

Synthesis, Characterization And Biological Activity Of Metal Complexes With Schiff Bases Derived From [4-Antipyrincarboxaldehyde] With [2-Amino-5-(2-Hydroxy-Phenyl)-1,3,4-Thiadiazole]

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ABSTRACT

New metal complexes of type $M_2(HL1)_2 \cdot 4H_2O$ [M=(M = Co(II), Ni (II), and Cu (II))] were prepared using the ligand (HL1) 4- [5-(2-hydroxy-phenyl) - [1, 3, 4-thiadiazol-2-ylimino methyl]-1,5-dimethyl-2-phenyl-1,2 - dihydro - pyrazol -3- one. The Schiff bases were condensed from [4 -antipyrincarboxaldehyde] with [2-amino-5 - (2-hydroxy-phenyl - 1, 3, 4 -thiadiazole)] in alcoholic medium. The prepared complexes were characterized by FTIR Spectroscopy, Electronic spectroscopy, elemental analysis, magnetic susceptibility measurements, thermal analysis, 1H -NMR spectra, and mass spectra. The activation thermodynamic parameters, such as ΔE^* , ΔH^* , ΔS^* and ΔG^* are calculated from the TGA curve using Coats-Redfern method. From the spectral measurements, structures for the complexes were proposed. Preliminary *in vitro* tests for antimicrobial activity show that all prepared compounds display good activity toward *Staphylococcus aureus*, *Escherishia coli*, *Pseudomonas aeruginosa* and *Candida albicans*.

Key Words: Schiff base, Microwave synthesis, Thermodynamic Parameters, Biological activity, Antipyrin.

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تحضير طيفية وفعالية بيولوجية لمعقدات بعض المعادن ودراساتها مع أسس شيف المشتقة من تفاعل 4-انتي بايرين كربوكسي الدهيد مع 2-أمينو - 5-(2-هيدروكسي فنييل)-4,3,1-ثياديازول

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المُلخَص

حُضِرَت معقدات جديدة نوع $M \cdot M_2(HL1)_2 \cdot 4H_2O$ حيث $M = (Co(II), Ni(II), \text{ and } Cu(II))$ واستُخدمت المرتبطة (HL1) = 4-[5-(2-hydroxy-phenyl)-[1,3,4-thiadiazol-2-ylimino methylen]-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one

التي حضرت من تفاعل 2-أمينو(2-هيدروكسي فنييل)-4,3,1-ثايوديازول مع 4-انتي بايرين كربوكسي الدهيد في الكحول النقي. شخّصت المعقدات المحضرة بتقنية الأطياف تحت الحمراء والأطياف الإلكترونية وطيف الكتلة والطنين النووي المغناطيسي البروتوني والتحليل الحراري، كما حددت الثوابت الترموديناميكية ΔE^* , ΔH^* , ΔS^* , ΔG^* باعتماد معادلة Coats-Red fern من أطياف التحلل الحراري الوزني للمركبات ولكل مرحلة من مراحل التحلل. وكذلك قيسَت الحساسية المغناطيسية. كما استخدم التحليل العنصري للمساعدة في عملية التشخيص، إذ اقترح شكل البنية الأساسية للمعقدات. قيسَت النسب المولية المتغيرة في المحلول فأعطت نتائج مطابقة مع تلك التي تم الحصول عليها في الحالة الصلبة ومن نتائج الاطياف اقترح شكل بنية المعقدات المحضرة. كما درست الفعالية البيولوجية للمركبات ضد أنواع منتخبة من البكتريا.

الكلمات المفتاحية: أسس شيف، التحضير الميكروويفي، أسس شيف، الثوابت الترموديناميكية، الفعالية البيولوجية.

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Introduction

Increasing physiological importance of nitrogen and sulphur donor organic compounds [1]. and active role played by coordination certain metal ions to them[2], have interesting use in synthesizing and studying structural aspects of metal complexes with some sulphur and nitrogen donor ligands [3].

The aromatic thiadiazole nucleus is associated with a variety of pharmacological actions, such as fungicidal, and leishmanicides activities. These activities are probably due to the presence of the $\text{N}=\text{C}-\text{S}$ group[4,5].

Pyrazole; thiadiazole and its derivatives form an important class of organic compounds due to their structural chemistry and biological activities as analgesic, antipyretics and anti-inflammatory [6]. Even the simplest pyrazolone derivatives like antipyrine and amidopyrine are widely used as analgesic medicines [7,8]. Pyrazolones are efficient extractants of metal ions and they have potential to form different types of coordination compounds due to tautomeric effect of enol and keto form[9]. Pyrazolones, especially pyrazolone, display several different coordination modes with respect to classical β -diketonates[10]. Microwave assisted organic reaction enhancement (MORE) is nowadays a well established technique for synthesis of various heterocyclic compounds [11-13]. In addition pyrazolones can form a variety of Schiff bases and are reported to be superior reagents in biological, clinical and analytical applications [14-20]. In continuation of our work on the metal complexes of Schiff bases, we report here the study of some new, Co(II), Ni (II) and Cu (II), complexes of Schiff bases derived from 4-antipyrincarboxaldehyde and 2-amino-5-(2-hydroxy-phenyl)-1,3,4-thiadiazole. Preparation, characterization and antibacterial activity of the above metal complexes with this Schiff bases are reported here. Where, HL1 is a Schiff base of 2-amino-5-(2-hydroxy-phenyl)-1,3,4-thiadiazole with 4-antipyrincarboxaldehyde.

