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RESEARCH ARTICLE

Synthesis and Biological activity of some complexes of (2-phenyl-4-arylidine imidazole-5-one) with some transition metal ions

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Abstract

A novel imidazole analogs of hipuric acids was synthesized by using acetic anhydride and acetic acid, then treated with hydrazine hydrate to give 3a-b. anew compounds were characterized by ^{1}HNMR,FTIR and UV spectroscopyand then were used as ligand and complication with some metals, these derivatives were investigated for their antimicrobial activity and antifungal. The prepared complexes were identified and their structural geometries were suggested by using elemental analysis (A.A), FT-IR and UV-Vis. spectroscopy, as well as magnetic susceptibility and conductivity measurements. Metal to ligand [M:L] ratio was obtained for all complexes in (ethanol) using molar ratio method, which gave comparable results with those obtained for the solid complexes.

Introduction:

The synthesis of 1,3-oxazoles is of considerableinterest due to their various biological activities. Reported damming these activities were: nervous system depression[1], analgesic[2,3], herbicidal[4], muscle relaxant[5],and tranquilizing[6] activities. The imidazole nucleus appears in a number of naturally occurring products like the amino acids, histidine and purines which comprise many of the most important bases in nucleic acids[7]. Imidazole derivatives possess a broad spectrum of pharmacological activities such as anticonvulsant[8] anti-Parkinson[9]**.** . In medicine, drugs based on benzimidazoles and benzimidazole derivatives have been patented, due to their antiviral and antihelmintic activity [10]. In metallurgy, benzimidazole has been used as a corrosion inhibitor[11]. Metal complexes play an important role in many biological systems [12]. It has been observed that metal ions have considerable effect on the antimicrobial activity of antibiotics [13-15]. Similarly metal ions are known for their antitumor activity [16]. Transition-metal ions play a number of critical roles in biology. However, the size and complexity of the metalloproteins which contain them makes it difficult to determine the properties that are responsible for their function [17-19]. Among these novel metal complexes derivatives which show considerable biological activity may represent an interesting approach for designing new antibacterial drugs. This may be due to the dual possibility of both ligands plus metal ion interacting with different steps of the pathogen life cycle [20].

Experimental

All chemicals were of highest purity and were used as received.

Physical measurements and analysis:

Melting point were determined in open capillary tubes on a Gallen Kamp melting point apparatus and were uncorrected. The FT-IR Spectra were recorded by KBr and CsI discs using a perkin-Elmer 1600FT-IR 8300 Shimadzu spectrometer in range of (4000-200)cm^{-1}. ^{1}HNMR Spectra were recorded on a Varian-Mercury 200 MHZ Spectrometer. Electronic spectra of ligands and their metal complexes wererecorded for their solution in ethanol at 200-1100 nm and obtained using UV-1650 PC Shimadzu spectrophotometer. The measurements were recorded using a concentration of 10^{-3}M of the complex in chloroform as a solvent. Atomic absorption analytical data were obtained using AA spectrophotometer phoenix-986. Conductivity measurements were obtained using WTW conductivity multimeter-740. These measurements were recorded in (DMSO) as a solvent using a concentration of 10^{-3}M of the complex at room temperature. Magnetic susceptibility measurements were obtained at 25°C on the solid state applying Faraday's method using Bruler BM6 instrument.

A- Synthesis of[(Phenyl-carbonyl amino]acetic acid (hipuric acid)(1)

To a stirring solution of glycine (0.75 g, 0.01 mol) and sodium hydroxide (10 ml,10% solution), benzoyl chloride (0.01 mol) was added. Then, the reaction mixture was shacked vigorously for 1h. ,a few grams of crushed ice was added with stirring. After that, the solution was acidified with conc. HCl and the product was collected and recrystallized from ethanol. (yield 67 %), (m.p, C°)(187-189), (IR. (KBr) (ν, cm^{-1}) 3280 (NH), 3178 (acid OH), 2983-2821 (C-H alph.) ,1746 (acid C=O),1667 (amide C=O);^{1}HNMR (DMSO-d^6) ς (ppm) 4.01 (s, NH), 4.67 (s, CO-$\underline{CH_2}$-NH), 6.84-7.98 (m, Aromatic protons).

B- Synthesis of4-(arylidene)-2-phenyl-1,3-oxazol-5(4*H*)-one(2a- b)

To a stirring mixture of compound 1 (1.8 g, 0.01 mol) acetic acid (5 ml) acetic anhydride (20 ml),aromatic aldehyde (0.01 mol) was added. The temperature of reaction was reached to 70 C° for 10 min. , then the mixture was poured in to crushed ice and stirred for 30 min. the product was collected and recrystallized from ethanol to afforded the desired compound.

2a. (yield 71 %), (m.p, C°)(143-146), IR. (KBr) (ν, Cm^{-1}) 3070 (C-H ar), 3146 (C-H olifen), 1795 (oxazole C=O), 1646 (oxazole C=N), 1600-1509 (C=CAr), 1245 (C-O) 825 (para substitution); ^{1}HNMR (DMSO-d6) ς(ppm) 8.69 (s,C=CH-), 6.57 – 7.88 (m, Aromatic protons).

2b. (yield 63 %), (m.p, C°)(167-169), IR. (KBr) (ν,cm^{-1}) 3055 (C-H ar), 3190 (C-H olifen), 1798 (oxazole C=O), 1640 (oxazole C=N), 1606- 1511 (C=C Ar), 1245 (C-O) 860 (para substitution); ^{1}HNMR (DMSO-d6) ς (ppm) 8.46 (s, C=CH-), 6.64 – 7.95 (m, Aromatic protons).

C- Synthesis of 3-amino-5-(arylidene)-2-phenyl-3,5-dihydro-4*H*-imidazol-4-one (3a – b)

To a mixture of compound (2a–b) (0.01 mol) in dry pyridine (5ml) hydrazine hydrate (99%) (10ml) was added. The reaction mixture was refluxed for 20hs. Then, the mixture was allowed to cool to room temperature and pyridine was removed. The product was recrystallized from ethanol to afford the desired compound.

3a. (yield 53 %), (m.p, C°)(167-168), IR. (KBr) (ν,cm^{-1}) 3350-3289 (NH_2), 3088 (C-H ar), 3215 (C-H olifen), 1637 (imidazole C=O), 1589 - 1527 (C=C Ar), 1232 (C-N) 810 (para substitution); ^{1}HNMR (DMSO-d^6) ς(ppm) 8.39 (s,C=CH-), 8.82 (s, NH_2), 6.76 – 8.00 (m, Aromatic protons).

