Synthesis And Characterization Of Some New Metals Complexes Of [1-benzoyl-3-(carbonyl Pyridin-2-yl)thiourea]

تحضير وتشخيص بعض المعقدات الفلزية الجديدة مع (١ - بنزويل -٣ - كربونيل بريدنايل)

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Abstract

A new ligand [1-benzoyl-3-(carbonyl Pyridin-2-yl)thiourea](HL) was synthesized by reaction of benzoylisothiocyanate with Nicotinamidein molar ratio(l:l).The ligand was characterized by elemental microanalysis C.H.N.S, FT-IR, UV-Vis and $^{1}H,^{13}C$-NMR spectra.The complexes of the bivalent ions (M^{+2} =Co, Ni, Cu, Pd, Cd andHg) have been prepared and characterized by C.H.N.S, FT-IR , UV-Vis spectra, conductivity measurements, magnetic susceptibility and atomic

absorption. from obtained results the molecular formula of all prepared complexes were $[M(HL)_2Cl_2]$ the proposedgeometrical structure for all complexes were octahedral, except palladium complex is have square planer.

Key Word: ligand, thiourea, benzoylisothiocyanate, Nicotinamide, complexes.

Introduction

In the recent years, thiourea derivatives have gained extensive applications in medicine, agriculture, and also as ligands in coordination chemistry[1],because benzoyl thioureas have suitable C=O and C=S function groups, they can be considered as useful chelating agents due to their ability to encapsulate into their coordinating moiety metal ions[2].

Specialized literature reveals that thiourea derivatives show a broad spectrum of biological activities. The thiourea skeleton can be effectively used to prepare a large number of new compounds with biological activities such as antiviral[3], anticancer [4], anti-inflammatory[5], antimicrobial[6], anticonvulsant[7], and anti-helmintic activities[8].

Thiourea derivatives are used as corrosion inhibitors[9], and as intermediates to obtain a great variety of heterocyclic compounds[10].

Although antibiotics have saved countless millions of lives, over the last decades, the emergence of antimicrobial resistance has limited their efficiency, becoming a serious global health problem thatrequires the development of new antimicrobial agents effective against pathogenic microorganisms resistant to currently available treatments[11].A distinguish biological activity was recorded for most investigated complexes especially with the presence of N, S and O heteroatom's[12,13].

Experimental

Chemicals: All regents used were annular or chemically pure grade by (BHD),Merk and Fluka. Metal salts ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $PdCl_2$,$CdCl_2.H_2O$ and $HgCl_2$), benzoyl chloride, ammonium thiocyanate , Nicotinamide, dimethyl sulphoxide, ethanol, acetone.

Instruments : ^1H and^{13}C–NMR was recorded using Ultra Shield 300 MH_zSwitzerl and atUniversity of Al al-Bayt, Jordan. Melting point was recorded by using Stuart- melting point apparatus. FT-IR spectra were recorded as KBr and CsI disc using 3800 Shimadzu in the range of (4000-400 and 400-200)cm^{-1}. Electronic spectra were obtained using UV-160 Shimadzu spectrophotometer at 25 ℃ for 10^{-3}M solution DMSO with 1.000 ± 0.001cm matched quartz cell. Molar Conductivity was measured at 25 ℃ for 10^{-3}M solution of DMSO by using PhilipsPW.Digital.Elemental micro analyses(C.H.N.S) were performed using AcrloErba 1106elemental analyzer. Magnetic susceptibility measurements were obtained by balance magnetic susceptibilityby model MSB-MKI. Metal contents of the complexes were determined by atomic absorption technique by using Shimadzu (AA680G).

The ligand prepared by two steps(scheme 1)[14]

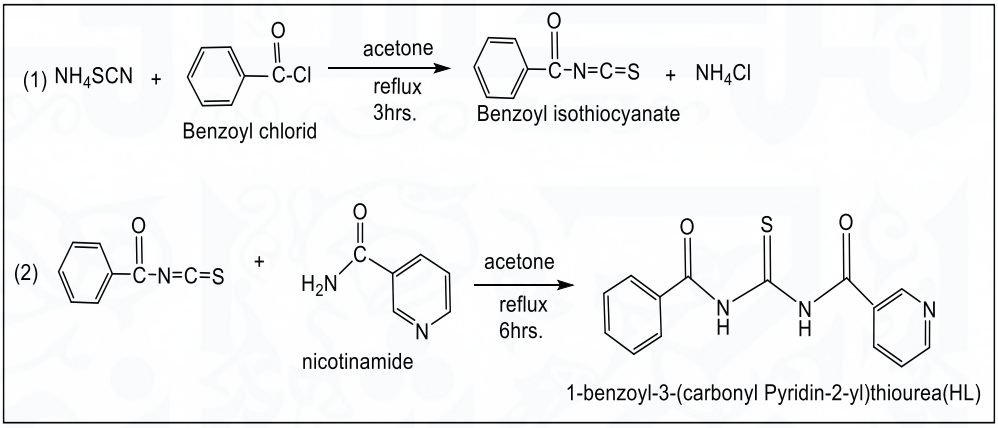
Step(1) Preparation of the (benzoyl isothiocyanate)

Mixture of benzoyl chloride (1.157ml, 0.01mole) and ammonium thiocyanate (0.76g,0.01mole) in (25ml) acetone was refluxed with stirring for (3) hours and then filtered; the filtrate was used for further reaction.