The Thermal analysis

From the TGA curves recorded for the successive steps in the decomposition process of these ligand and complexes it was possible to determine the following characteristic thermal parameters for each reaction step: Initial temperature point of decomposition (T_i): the point at which TG curve starts deviating from its base line. Final temperature point of decomposition (T_f): the point at which TG curve returns to its base line. Peak temperature, i.e. temperature of maximum rate of weight loss: the point obtained from the intersection of tangents to the peak of TG curve. Mass loss at the decomposition step (D_m): it is the amount of mass that extends from the point T_i up to the reaction end point T_f on the TG curve, i.e. the magnitude of the ordinate of a TG curve. The material released at each step of the decomposition is identified by attributing the mass loss (D_m) at a

given step to the component of similar weight calculated from the molecular formula of the investigated complexes, comparing that with literatures of relevant compounds considering their temperature. This may assist in identifying the mechanism of reaction in the decomposition steps taking place in the complexes under study. Activation energy (E) of the composition step: the integral method used is the Coats-Redfern equation[21-23]. for reaction order $n \neq 1$ or $n = 2$, which when linearised for a correctly chosen n yields the activation energy from the slop;

$$\log \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \log \frac{ZR}{qE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \dots\dots\dots n \neq 1$$

$$\log \left[\frac{-\log(1-\alpha)}{T^2} \right] = \log \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{2.303RT} \dots\dots\dots n = 1$$

$\Delta S^* = 2.303R[\text{Log}(Ah/K T_{\max})]$, $\Delta H^* = E - RT_{\max}$, $\Delta G^* = \Delta H^* - T_{\max} \Delta S^*$ where: α = fraction of weight loss, T = temperature ($^{\circ}\text{K}$), n = order of reaction, A or Z = pre-exponential factor, R = molar gas constant, E = activation energy and q = heating rate. Order of reaction (n): it is the one for which a plot of the Coats-Redfern expression gives the best straight line among various trial values of n that are examined relative to that estimated by the Horovitz-Metzger method[24,25].

Experimental

All used chemicals were of reagent grade (supplied by either sigma Aldrich or fluka) and used as supplied. The FTIR spectra in the range (4000-400) cm^{-1} cut were recorded as KBr disc on FTIR.4200 Jasco Spectrophotometer. The Uv-visible spectra were measured in ethanol using Shimadzu Uv-vis. 160 A-Ultra-violet Spectrophotometer in the range (200-1000) nm. Magnetic susceptibility measurement for complexes were obtained at room temperature using (Magnetic Susceptibility Balance) Jhonson Matthey catalytic systems division. Gallencamp M.F.B600.010 F melting point apparatus were used to measure the melting point of all the prepared compounds. Elemental microanalysis was carried out using CHNOS elemental analyzer model 5500 Carlo-Erba instruments (Italy).

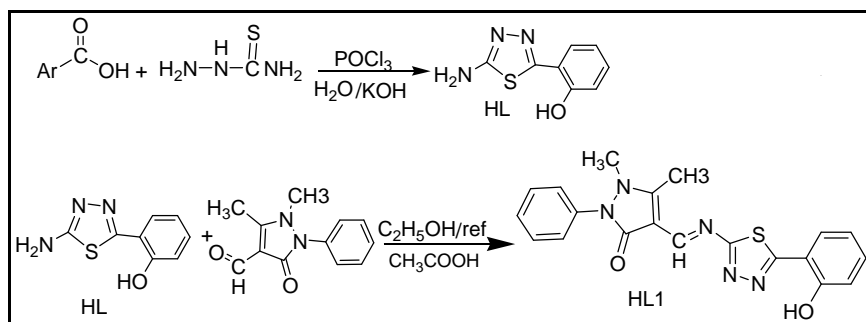
1- Synthesis of [2-amino-5-(2-hydroxy-phenyl-1,3,4-thiadiazole] [HL]

A mixture of benzoic acid (0.1 mol 12.2g), thiosemicarbazide (0.1 mol 9.1 g) and (40ml) of POCl_3 was heated gently for 3 hours. After cooling than (250 ml) of water was added then refluxed for 4 hours. The mixture was cooled filtered and the filtrate neutralized with KOH and recrystallization solvent ethanol. M.p. yield, C.H.N.S analysis in Table (1).

2-4-[5-(2-hydroxy - phenyl) - [1, 3, 4 - thiadiazol - 2 - ylimino methyl] - 1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one [HL1]

Method(1) A mixture of equimolar amounts (0.09 mol) of appropriate (4-antipyrincarboxaldehyde) and the (2-amino-5-(2-hydroxy-phenyl-1,3,4-thiadiazole), in absolute ethanol (15 ml) with (2) drops of glacial acetic acid was refluxed 3- hours. The reaction mixture was then allowed to cool at room temperature, and the precipitate was filtered and dried, recrystallized from ethanol to give yellow powder.

Method(2): A mixture of equimolar amounts (0.09 mol) of appropriate (4-antipyrincarboxaldehyde) and the (2-amino-5-(2-hydroxy-phenyl-1,3,4-thiadiazole), were ground with a mortar, mixed, dried and subjected to microwave irradiation 700W for (30) minutes, after completion the reaction the mixture was cooled to room temperature and the obtained solid was recrystallized twice from absolute ethanol, some of physical data for these four compounds are listed in table. Yield, C.H.N.S analysis in Table (1).



(Scheme-1) Synthesis of Schiff base ligand

Preparation of complexes

Method(1) :Addition of ethanol solution of the hydrated metal chloride Ni(II), Co(II) and Cu(II) to an ethanol solution of (HL1) in 1:1 (ligand : metal) molar ratios. After stirring for 2 hours with heating 50 °C, crystalline colored precipitates formed then cooling at room temperature, the resulting solids were filtered off, washed with distilled water, dried and recrystallized from ethanol and dried at 50 °C

Method(2) : Addition of ethanol solution of the hydrated metal chloride Ni(II), Zn(II) and Cu(II) to an ethanol solution of (HL1) in 1:1 (ligand : metal) molar ratios. The reaction mixture was placed in ultrasonic bath for 30 mints crystalline colored precipitates formed when cooled at room temperature, the resulting solids were filtered off, washed with distilled water, dried and recrystallized from ethanol and dried at 50 °C. Yield, C.H.N.S analysis in (Table-1).