3b. (yield 46 %), (m.p, C°)(200-201), IR. (KBr) (ν,cm^{-1})3277-3223 (NH_2), 3061 (C-H ar), 3222 (C-H olifen), 1712 (imidazole C=O), 1604- 1519 (C=C Ar), 1249 (C-N) 823 (para substitution); ^{1}HNMR (DMSO-d^6) ς(ppm) 8.19 (s, C=CH-), 8.77 (s, NH_2), 754 – 7.91 (m, Aromatic protons).

D- Preparation of hipuric acid complexes of L_1 (M_1-M_5) and L_2(F_1-F_5):

Ethanolic solution of each of the following metal ion salts (1mmol) [$PdCl_2$(Na_2PdCl_4), $CoCl_2$, $NiCl_2$, $LaCl_3$, $CrCl_3$, $PtCl_4$]; [$CuCl_2$, $CoCl_2$, $NiCl_2$, $LaCl_3$, $CrCl_3$, $FeCl_3$] were added to an ethanolic solution of (0.3074gm, 1mmol) of L_1 and (0.3433 gm, 1mmol) of L_2 with stirring. The mixture was heated under reflux for one hour during this time a precipitate was formed. The product was isolated by filtration, washed several times with distilled water and hot ethanol then dried in oven. The physical data of the prepared complexes are shown in table (1)& (2).

E- Study of Complexes Formation in Solution :

Complexes of (L) with metal ions were studied in solution using ethanol as solvents in order to determin [M:L] ratio in the complex following molar ratio method[21]. Series of solutions were prepared having a constant concentration 10^{-3}M of the metal ion and (L). the [M:L] ratio was determined from the relationship between the absorption of the absorbed light and the molar ratio of [M:L]. the results of complexes formation in solution were listed at table (1).

F- Biological activity

1) Microbial isolates:-

Isolates of *Esherichia coli*, *Pseudomonas aeruginosa* and *Klebsiella pneumonia*[Gram (-ve) bacteria] and *Staphylococcus aureus*, *Enterococcus faecalis* [Gram (+ve) bacteria] were collected from different infections sources from Central Medicine City hospital in Baghdad, and isolate for Candida albicans. Isolates were identified according to that reported in [22].

2) Antimicrobial activity of (L_1,L_2) and their complexes against pathogenic isolates:-

Antimicrobial activity of (L_1,L_2) and their complexes were screened for their inhibitory activity against [Gram –ve bacteria], [Gram +ve bacteria] isolates and Candida albicans, using agar well diffusion method plates were prepared by spreeding Approximately (105 cFu/ml) culture broth of each indicator isolates on Muller- Hinton agar surface for bacterial isolates and Saboroud - agar surface for Candida albicans Isolate. The agar plates were left for about (15 mins) before a septically dispensing. The (50 µL) of each compound into the agar wells already bored in the agar plates. The plates were then incubated at (37 ºC) for (24hs). Zones of inhibition were measured and recorded in millimeter diameter.

3) Synergism effect of (L_1,L_2) and their complexes against bacterial isolates:-

Synergism effect of (L_1,L_2) and their complexes against Staphylococcus aureus and Esherichia coli were tested by using agar well diffusion Method

Results and discussion

A-Elemental Analysis

The physical analytical data of (L_1,L_2) and their metal complexes are given in table (1) and table (2). In a satisfactory agreement with the calculated values, the suggested molecular which are formulas also supported by subsequent spectral and elemental analysis as well as magnetic moment and conductivity.

Table (1): Physical analytical data of (L_1) and their metal complexes (M_1-M_5)

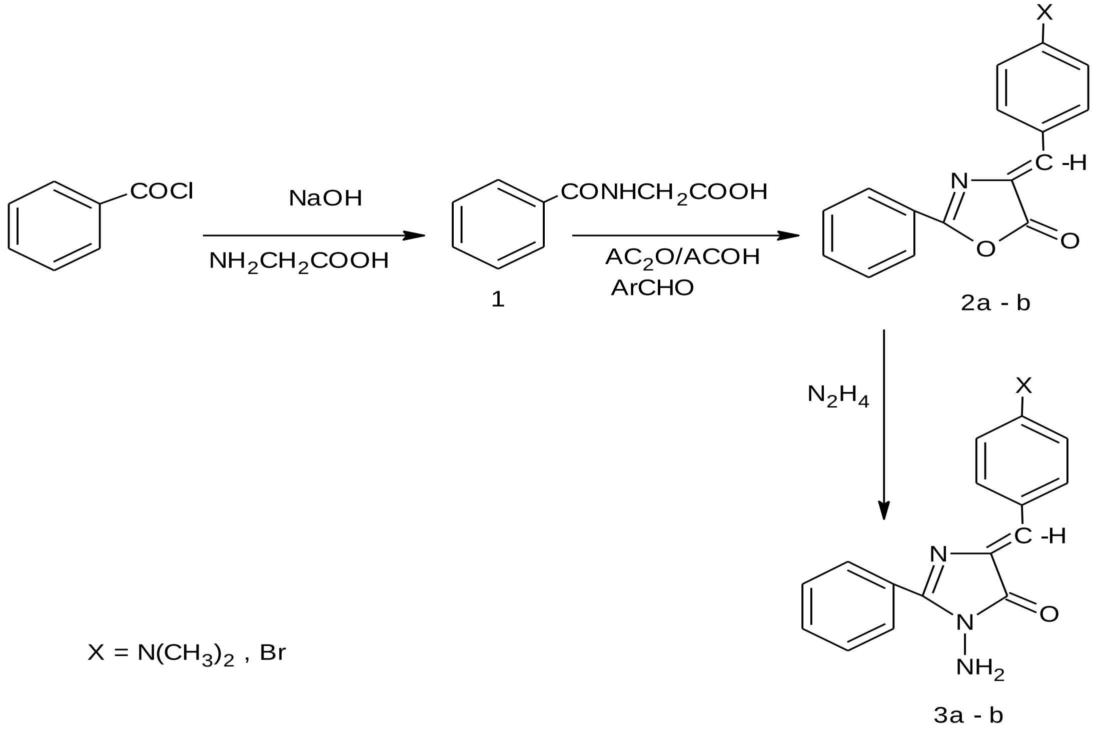
Comp. symbol	Colour	Melting point ºC	Yield %	M:L in EtOH	Elemental analysis		Suggested formula
					Found	Calculate	
L_1	Greenish-yellow	(167-168)	53	–	–	–	$C_{18}H_{18}N_4O$
M_1	Reddish-brown	190 dec.	79	1:1	17.71	18.45	$[Pd(C_{18}H_{18}N_4O)Cl.EtOH].Cl.EtOH$
M_2	Deep red	(110-112)	87	1:1	10.27	11.09	$[Ni(C_{18}H_{18}N_4O)Cl.EtOH].Cl.EtOH$
M_3	Brownish-black	(154-156)	80	1:1	16.36	13.5	$[Co(C_{18}H_{18}N_4O)Cl_3.EtOH].Cl$
M_4	Deep brown	216 dec.	48	1:1	12.7	10.37	$[Cr(C_{18}H_{18}N_4O)Cl_3.EtOH]$
M_5	Reddish-brown	(225-226)	75	1:1	27.996	26.5	$[Pt(C_{18}H_{18}N_4O)Cl_2.2EtOH].2Cl$

