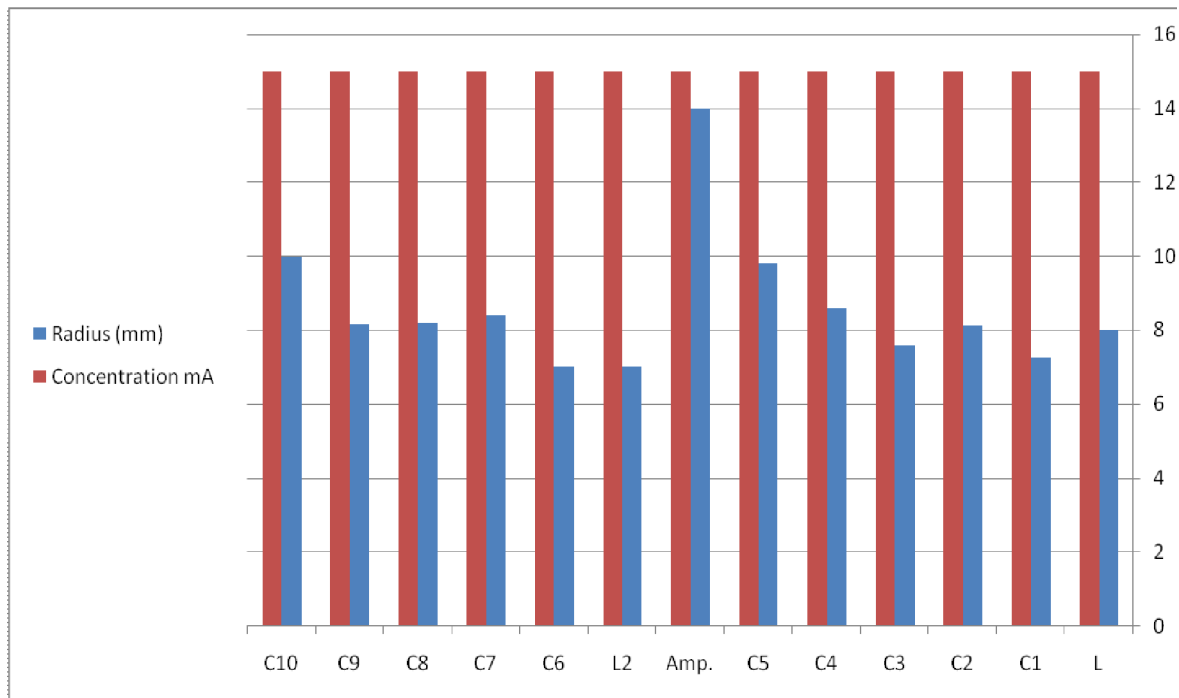
Compound	Radius (mm)	Concentration mA
L ₁	0.2,0.5,0.6,0.8,1.1	5,10,15,20,25
C ₁	0.2, 0.3,0.7,0.1,1.3	5,10,15,20,25
C ₂	0.3, 0.6,0.8,0.8,1.3	5,10,15,20,25
C ₃	0.3,0.6,0.8,0.8,1.1	5,10,15,20,25
C ₄	0.3,0.5,0.6,0.8,1.0	5,10,15,20,25
C ₅	0.2,0.4,1.0,1.6,2.0	5,10,15,20,25
Amp.	0.4,0.9,1.4,1.9,2.2	5,10,15,20,25
L ₂	0.4,0.6,0.9,1.2,1.3	5,10,15,20,25
C ₆	, 0.4,0.7, 1.0,1.3 0.3	5,10,15,20,25
C ₇	0.2, 0.5,0.8,1.0,1.3	5,10,15,20,25
C ₈	0.3,0.4,0.6,0.9,1.3	5,10,15,20,25
C ₉	0.3,0.6,0.9,1.3,1.6	5,10,15,20,25
C ₁₀	0.2,0.6,1.3,1.7,2.0	5,10,15,20,25

Table (8): The effect of *Pseudomonas*, bacteria toward Ligands and their complexes (C₁-C₁₀)