(Table-1) Analysis data of prepared compounds

Molecular formula (Color)	Yield%	M	% element analysis found(calculated)			
			N	H	C	S
HL C ₈ H ₇ N ₃ OS	76	-	(49.37) 49.51	(3.65) 3.55	(21.75) 21.69	(16.59) 16.63
HL1 C ₂₀ H ₁₇ N ₅ O ₂ S	67	-	(61.37)	(4.38)	(17.89)	(8.19)
[Ni ₂ (HL1) ₂ 4H ₂ O] ⁺⁴	58	(12.07) 12.03	(14.41) 14.39	(4.35) 4.33	(49.41) 49.44	(6.60) 6.57
[Co ₂ (HL1) ₂ 4H ₂ O] ⁺⁴	75	(12.12) 12.15	(14.40) 14.44	(4.35) 4.31	(49.39) 49.42	(6.59) 6.56
[Cu ₂ (HL1) ₂ 4H ₂ O] ⁺⁴	79	(12.94) 12.89	(14.26) 14.21	(4.32) 4.31	(48.92) 448.95	(6.53) 6.55

Result and discussion

(Table-2) shows the decomposition point, color and electronic Absorption bands for ligand and complexes. The bands are classified into three distinct groups: The intermolecular transitions appear in the region, charge transfer from ligand to metal, and d-d transitions appear in the visible region show in. These transitions are assigned in relevant to the structures of complexes, and also Uv-viss spectrum of compound shown in (Fig-1).

1-[2-amino-5-(2-hydroxy-phenyl-1,3,4-thiadiazole)] [HL]

The reaction of thiosemicarbazide with benzoic acid in presence of phosphorus oxychloride afforded 2 – amino – 5 – phenyl-1, 3, 4 - thiadiazole (P. Coudert, (1994). The structural assignment of the product was based on it's melting point and spectral (FT-IR, ¹H-NMR and Uv/Vis.) data. Besides the C.H.N.S. analysis (Table-1). The FT-IR spectrum of compound (HL) (Fig-2) exhibited significant two band in the range (3396–3283)cm⁻¹ which could be attributed to asymmetric and symmetric stretching vibrations of NH₂ group band in the (3101) stretching vibrations of (OH). Besides this, band at about (1626 cm⁻¹) due to cyclic (C=N) stretching is also observed. Bands at (1518 cm⁻¹) and (1484cm⁻¹) are due to the (N-H) bending and (C-N) stretching vibrations, respectively (Silverstein, R.M. Bassler, G.C. and Movril, T.C., 1981).

¹H-NMR spectrum of compound (HL) shows the following characteristic chemical shifts (DMSO-d₆, ppm). The five aromatic protons appear at: (δ 7.40-7.94) were due to aromatic protons. Amino protons (NH₂) absorbed at (δ 3.38). Furthermore, the small peak at (δ 2.5) was due to DMSO.

(Table-2) Some physical data of electronic spectra for ligand and complexes in ethanol.

Symbol	Dec. Point °C	Conductivity ohm ⁻¹ cm ² mol ⁻¹	Magnetic Moment (B.M)	Color	Absorption Bands (nm)	Assigned Transition
HL	238	-	-	White-pink	295	$\pi \rightarrow \pi^*$
					320	$n \rightarrow \pi^*$
HL1	280	-	-	Green	250	$\pi \rightarrow \pi^*$
					370	$n \rightarrow \pi^*$
Co(II)	285	12.34	4.47	Red blue	225	$\pi \rightarrow \pi^*$
					243	$n \rightarrow \pi^*$
					320	Charge Transfer
					380	${}^4T_{1g}^{(F)} \rightarrow {}^4t_{1g}^{(P)}$
Ni(II)	310	15	2.9	Pale green	910	${}^4T_{1g} \rightarrow {}^4A_{2g}$
					235	$\pi \rightarrow \pi^*$
					295	$n \rightarrow \pi^*$
					320	Charge Transfer
					633	${}^3A_{2g} \rightarrow {}^3t_{1g}^{(P)}$
Cu(II)	320	11.8	1.84	Dark Green	960	${}^3A_{2g} \rightarrow {}^3t_{1g}^{(F)}$
					230	$\pi \rightarrow \pi^*$
					295	$n \rightarrow \pi^*$
					360	Charge Transfer
					675	${}^2E_g \rightarrow {}^2T_{2g}$
					595	${}^4A_{2g} \rightarrow {}^4t_{1g}$
655	${}^4A_{2g}^{(F)} \rightarrow {}^4t_{1g}^{(P)}$					

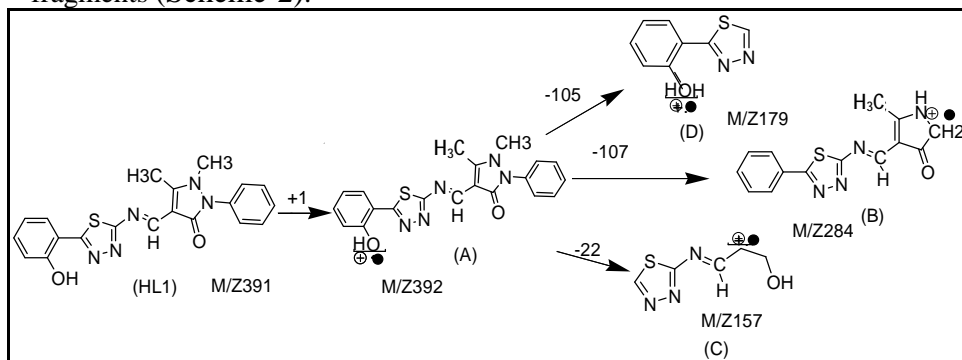
2)4-[5-(2-hydroxy-phenyl)- [1, 3, 4- thiadiazol – 2 - ylimino methyl]-1,5 dimethyl -2-phenyl-1,2-dihydro-pyrazol-3-one [HL1]