Table (2): Physical analytical data of (L_2) and their metal complexes (F_1-F_5)

Comp. symbol	Colour	Melting point ºC	Yield %	M:L in EtOH	Elemental analysis		Suggested formula
					Found	Calculate	
L_2	reddish-orange	(200-201)	46	–	–	–	$C_{16}H_{12}N_2OBr$
F_1	light-green	160 dec.	73	1:2	5.9	7.7	$[Cu(C_{16}H_{12}N_2OBr)_2.Cl_2]$
F_2	Brown-gray	172 dec.	81	1:1	12.58	11.31	$[Ni(C_{16}H_{12}N_2OBr)Cl.EtOH].Cl$
F_3	Greenish-gray	(127-129)	74	1:2	6.56	6.83	$[Co(C_{16}H_{12}N_2OBr)_2Cl.EtOH].Cl$
F_4	Yellow	150 dec.	54	1:2	6.5	6.4	$[Cr(C_{16}H_{12}N_2OBr)_2Cl_2]$
F_5	Brown-Black	117 dec.	82	1:2	6.5	8.31	$[Fe(C_{16}H_{12}N_2OBr)_2Cl.EtOH].Cl$

B-The Infrared spectra of (L_1,L_2) and their complexes:

Schemes (1) were summarized the synthesis of different derivatives of hipuric acid (compound 1).



Scheme 1

[phenyl-carbonyl amino]acetic acid **(1)** have been

synthesized by the reaction of benzoyl chloride with glycine in the presence of sodium hydroxide. The reaction is followed by decreasing of absorption band for ($\upsilon_{C=O}$) at 1741 cm^{-1} and appearance of new absorption band at 3280 cm^{-1} due to (υ_{NH}). Inthe ^{1}H NMR spectra, the proton signals due to (CO-$\underline{CH_2}$-NH) was recorded at 4.67 ppm integrating for two protons. The treatment of compound (1) with aryl aldehyde in presence of acetic acid and acetic anhydride led to the formation of 4-(arylidene)-2-phenyl-1,3-oxazol-5(4*H*)-one(2a-b). Compounds (2a-b) have been identified by IR spectrum which it showed the appearance of characteristic absorption bands near 1795-1798 cm^{-1} which belonged to the oxazol-5(4H)-one carbonyl group (oxazole,$\upsilon_{C=O}$), and at 3146-3190 cm^{-1} due to (olifinicυ_{CH}), ^{1}H NMR spectra showed signals at 8.46-8.69 ppm due to (CH, olifenic) and at 6.57-7.95 ppm which belonged to aromatic protons.Refluxing compounds (2a-b) with hydrazine hydrate (99%) for 20 hrs offered good yields of the corresponding derivatives (3a-b). The IR spectra of compounds (3a-b) displaced peaks at 1637-1712 cm^{-1}, 3223-3350 cm^{-1} for (imidazole, $\upsilon_{C=O}$) and (υ_{NH2}) functions respectively. ^{1}H NMR spectrashowed signals at 8.77-8.82 ppm due to (NH_2), at 8.19-8.89 ppm for (CH, olifenic) and at 6.76 – 8.00ppm which belonged to aromatic protons.

Important information obtained from the FTIR spectrum of L_1 and L_2complexes which are summarized in tables 3 & 4. Some bands which were appeared at 1708(v.sh) in L_1 and at 1712(sh) in L_2were shifted to lower frequencies in comparison with ligands were appearing at about 1645(sh) in M_1, 1643(w) in M_2, 1641(w) in M_3, 1640(w) in M_4 and at 1645(m) in M_5 also bands appeared at 1627(sh) in F_1, 1643(sh) in F_2, 1637(sh) in F_3, 1647(v.sh) in F_4 and at 1641(w) in F_5 that belong to the typical$\upsilon_{(C=O)}$ of imidazol ringthat indicated coordination of ligands with metal ions through the O atom of C=O group[23,24].

The typical $\upsilon_{(N-NH2)}$ band for lactam in L_1 appeared at 3327(sh) wasshifted to 3444(br) in M_1, 3414(br) in M_2, 3404 in M_3, 3383 in M_4 and at 3452 in M_5 , also the band appeared in L_2 at 3277(m) was shifted to 3360(w) in F_1, 3336(br) in F_2, 3308(br) in F_3, 3327(w) in F_4 and at 3329(br) in F_5 that indicated coordination of ligands with metal ions through the N atom of NH_2group[25,26].

At last, the new bands appearing at 542(w), 496(w) and 415(w) in M_1; at 532(w), 462(w), 425(w) in M_2; 530(w), 470(w), 424(w) in M_3, 545(m), 482(w), 403 in M_4 and at 561(w), 488(w) and 430(m) in $M_5$and at about 499(sh), 434(m) and 420(w) in F_1; at 500(w), 453(w), 435(w) in F_2; 501(m), 457(w), 405(m) in F_3, 504(m), 447(w), 422(m) in F_4 and at 498(sh), 434(m) and 410(m) in $F_5$are attributed to (M-O), (M-N) and (M-Cl) stretching vibration respectively in complexes of L_1&L_2 which are absent in ligands spectra[27,28].