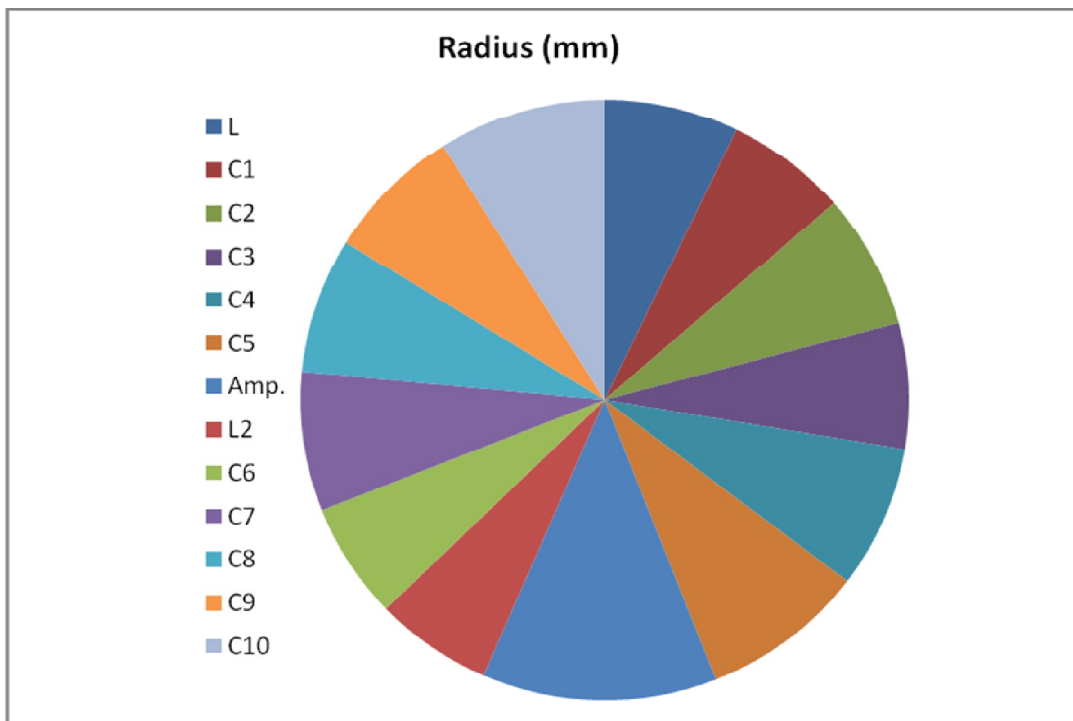
Compound	Radius (mm)	Concentration mA
L ₁	0.3,0.6,0.8,1.0,1.3	5,10,15,20,25
C ₁	0.3, 0.5,0.8,1.1,1.4	5,10,15,20,25
C ₂	0.3, 0.6,0.9,1.2,1.5	5,10,15,20,25
C ₃	0.3,0.6,0.9,1.3,1.9	5,10,15,20,25
C ₄	0.3,0.4,0.7,1.3,1.9	5,10,15,20,25
C ₅	0.3,0.5,1.1,1.6,2.2	5,10,15,20,25
Amp.	0.3,0.6,1.5,1.9,2.4	5,10,15,20,25
L ₂	0.3,0.6,0.8,1.0,1.1	5,10,15,20,25
C ₆	, 0.4,0.6, 1.1,1.3 0.3	5,10,15,20,25
C ₇	0.3, 0.5,0.7,1.0,1.4	5,10,15,20,25
C ₈	0.3,0.6,0.8,1.2,1.5	5,10,15,20,25
C ₉	0.3,0.4,0.8,1.3,1.5	5,10,15,20,25
C ₁₀	0.4,0.9,1.3,1.6,2.1	5,10,15,20,25

Table (9): the effect of *Klebsiella* bacteria toward complexes (C₁—C₁₀)

Compound	Radius (mm)	Concentration mA
L ₁	0.3,0.5,0.8,1.1,1.3	5,10,15,20,25
C ₁	0.3, 0.5,0.8,1.1,1.6	5,10,15,20,25
C ₂	0.3, 0.6,1.0,1.6,2.0	5,10,15,20,25
C ₃	0.3,0.5,0.7,0.9,1.4	5,10,15,20,25
C ₄	0.3,0.6,0.8,1.0,1.4	5,10,15,20,25
C ₅	0.4,0.8,1.4,1.8,2.4	5,10,15,20,25
Amp.	0.3,0.8,1.6,2.0,2.4	5,10,15,20,25
L ₂	0.2,0.4,0.8,1.0,1.1	5,10,15,20,25
C ₆	, 0.5,0.7, 1.1,1.2 0.3	5,10,15,20,25
C ₇	0.3, 0.5,0.8,1.0,1.2	5,10,15,20,25
C ₈	0.3,0.5,0.7,0.9,1.2	5,10,15,20,25
C ₉	0.4,0.7,1.0,1.1,1.4	5,10,15,20,25
C ₁₀	0.4,0.9,1.5,1.8,2.1	5,10,15,20,25



A



B

Figure (1): The effect of *Staphylococcus aureus* bacteria toward the ligands (L₁ & L₂) and their complexes (C₁—C₁₀).

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