The FT-IR spectra (Fig-3), show the disappearance of the two absorption bands due to (-NH₂) stretching of amino thiadiazole [HL] showed all the suggested bonds for olefinic (C-H), (C=C) aromatic, endocyclic (C=N) and exocyclic imine group. Stretching vibrations in addition to out of plane bending of substituted aromatic ring. All the prepared compounds (Schiff bases) exhibited the stretching band near the region (1213-1253) cm⁻¹ this is due to (=N-N=C-) cyclic group; 3429 cm⁻¹ (ν OH stretching of alcohol), 1651cm⁻¹ (ν C=N Stretching of imine), 1554 cm⁻¹, 1498 cm⁻¹ (Characteristic bands of pyrazolone ring) 1432 cm⁻¹, 1267 cm⁻¹ (Characteristic bands of thiazole ring), 1142 cm⁻¹ (ν C-O Stretching of alcohol).

All the spectral data for other compounds are listed in (Table-3).

$^1\text{H-NMR}$ spectrum of compounds [HL1], Fig (4), shows the following characteristic chemical shift, ($\text{CDCl}_3\text{-D}_6$) ppm. The methyl protons resonate at [$\delta= 1.5, 2.4,$] (s, 3H, CH_3), OH proton resonates at ($\delta 3.4$), five aromatic ring protons of phenyl and four aromatic ring protons appeared at ($\delta 6.9 - 7.6$) ppm, proton C appears at ($\delta 7.8$) Furthermore, the signal at ($\delta 8.8$) attributed to ($\text{CH}=\text{N}$) proton.

(Fig-5) The positive ion mass spectral analysis of (HL1) MS observes at m/z 392.0 ($\text{M}+1$) (Fig-5), confirms the theoretical molecular weight i.e. 391.11., The series of peaks in the table 2 may be assigned to various fragments (Scheme-2).



Scheme. 2

Infrared spectral analysis of metal complexes

The infrared spectra of the ligands show $\nu\text{O-H}$ (weakly H-bonded) at 3429cm^{-1} . The absence of this band in all the metal complexes indicates the removal of proton of hydroxyl group of benzene ring during the chelation. The FT-IR spectra (Fig-6,7) of complexes are further supported by the shift of C-O frequency from 1342cm^{-1} (in ligand) to the higher frequency 1379cm^{-1} (in complexes)[26-28]. The sharp intense band at 1651cm^{-1} in the ligands can be assigned to $\nu\text{C}=\text{N}$ (azomethine). A downward shift ($\Delta\nu = 10\text{-}18\text{cm}^{-1}$) in $\nu\text{C}=\text{N}$ (azomethine) is observed upon coordination indicating that the nitrogen of azomethine group is involved in coordination. All the complexes show broad band in the region ($3285\text{-}3378$) cm^{-1} which may be assigned to $\nu\text{O-H}$ of coordinated water[29-31]. To account for the octahedral stereochemistry of the metal complexes, the coordination of two water molecules is expected.

The bands at 476cm^{-1} in Co(II) complexes, 498cm^{-1} in Ni(II) complexes and 514cm^{-1} in Cu(II) complexes may be due to metal-nitrogen stretching vibration[19,20]. All the metal complexes involved in coordination. In the free ligand, the band at 1606cm^{-1} is assigned to the stretching of $\text{C}=\text{N}$ (thiazole ring). on complexation, this band is shifted to a lower frequency

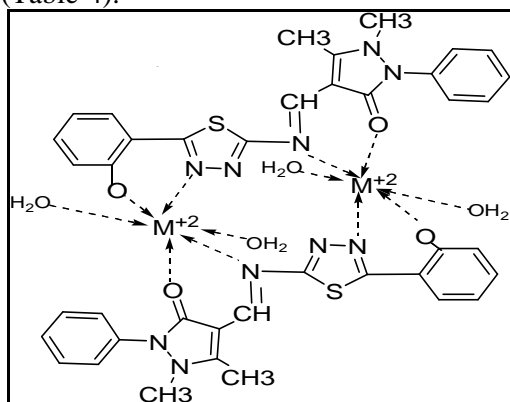
region. This shift is probably due to the lowering of bond order of the carbon-nitrogen bond resulted from complexation of the metal to the ligand through nitrogen in ν C=N compared to its respective ligands. This suggests that the nitrogen atom of the ring has not participated in the chelation. However, in water containing chelates, this band is observed as a broad with structure and this may be due to coupling of the bending mode of coordinated water molecules with metal[32-35].