Finally there are broad absorption bands appearing at about 3449(br) cm^{-1} in M_1, 3414(br) cm^{-1} in M_2, 3408(br) cm^{-1} in M_3, 3400(br) cm^{-1} in M_5 and about 3335(br) cm^{-1} in F_2, 3377(br) cm^{-1} in F_3, 3379(br) cm^{-1} in F_5

attributed to the $\upsilon_{(OH)}$, indicate the presence of coordinated solvent molecules (Ethanol) in those complexes[29]. In addition, the bands appearing at 696(m) cm^{-1} in M_1, 698(m) cm^{-1} in M_2, 692(m) cm^{-1} in M_3, 650(m) in M_5 and 692(m) in F_2, 690(m) in F_3, 694(m) in F_5 resulting from $\delta_{(OH)}$ bends also supports this conclusion[30,31].

Table (3): Characteristic stretching vibration frequencies (cm^{-1}) located in FT-IR of (L_1) and their metal complexes (M_1-M_5)

Compound symbol	$\nu_{C=O}$for Imidaol	ν_{C-N}forImidaol	$\nu_{N-NH2}$for lactam	ν_{M-O}	ν_{M-N}	ν_{M-Cl}
L_1	1651(s)	1257(m)	3298(sh)	–	–	–
M_1	1599(s)	1231(w)	3228(m)	542(w)	496(w)	415(w)
M_2	1645	1236(m)	3323(br)	532(w)	462(w)	435(w)
M_3	1641	1236(w)	3383(br)	530(w)	470(w)	424(w)
M_4	1641(w)	1225(w)	3283(br)	545(m)	482(w)	403(w)
M_5	1645(m)	1298(m)	3186(w)	561(w)	488(w)	430(m)

Table (4): Characteristic stretching vibration frequencies (cm^{-1}) located in FT-IR of (L_2) and their metal complexes (F_1-F_5)

Compound symbol	$\nu_{C=O}$for Imidaol	ν_{C-N}forImidaol	$\nu_{N-NH2}$for lactam	ν_{M-O}	ν_{M-N}	ν_{M-Cl}
L_2	1712(sh)	1249(m)	3277(w)	–	–	–
F_1	1627(sh)	1273(w)	3360(w)	499(sh)	434(m)	420(w)
F_2	1643(m)	1213(m)	3303(br)	500(w)	453(w)	435(vw)
F_3	1637(sh)	1213(w)	3308(br)	501(m)	457(vw)	405(m)
F_4	1647(sh)	1298(m)	3221(br)	504(m)	447(w)	422(m)
F_5	1641(sh)	1250(w)	3329(br)	498(sh)	434(m)	410(m)

Note: sh=sharp, br=broad, m=medium, w=weak

The Electronic spectra of (L_1) and their complexes:

The UV spectrum of (L_1) showed intense bands at 47619 cm^{-1} belong to $\pi \rightarrow \pi^*$ and at 28735 cm^{-1} and at 21645 cm^{-1} belong to $n \rightarrow \pi^*$ [25], table 5.

[M_1]:- The UV-visible spectrum of deep- reddish brown of palladium complex with (L_1) exhibited a weak shoulder at (12658cm^{-1}, 790nm) due to [$^1A_1g \rightarrow {}^1E_1g$] transition, which is equal to the value (10Dq) for square planner configuration[32]. It is also gave another band at (15151cm^{-1}, 660nm) due to [$^1A_1g \rightarrow {}^1B_1g$] transition, and another strong band at (38461cm^{-1}, 260nm) due to charge transfer between metal and ligand[33]. The diamagnetic propertyof the complex agree well with electronic transition of low spin (d^8) of palladium (II) complexes, which is the only case in square planner environment[34,35]. The conductance measurements indicate that this complex was to be ionic, table (5).

[M_2]:- The electronic spectrum of deep- red complex of nickel with (L_1) exhibited two bands one at (21052cm^{-1}, 475nm) due to [$^3T_1g \rightarrow {}^3A_2g$] transition and another band at (15873cm^{-1}, 630nm) due to [$^3T_1g(F) \rightarrow {}^3T_2g(P)$] transition[32], which is equal to the value (10Dq) for octahedral configuration[36]. In addition the effective magnetic moment at room temperature for the prepared complex was found to be (2.2 B.M), that refers to high spin (d^8) of nickel (II) complexes[37].The conductivity measurements in (DMSO) showed a electrolytic behavior for complex, which is in a good agreement with that reported for tetrahedral geometry[38]. Table (5).

[M_3]:- The UV-visible spectrum of brownish-black of cobalt complex with (L_1) exhibited a weak shoulder at (14619cm^{-1}, 684nm) due to [$^4A_2g(F) \rightarrow {}^4T_2g(F)$] transition, which is equal to the value (10Dq) for distorted octahedral configuration[36]. It is also gave another two bands, one at (17985cm^{-1}, 556nm) due to [$^4A_2g(F) \rightarrow {}^4T_1g(F)$] transition, and another band at (21834cm^{-1}, 258nm) due to [$^4A_2g(F) \rightarrow {}^4T_1g(P)$] transition[39]. The measured effective magnetic moment at room temperature for this complex was found to be (3.84 B.M), which refers to high spin (d^7) of cobalt (II) complexes[40].The conductivity measurements showed a electrolytic behavior for complex, which is in a good agreement with that reported for octahedral geometry[41,42].

[M_4]:- The electronic spectrum of this deep brown of chromium complex with (L_1) gave a shoulder band at (20833cm^{-1}, 480nm) due to [$^4A_2g(F) \rightarrow {}^4T_2g(F)$] transition, which is equal to the value (10Dq) for octahedral configuration[43]. It is also gave another two bands at (27700cm^{-1}, 361nm) due to [$^4A_2g(F) \rightarrow {}^4T_1g(F)$] transition, (38759$cm^{-1}$, 258nm) due to [$^4T_2g(F) \rightarrow {}^4T_1g(F)$] transition[38]. The measured effective magnetic moment at room temperature for the prepared complex was found to be (4.23 B.M), which refers to (d^3) of chromium (III) complexes[44].The conductivity measurements in (DMSO) showed a non- conductive behavior for this complex, table (5).