Table (3) Infrared data of Ligand and its metal complexes (cm^{-1})

Symbol	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N}=\text{N}-\text{C})$	$\nu(\text{M}-\text{O})$	$\nu(\text{O}-\text{H}) \text{H}_2\text{O}$	$\nu(\text{O}-\text{H})$	$\nu(\text{M}-\text{N})$
HL1	1651(s)	1606	1219-1253	-	-	3429	-
Co(II)	1662(s)	1521	1238-1311	425(s)	3292	-	476(s)
Ni(II)	1661(s)	1593	1585	442(s)	3285	-	498(s)
Cu(II)	1633(s)	1607	1240-1308	481(s)	3378	-	570(s)

Thermal analysis

To understand thermal decomposition process, Schiff and its metal complexes were examined by thermo gravimetric analysis in the temperature range of 35–700 °C. The obtained thermo analytical results from TGA curves (Fig-8) for all these compounds are given in (Table-4). The decomposition was completed at 693 °C for all the complexes. The data from the thermo gravimetric analyses indicated that the decomposition of the complexes and the ligand proceeds in (two – four) steps. The comparison of ligand and the complexes shows that the complexes. the first step of decomposition was started at (250 °C) and completed at 693 °C for all the complexes. The final stage of the thermal decomposition of given metal oxides mixture formed above 598 °C for the metal[22]. (Fig-9) shows Coats-Redfern pattern of Ligand and complexes. The thermal data have been analyzed for thermodynamic parameters by using Coats-Redfern[36,37] (Table-4).



Scheme the structure of complex ML :
M=Cu(II),Ni(II) and Co(II)

(Table-4) Thermodynamic parameters of the ligand and metal complexes

Sample (step)	T.range °C	N	R ²	T _{max} °K	E _a K.J mol ⁻¹	Δ H [*] KJ mol ⁻¹	ZSec ⁻¹ x10 ⁵	Δ S [*] J mol ⁻¹ K ⁻¹	Δ G [*] KJ mol ⁻¹
L ₁ (1)	37-390	1	0.99	535	13.1101	8.661971	1.4969	-342.153	192.0284
L ₁ (2)	390-598	1	0.99	798.51	-6.0569	-12.6845	5.84	-353.297	269.4266
Co(1)	37-108	1	0.99	388	91.198	88.393	2.8	-84.2368	116.8635
Co(2)	108-295	0.9	0.99	479.08	29.024	25.0477	9.21	-287.826	162.939
Co(3)	395-479	0.9	0.99	675	-8.0246	-13.6271	5.57	-352.282	224.1636
Co(4)	479-700	0.9	0.99	792.94	-9.98489	-16.5663	3.98	-356.422	266.0552
Ni(1)	37-115	0.9	0.99	342	30.5012	27.6626	0.4155	-272.491	120.8546
Ni(2)	115-289	0.9	0.99	473.3	33.2497	29.3213	0.2126	-285.063	164.242
Ni(3)	289-700	0.9	0.99	669.2	12.19515	-10.843	9.05	-348.184	222.1616
Cu(1)	37-216	0.9	0.99	423	16.49479	12.98389	7.68	-326.581	151.1275
Cu(2)	216-389	0.9	1	554	54.214	49.616	0.5357	-255.25	191.025
Cu(3)	389-700	0.9	0.99	726.35	-8.14044	-14.1691	4.91	-353.949	242.9219

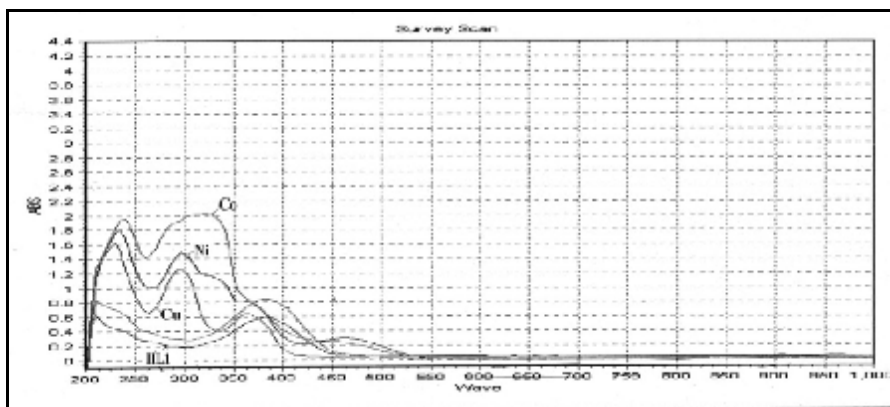
Biological Activity

With a view to explore the possibility of obtaining biologically useful complexes that contain 1,3,4- thiadizole and pyrazolone ring system, such biological activity prompt us to prepare some new series containing the above mentioned units. The antimicrobial activity of these compounds was determined by the agar diffusion method using *Staphylococcus aureus*, *Escherishia coli*, *Pseudononas aeruginosa* and *Cndida albicans*[38,39]. In this method a standard 5mm diameter sterilized filter paper disc impregnated with the compound (1 mg per 1 ml dimethyl sulfoxide) was placed on an agar plate seeded with the test organism. The plates were incubated for 24 hours at 37 °C. The zone of formed inhibition was measured in mm and are represented by (+), (++) and (+++) depending upon the diameter and clarity, (Table-5).The preliminary screening result reveal that compound contained thiadizole and pyrazolone complexes exhibits highest antibacterial activity against *Escherishia coli*[40,41].

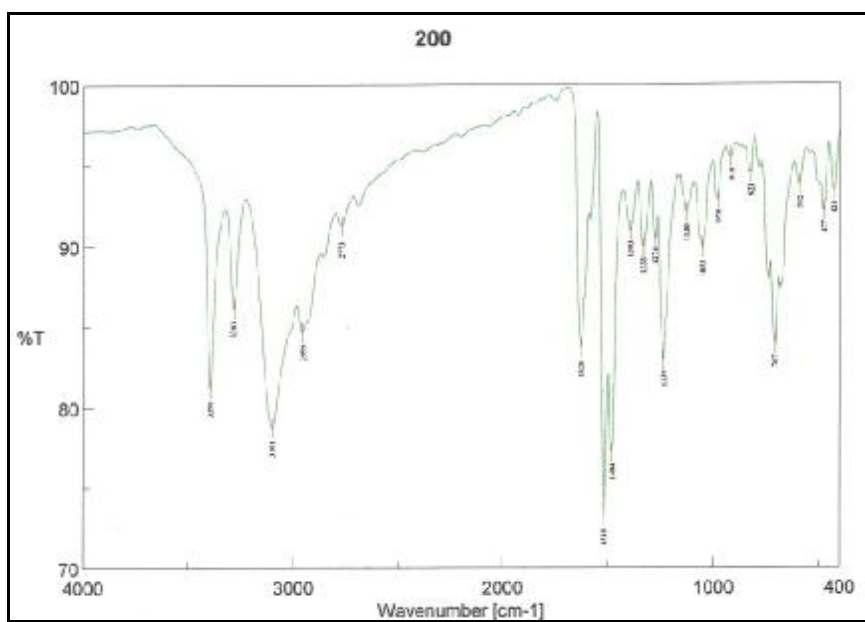
(Table-5) Antibacterial activity of the prepared compounds.

Symbol	Staphylococcus aureus	Escherishia coli	Pseudononas aeruginosa	Cndida albicans
HL1	-	+	-	-
Co(II)	-	+++	+	+
Ni(II)	+	+++	-	+
Cu(II)	+	+++	+	+

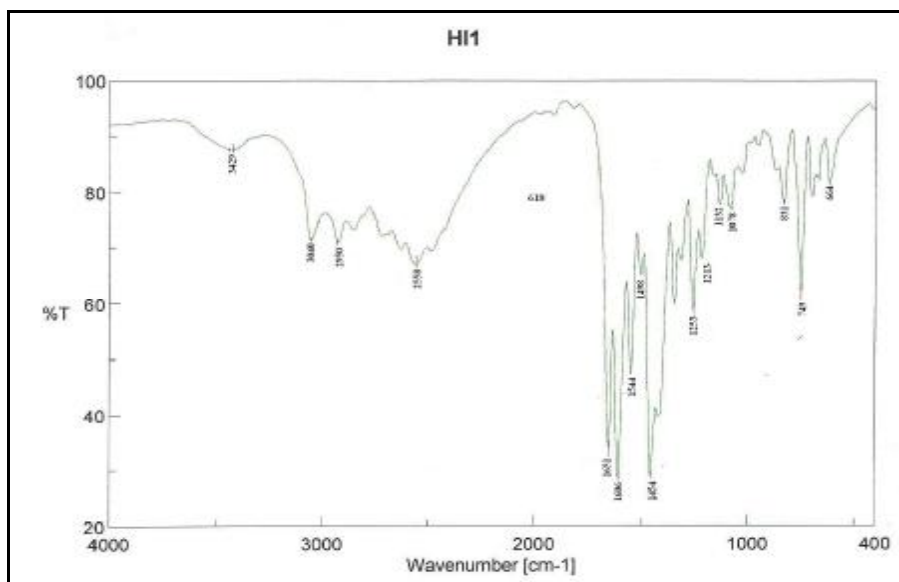
Note (-) = no inhibition, (+) = (5-10) mm, (++)=(11-20) mm, (+++) = more than (20)mm