[M_5]:- The UV-visible spectrum of this deep brown of platinum complex with (L_1) showed three bands, the first one appeared at (15197cm^{-1}, 658nm) due to (d-d) transition, which is equal to the value (10Dq) for octahedral configuration[39].The second band appeared at (20533cm^{-1}, 487nm) due to [$^3A_1g(F)\rightarrow{}^3T_2g(F)$] transition[45]. While the third one which refers to charge transfer transition appeared at (28653cm^{-1}, 349nm). The effective magnetic moment at room temperature for this complex showed low spin octahedral (d^6) of Platinum (IV) complexes which found to be (0.0 B.M)[46].The conductivity measurements in (DMSO) showed a a electrolytic behavior for complex, table (5).

The Electronic spectra of (L_2) and their complexes:

The UV spectrum of (L_2) showed intense bands at 48780 cm^{-1} and at 44642cm^{-1} belong to $\pi \rightarrow \pi^*$ and at 33670 cm^{-1} belong to $n \rightarrow \pi^*$ [25]. Table 6.

[F_1]:- The electronic spectrum of light- green cupper complex with (L_2) exhibited only a broad overlapping band at (12500cm^{-1}, 800nm) due to [$^2Eg\rightarrow{}^2T_2g$] transition[47]. In addition the measured effective magnetic moment at room temperature for complex was found to be (1.67 B.M), which refers to low spin distorted octahedral (d^9) of cupper (II) complexes[44]. The complex was paramagnetic and the conductance measurements indicate that this complex was to be a nonionic, table (6).

[F_2]:-The electronic spectra of L_2 and its brown- red complex of nickel are similar. The complex spectrum exhibited two bands at (31948cm^{-1}, 313nm) due to [$n\rightarrow\pi^*$] transition and at (43290cm^{-1}, 231nm) due to [$\pi\rightarrow\pi^*$] transition that shifted to upper frequency.Thishypsochromic shifts of about (16&7) nm respectively are caused by the coordination of N and O atoms of imidazole ring to Ni ion, which can also provide the conclusion evidence for the coordination[30].The d-d transitions corresponded to [$^1A_1g\rightarrow{}^1B_1g$] and [$^1A_1g(F)\rightarrow{}^2B_2g(P)$] for square planner were masked by high intensity band of intra-ligand charge transfer (INCT)[48]. The diamagnetic property of complex agree well with electronic transition of low spin (d^8) of nickel (II) complexes, which is the only case in square planner environment[36,49].The conductance measurements in (DMSO) showed electrolytic behavior in (1:1) ratio. This data was considered to cooperate with proposed formula [Ni(L_2)(EtOH)Cl]Cl, table (6).

[F_3]:- The electronic spectrum of greenish-gray complex of cobalt with (L_2) exhibited three absorption bands. The first band appeared at (15290cm^{-1}, 654nm) due to [$^4A_2g(F)\rightarrow{}^4T_1g(F)$] transition, which is equal to the value (10Dq) for destroyed octahedral configuration[32]. The second band appeared at (16447cm^{-1}, 608nm) due to [$^4T_1g(F)\rightarrow{}^4T_1g(P)$] transition, while the third band appeared at (17699cm^{-1}, 565nm) due to [$^4T_1g(F)\rightarrow{}^4T_2g(P)$] transition[43]. The position of these bands are in a good agreement with that reported for octahedral geometry[36]. The measured effective magnetic moment at room temperature for complex was found to be (3.77 B.M), which refers to high spin (d^7) of cobalt (II) complexes[47,50]. Conductivity measurements in (DMSO) indicate electrolytic behavior for complex, Table (6).

[F_4]:- The UV-visible spectrum of yellow complex of chromium with (L_2) showed a two bands, one appeared at (16666cm^{-1}, 600nm) due to [$^4A_2g(F)\rightarrow{}^4T_2g(F)$] transition, the other broad band appeared at (24937cm^{-1}, 401nm) due to [$^4A_2g(F)\rightarrow{}^4T_1g(F)$] transition[32]. while the third one which refers to charge transfer transition appears at (25839cm^{-1}, 387nm). The measured effective magnetic moment at room temperature for the prepared complex was found to be (4.5 B.M), which is in agreement with (d^3) octahedral geometry of chromium (III) complexes[44]. Conductivity measurements in (DMSO) showed a non- conductive behavior for this complex, table (6).

[F_5]:- The electronic spectrum of black complex of Iron with (L_2) showed three absorption bands appeared at (16051cm^{-1}, 623nm), (16447cm^{-1}, 608nm) and (14164cm^{-1}, 706nm) due to [$^4A_{1g}\rightarrow{}^4T_1g(G)$], [$^4A_{1g}\rightarrow{}^4Eg,{}^4A_1g(G)$] and [$^4A_{1g}\rightarrow{}^4T_1g(P)$]transition respectively[51]. The paramagnetic property at room temperature of the complex indicate a low spin octahedral (d^5) of ferric (III) complexes and it was found to be (1.8 B.M)[52].The conductivity measurements in (DMSO) showed anelectrolytic behavior in (1:1) ratio, table (6).

Table (5): Electronic spectra, Conductance in (DMSO) and Magnetic moment (B.M) for (L_1) and their metal complexes (M_1-M_6)

Compound symbol	Bands (cm^{-1}) (nm)	Assignment	Molar conductivity (µs.cm^{-1})	µeff. (B.M)	Suggested structure
L_1	47619 (210) 28735 (348) 21645 (462)	π→π n→π n→π	19.9	–	–
M_1	38461 (260) 15151 (660) 12658 (790)	C.T. [$^1A_1g\rightarrow{}^1B_1g$] [$^1A_1g\rightarrow{}^1E_1g$]	32.5	0.0	Square planner

M_2	21052 (475) 15873 (630)	$[^3A_2g \rightarrow {}^3T_1g(F)]$ $[^3T_1g(F) \rightarrow {}^3T_1g(P)]$	43	2.2	Tetrahedral
M_3	21834 (458) 17985 (556) 14619 (684)	$[^4A_2g(F) \rightarrow {}^4T_1g(P)]$ $[^4A_2g(F) \rightarrow {}^4T_1g(F)]$ $[^4A_2g(F) \rightarrow {}^4T_2g(P)]$	42.8	3.9	Distorted octahedral
M_4	17921 (558) 15015 (666) 12771 (783)	C.T. $[^4A_2g(F) \rightarrow {}^4T_1g(F)]$ $[^4A_2g(F) \rightarrow {}^4T_2g(P)]$	24.1	4.1	Octahedral
M_5	12658 (790)	$[^3A_1g(F) \rightarrow {}^3T_1g(F)]$	63.3	0.0	octahedral