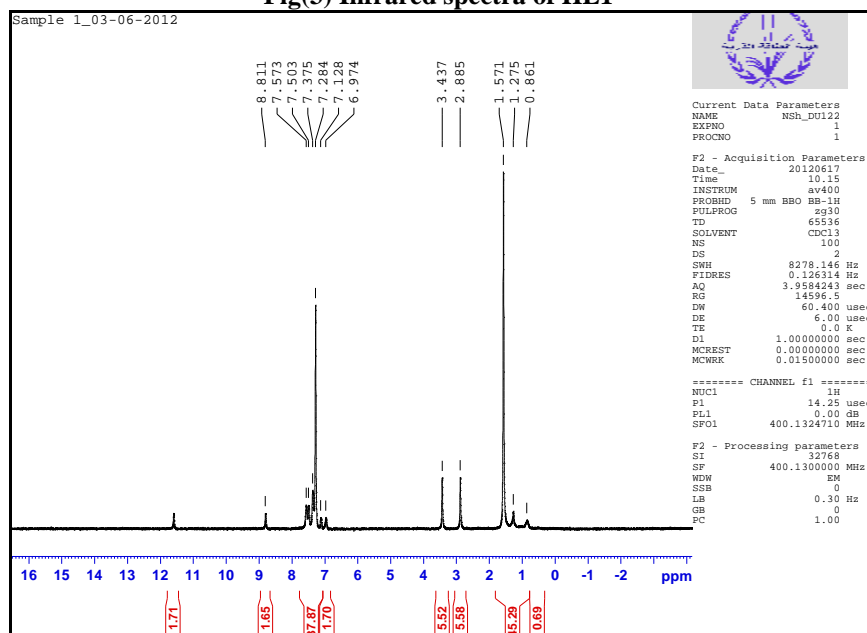
Fig(1)Uv-vis of ligand and complexes



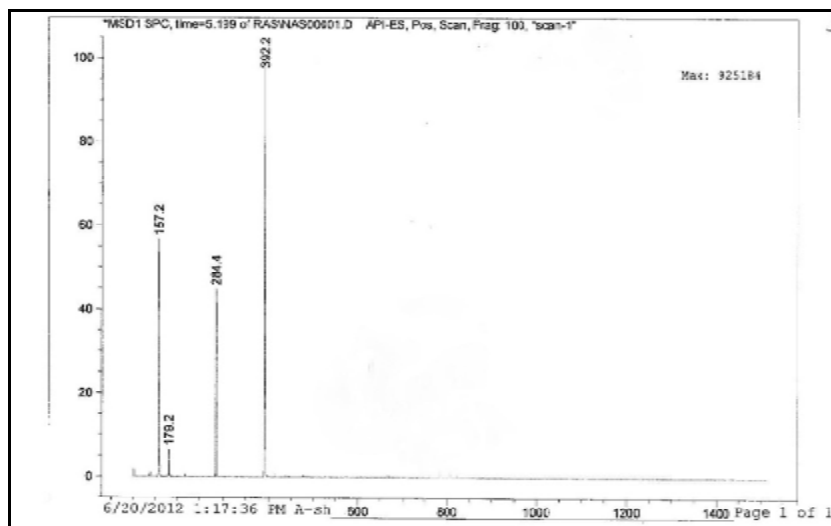
Fig(2) Infrared spectra of HL



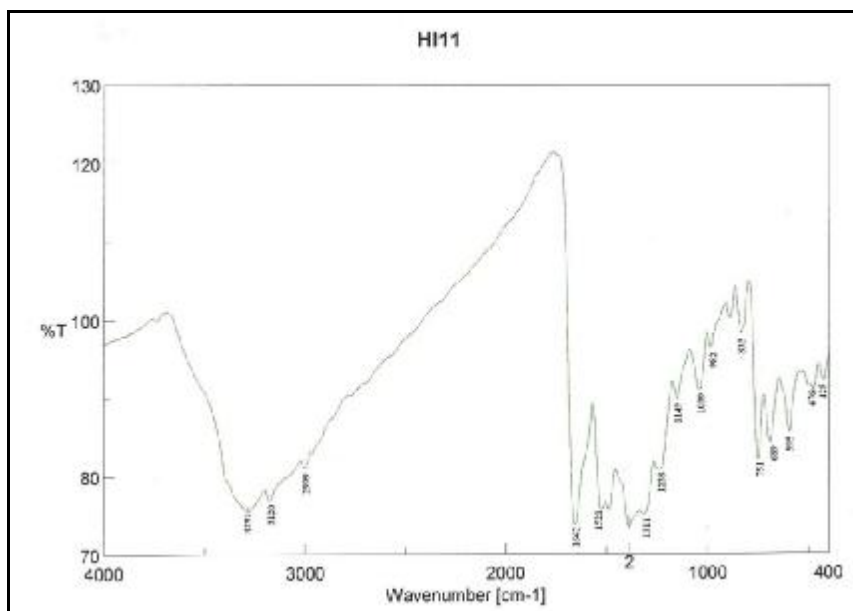
Fig(3) Infrared spectra of HL1



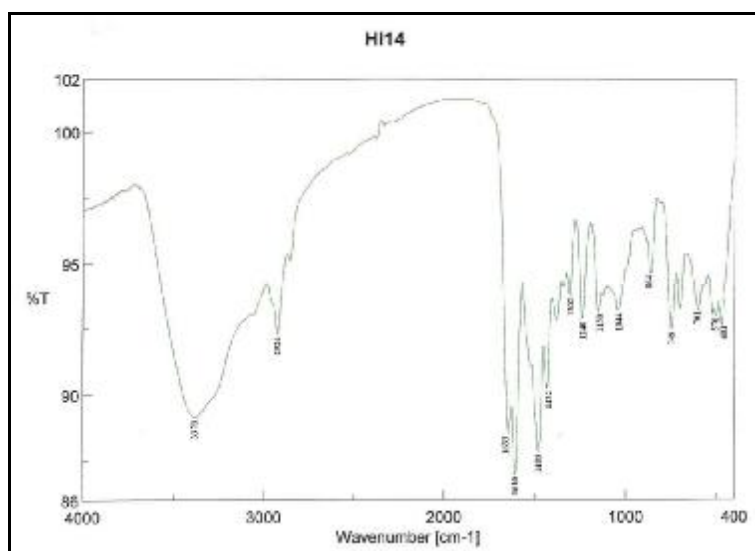
Fig(4) ¹H NMR spectra of HL1



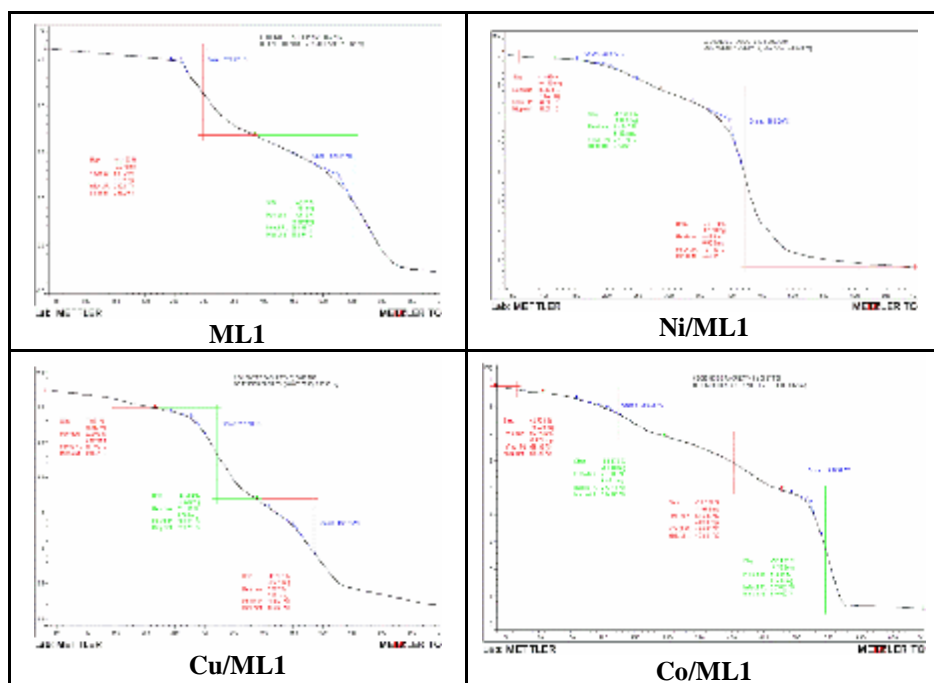
Fig(5) Electron impact mass spectrum of HL1