Table (6): Electronic spectra, Conductance in (DMSO) and Magnetic moment (B.M) for (L_2) and their metal complexes (F_1-F_6)

Comp. symbol	Bands (cm^{-1})(nm)	Assignment	Molar conductivity ($\mu s.cm^{-1}$)	µeff. (B.M)	Suggested structure
L_2	48780 (205) 44642 (224) 33670 (297)	$\pi \rightarrow \pi$ $\pi \rightarrow \pi$ $n \rightarrow \pi$	22.7	–	–
F_1	12500 (800)	$[^2Eg \rightarrow {}^2T_2g]$	20.2	1.67	Distorted Octahedral
F_2	33783 (296) 11248 (889)	$[^3A_2g \rightarrow {}^3T_1g(F)]$ $[^3T_1g(F) \rightarrow {}^3T_1g(P)]$	50.8	0.0	Square planner
F_3	17699 (565) 16447 (608) 15290 (654)	$[^4A_2g(F) \rightarrow {}^4T_1g(P)]$ $[^4A_2g(F) \rightarrow {}^4T_1g(F)]$ $[^4A_2g(F) \rightarrow {}^4T_2g(P)]$	44.5	3.77	Octahedral
F_4	16666 (600) 13793 (725)	$[^4A_2g(F) \rightarrow {}^4T_1g(F)]$ $[^4A_2g(F) \rightarrow {}^4T_2g(F)]$	5.7	4.5	Octahedral
F_5	16447 (608) 16051 (623) 14164 (706)	$[^4A_1g(F) \rightarrow {}^4T_1g(P)]$ $[^4A_1g(F) \rightarrow {}^4T_1g(G)]$ $[^4A_1g(F) \rightarrow {}^4Eg, {}^4A_1g(G)]$	45.9	1.8	Octahedral

The Antimicrobial Activity of(L_1, L_2) and their complexes were tested against pathogenic isolates(*Esherichia coli*, *Pseudomonas aeruginosa*, *Klebsiella pneumonia*, *Staphylococcus aureus*, *Enterococcus faecalis* and *Candida albicans*) using well diffusion technique. The diameter of inhibition zones around each well with (L_1, L_2) and their complexes is represented in table (7). The highest Antimicrobial Activity was observed against *Pseudomonas aeruginosa*. No inhibition activity was noticed from all prepared compounds against *Candida albicans*.(Ni+L_1) and (La+L_1) complexes were found to be the most effective agent against bacterial isolates, while (Fe+L_2) was the lowest effective agent.

On the other hand the synergism effect of (L_1, L_2) and their complexes were tested against *Staphylococcus aureus* and *Esherichia coli*. The results showed non effect for all compound against *Staphylococcus aureus*. (Ni+L_2) + (Pd+L_1) and (Co+L_1) + (Fe+L_2) complexes mixtures were effected with *Esherichia coli*, the inhibitor zone diameter was (11mm, 10mm) respectively, table (8).

Table (7):- Antimicrobial Activity of (L_1, L_2) and their complexes

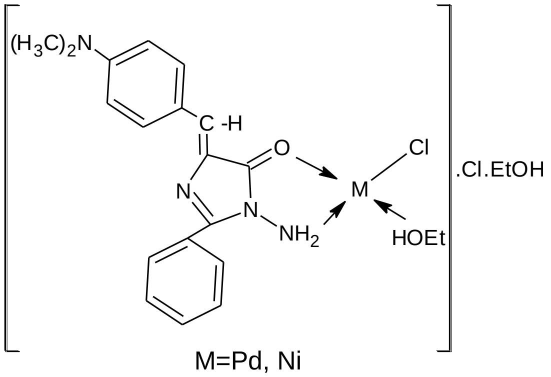
Isolate compounds	**Inhibition Zone diameters (mm) aganist**				
	Pseudomonas aeruginosa (G-ve)	*Esherichia coli* (G-ve)	*Enterococcus faecalis* (G+ve)	*K. pneumemae*(G-ve)	*Staphylococcus aureus* (G+ve)
Pt+L_1	18	14	–	16	11
Co+L_1	22	14	–	15	11
Cr+L_1	21	15	–	15	–
Ni+L_1	25	15	–	13	12
La+L_1	25	15	–	13	13
Pd+L_1	21	15	–	13	13
L_1	20	15	12	15	15

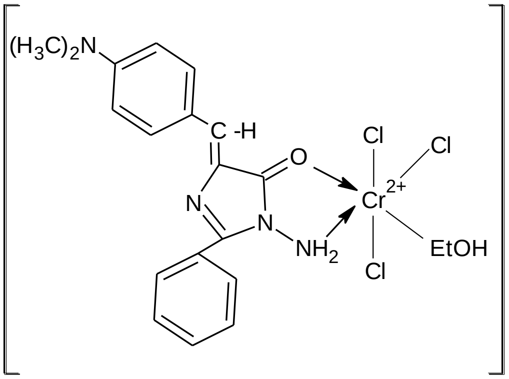
Cu+L_2	20	15	14	16	12
La+L_2	20	14	−	12	13
Fe+L_2	−	14	−	12	−
Cr+L_2	17	14	−	11	−
Co+L_2	17	14	−	11	11
Ni+L_2	−	14	15	12	12
L_2	−	13	−	−	−

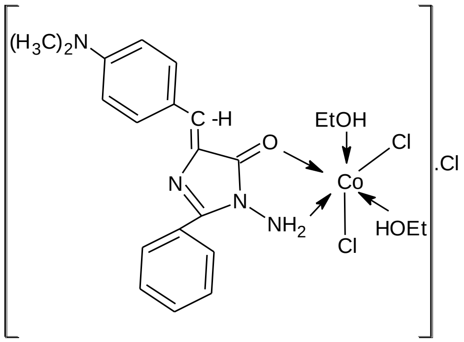
Table (8):- Synergism Affectof (L_1, L_2) and their complexes

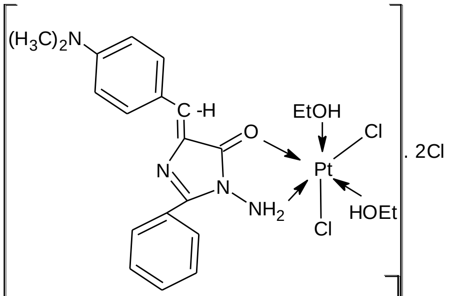
Mixture	*Staphylococcus aureus*	*Esherichia coli*
(Pt+L_1)&(Cu+L_2)	−	−
(Co+L_1)&(La+L_2)	−	−
(Cr+L_1)&(Fe+L_2)	−	−
(Ni+L_1)&(Cr+L_2)	−	−
(La+L_1)&(Co+L_2)	−	−
(Pd+L_1)&(Ni+L_2)	−	**11mm**
(L_1)&(L_2)	−	−
(Co+L_1)&(Fe+L_2)	−	**10mm**
(Ni+L_1)&(Cu+L_2)	−	−
(Pd+L_1)&(Cr+L_2)	−	−
(Ni+L_1)&(Fe+L_2)	−	−
(Pd+L_1)&(Cu+L_2)	−	−
(Pd+L_1)&(Fe+L_2)	−	−
(La+L_1)&(Fe+L_2)	−	−

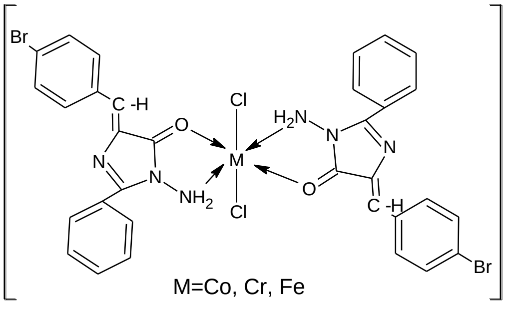
The suggested stereo geometrical structure of L_1& L_2 with their metal complexes (M_1-M_5) and (F_1-F_5):

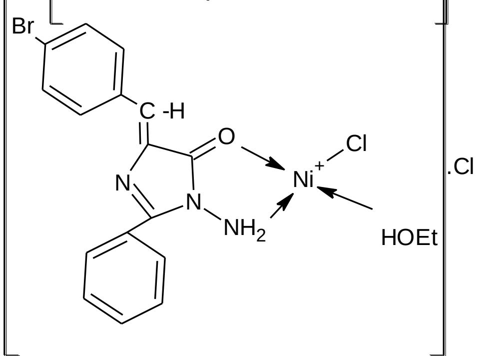


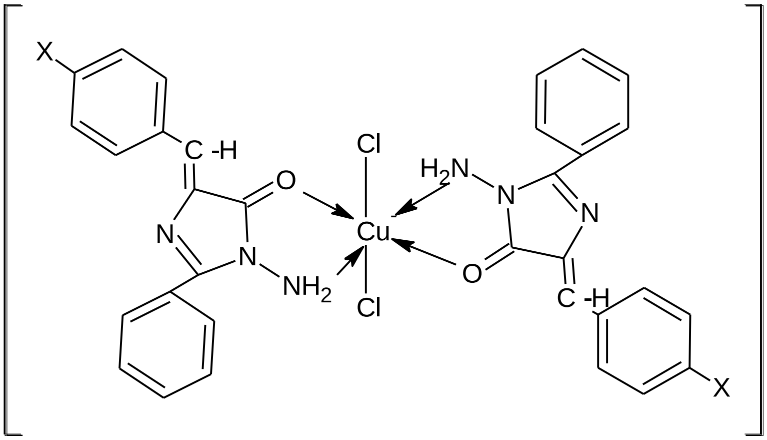












`**References**

1 –.Maillard J., Vincent M., Morin R., Benard M. : Hypnotic and sedative drug, 2-(O-hydoxyphenyl) -1,3,4-oxadiazole. FrenchPatent M 379: ChemAbstr: 57, 15251, (1962).

2- Angilini I., Angilini L., Sparacc F : 2-Phenyl-5-chloroalkyl- 1,3,4-oxadiazoles, British Patent, 1:161, 801, 1969; ChemAbstr71:112936, (1969).

3- Najer H, Giudicelli R, Moral C, MeninM : Synthesis of some 5-aryl-2-dimethylamino-1,3,4-oxadiazoles with antiinflammatory

4- Kennedy D.A., Summers L. A. : Chemical constitution and activity of Herbicides. Part XIV. Reduction potential and herbicidal activity of 4,4-(1,3,4-thiadiazole-2,5-diyl)-and 4,4-(1,3,4-oxadiazole-2,5-diyl) bis (1-methylpyridinium) diiodides, J.HeterocyclChem 409-410, (1981).

5- Yale HI, LoseeK : 2-Amino-5-substituted 1,3,4-oxadiazoles and 5-imino-substituted Δ 2- 1,3,4-oxadiazolines. A groupof novel muscle relaxants. J Med Chem 9:478-483, (1966).

6- Piala JJ, Yale HL : 2-Amino-5-aryl 1,3,4-oxadiazoles, USPatent: 3,141, 022, 1964. ChemAbstr: 61, 8317, (1964).

7- PRIYA V. F., GIRISH K. S. and BALAKRISHNA K. Solvent-free microwave-assisted synthesis of oxadiazoles containing imidazole moietyJ. Chem. Sci., Vol. 119, No. 1, , pp. 41–46 January (2007).

8 - Eduardo A. Ve´liz and Peter A. Beal 6-Bromopurine Nucleosides as Reagents for Nucleoside AnalogueSynthesis J. Org. Chem. (2001), 66, 8592-8598.

9- Sahar A. Kadem Synthesis of New Imidazole Derivative Mustansiriya J. Sci., 3(17), 50-58(2010).

10- J. Valdez; R. Cedillo; A. Hernandez-Campos; L. Yepez; F. Hernandez- Luis; G. Navarrete-Vazquez; A. Tapia; R. Cortes; M. Hernandez; R. Castillo. *Bioorg Med Chem Let*., **(2002)**, 12, 2221.

11- KF Khaled. *ElectrochimActa*, **(2003)**, 48, 2493.

12-Kamalakannan, P.; Venkappaya, D. *J. Inorg. Biochem.* **2002**, 90, 22.

13- Newman, E.C.; Frank, C.W. *J. Pharm. Sci.* **1976**, 65, 1728.

14- Collin, F.B. "*Metal Chelation Principles and Applications"*, Oxford Chemistry Series,Clarendom Press: Oxford; **1977**, p 124.