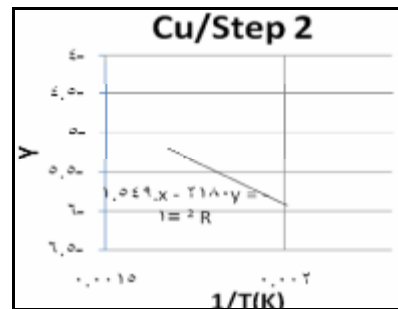
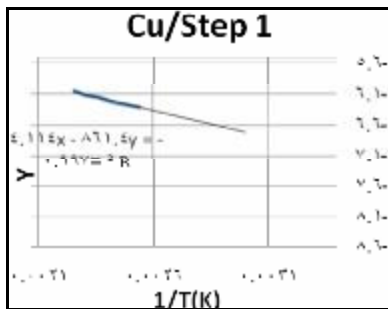
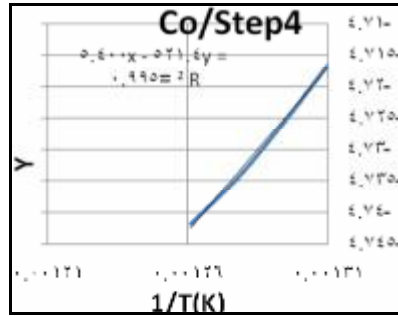
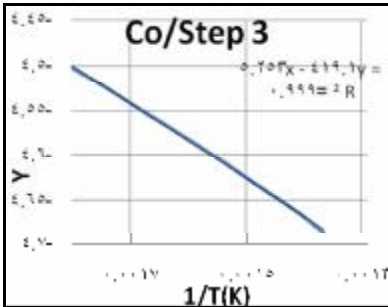
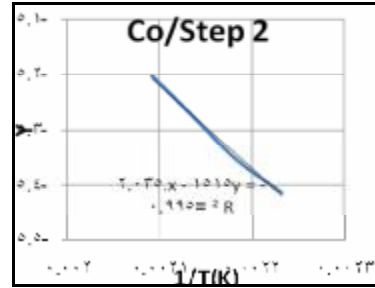
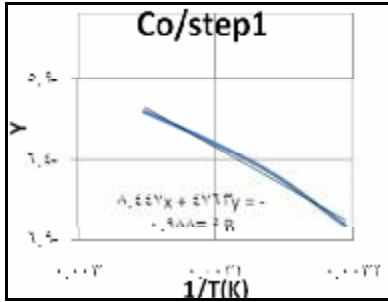
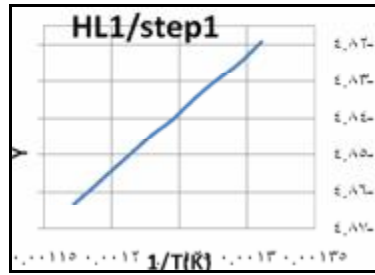
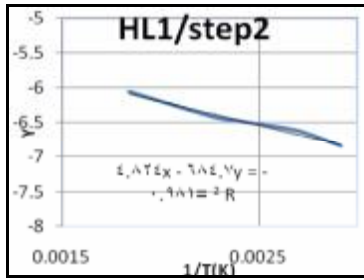
Fig(6) Infrared spectra of Cu complexes

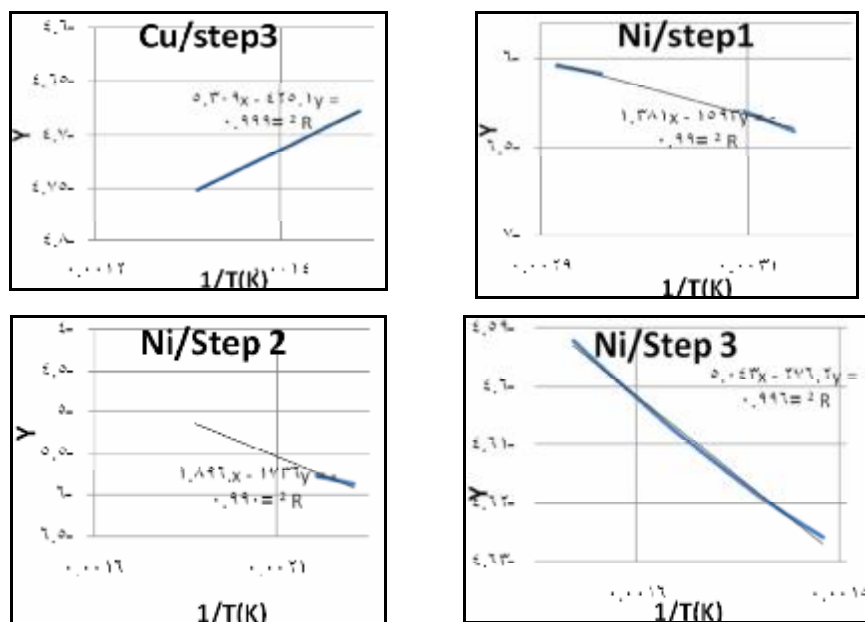


Fig(7) Infrared spectra of Cu complexes



Fig(8) TGA of Ligand and complexes





Fig(9) Coats-Redfern pattern of Ligand and complexes

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