15-Beur, A.W.; Jkirby, W.M.M.; Turck, M. *Am. J. Clin. Pathol.* **1996**, 44, p 493.

16- Shrivastav, A.; Singh, N.K.; Srivastava, G. *Bioorg. Med. Chem.* **2002**, 10, 2693.

17- A. Neves, L.M. Rossi, A.J. Bortoluzzi, A.S. Mangrich, W. Haase,R. Werner, J. Braz. Chem. Soc. 12 (2001) 747.

18- Z. Hu, R.D. Williams, D. Tran, T.G. Spiro, S.M. Gorun, J. Am.Chem. Soc. 122 (2000) 3556.

19- C. Fernandes, A. Neves, A.J. Bortoluzzi, A.S. Mangrich, E.Rentschler, B. Szpoganicz, E. Schwingel, Inorg. Chim. Acta(2001) 12.

20- Travis, J.; Potempa, J. *Biochim. Biophys. Acta*,(**2000)**, 14, 35.

21- Douglas, A. S., Donald, M. N., Holler, F. J., Crouch, S. R. and Chen, S. C. 2011. "Introduction to Analytical Chemistry", Case bound, 1st Ed.

22- Green Wood, D.; Slack, R.C. and Peutherer, J.F. (2002). Churchill Livingston, 16th Ed.

23-Deepa, K., Madhu, N. and Radhakrishnan, P. 2005. "Cadmium(II) Complexes of 1,2-Di (imino-4'-antipyrinyl) ethane", Synth. React. Inorg. Met.-Org. Nano-Met. Chem., 35 :883-888.

24- Aswar, A. S., Bansod, A. D., Aswale, S. R. and Mandlik, P. R. 2004. "Synthesis, Charactization, electrical and biological Studies of Cr(III), Mn(II), Fe(III), Ti(III), VO(IV), Th(IV), Zr(IV) and UO_2(VI) polychelates with bis-bidentate Schiff base", Indian J. Chem., 43A :1892-1899.

25- R.M. Silvershtein, G.C.Bassler and T.G.Morrill, “Spectrometric Identification of Organic Compounds”, 4th Ed., John Wiley and Sons, Inc., New York, London, (1981).

26- El-Ajaily, M. M. and El-Ferjani, R. M. 2007. "Preparation and Physical Investigation of Complexes derived from 4-Dimethyl amino benzaldehyde and 4-amino antipyrine Schiff Base with Ni(II), Cu(II), Rh(III) and Pt(IV) Ions", Jordan J. Chem., 2(3) :287-296.

27-Nakamoto, K. “Infrared and Raman spectra of Inorganic and Coordination Compounds”, 5th Ed., John Wiley and Sons: New York, NY, USA, (1986): 232-234.

28- Nakamoto, K. “Infrared of Inorganic and Coordination Compounds”, 6th Ed., John Wiley, Inc., New York, London, (1997).

29- Nakamoto, N. “Infrared and Raman spectra of Inorganic and Coordination Compounds”, 7th Ed., John Wiley and Sons, Inc., New Jersey, (2009).

30- Yan-Fang Wang, Jian-Feng Liu, Hui-Duo Xian and Guo-Liang Zhao “Synthesis, Crystal Structure, and Kinetics of the Thermal Decomposition of the Nickel(II) complex of the Schiff base 2-[(4-Methyl phenylimino) methyl]-6-methoxyphenol” Molecules, 14 (2009).

31-G.Kumar, M.Srivastava, Rev. Chim, Miner, 16, 14(1979).

32- D.Sutton, “Electronic spectra of transition metal complexes” 1st Ed., Mc.Graw- Hill publishing, London, (1968).

33- A.B.P. Lever, “Inorganic Electronic Spectroscopy”, Elsevier, Amsterdam (1968).

34-A. Earnshaw, “Magneto chemistry”, New York, p.6-7 (1968).

35-R.C.Saxen, R.Benjamin and S.K.Sangal, “Magnetic and spectral behavior of Pd(II), Pt(IV) and Ru(II) complexes with some tridentate substituted thiosemicarbazones”, J.Ind. Chem. Soc., LXIII (2), (1986).

36- A.Antipas and M.Gouterman, “Electronic states of Co(II), Ni(II), Rh(II) and Pd(II) complexes”, J. Am. Chem. Soc., 105(23), (1983).

37- N.N.Greenwood and A.Earn chaw, “Chemistry of the Elements”, 2nd Ed., Pergaman Press, (1998).

38- B.N.Figgis, “Introduction to Ligand Fields”, John Wiley and Sons, Inc., New York, (1966).

39- G. Deveto, G. Ponticelli and C. Preti, J. Inorg. Nucl. Che., 37, 1635 (1975).

40-Bipin, B.M. and M.K. Raval, Indian J. of chem., 28A, 434 (1989).

41- R.A.M. Al-Hasani, “Synthesis and study of some transition metal complexes of some 1,3,4- oxadiazole derivatives”, M.Sc. Thesis, Al-Mustansirya University, Baghdad, Iraq, (1999).

42- A. Wasey, R.K. Bansal, B.K.F. Kmil and S. Chandra, Transition Met. Chem., 8, pp. 341-342 (1983).

43-J. Carl Ballhausen, “Introduction to Ligand Field Theory”, New York, Toronto, London (1962).

44- David Nicholis, “Complexes and first-row transition elements”, 1st Ed., The Mac Millan Press LTD. (1974).

45-C.K.Demertzi, “Platinum(II) and Platinum(IV) complexes of 2-amino-4,6-dimethyl pyrimidine”, Trans. Met. Chem., 15(23), (1990).

46- F.Wilson and P.Merchant, “The interaction of (2-mercapto-benzothiazole with certain platinum group element derivatives”, J. Inorg. Nucl. Chem., 29(18), (1993).

47- F.A. Cotton and G. Wilkinson “Advanced Inorganic Chemistry”, 5th Ed., Interscience publishers, New York (1988).

48- W.J. Gerry, (1971).

49-L.N. Mulay, “Magnetic Susceptibility”, John Wiley & Sons, New York, Part I, vol.4 (1963).

50- L.E. Orgel, J. Chem. Phys., 23, p.1004 (1955).

51- C.K. Jorgenson, “Absorption Spectra and Chemical Bonding in Complexes” Perganmon Press (1964).

52- F.E. Mabbs and D.J. Machin, “Magnetism and Transition Metal Complexes” Chopman and Hall, London (1973