Step(2) Preparation of [1-benzoyl-3-(carbonyl Pyridin-2-yl)thiourea]

(1.22g,0.01mole) of , Nicotinamidein(20ml) acetone were rapidly added to benzoyl isothiocyanate solution and maintaining refluxfor (6) hours. The resulting solid was collected, washed with acetone and recrystallized from ethanol (m.p =242-245^oC), Yield(75%), %C found (58.65)

calc.(58.94), %H found (3.84 calc.(3.89), %N found (14.84) calc.(14.7) and %S found (11.13) calc.(11.24).



Scheme (1) preparation of [1-benzoyl-3-(carbonyl Pyridin-2-yl)thiourea]

Synthesis ligand (HL) complexes[15]

(0.285g, 0.001mole) of the ligand (HL) was dissolved in (20ml) of ethanol containing (0.12gm, 0.002mole) of KOH. A solution of (0.5mmole) metal salt ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $PdCl_2$, $HgCl_2$, $CdCl_2.H_2O$) (0.119g, 0.118g, 0.085g, 0.088g, 0.135g, and 0.1g) respectively, in ethanol was added drop wise to the mixture and precipitate formed immediately. After stirring the mixture at room temperature for (2)hours, washed with (1:1) mixture of water: ethanol, recrystallized from ethanol anddried. Physical properties were given in Table (1).

Results and Discussion

Ligand (HL):

IR spectrum (KBr) $\upsilon(cm^{-1})$: 3244-3124 m(N–H thioamide, sec amide), 3066 m($C–H_{Ar,}$), 1666-1716 m, vs(C=O), 1600-1546 s($C=C_{Ar,\ Py}$), 1485 s($C=N_{py}$), 1385 s(C=S), 1400-1257 vs, m(C–N)[6,16],Fig.(1) showed the FTIR spectrum of (HL).

UV-Visible spectrum in DMSO solution exhibited absorption band at (225nm, 44444cm^{-1}) which is due to

(π→π*) transition, other band appeared at (262nm, 38167cm^{-1}) was expressed at the (n→π*)[16].

^{1}H, ^{13}C NMR spectra (DMSO-d^{6}) δppm: 2.57 (6H, t, CH DMSO), 7.60 (2H, d, CHAr), 7.76 (3H, t, CHAr), 8.126(H, t, CHpy), 8.95,9.07 (2H, d, CHpy), 9.38 (H, s, CHpy),10.83 (1H, s, NH thioamide), 11.40 (1H,s, NH sec amide), ^{13}C NMR: 38.83 (2C, s, DMSO), 123.4 -137.8 (6C, s, CHAr), 144.2-159.2 (6C, s, CHpy), 162.3 (C=S), 176.7, 177.6 (2CONH)[17].

Complexes of the Ligand (HL):

The solid complexes soluble in some common solvent such as dimethylformamide, dimethylsulphoxide and relatively thermally stable. The molar conductivity values of all complexes in DMSO solvent in 10^{-3}M at 25˚C.the atomic absorption measurements for all complexes gave approximated values when its comparison with theoretical values, the values of measured magnetic susceptibility and effective magnetic moment (μeff) for the Co(II), Ni(II), Cu(II)complexesexhibit μeff (4.75, 2.71, 1.7) B.M respectively ,which can be a normal values for high spin octahedral complexes[18],Table (1) includes the physical properties for the ligand and its complexes.

FT-IR Spectra

These spectra exhibited marked difference between bands belonging to the stretching vibration of υ(C=O) in the range between (1697-1708)cm^{-1}shifted lower frequencies by(11-20)cm^{-1} suggesting of the possibility of the coordination of ligand through the oxygen atom at the carbonyl group[14]while the band caused by υ(C=S) appearedbetween (1346-1446)cm^{-1}shifted to higher frequencies by (75-95)cm^{-1}which indicates to the coordination of ligand through the sulfur atom at the thiol group to the central ion[15] Metal-oxygen and metal-sulfur bonds were confirmed by the presence of the stretching vibration of υ(M-O), (M-S)[16] around (432-455), (346- 371)cm^{-1} respectively the spectra of

complexes. scheme (2), table (2) describe the important bands and assignment for all prepared complexes.

Electronic spectra of complexes:

$[Co(HL)_2Cl_2]d^7$ The spectrum of the light purple complex gave five bands at (42553)cm^{-1}, (38167)cm^{-1} attributed to (L.F),(24330)cm^{-1},attributed to (C.T), (15625)cm^{-1} and (12658)cm^{-1}electronic transfer$^4T_1g_{(F)} \longrightarrow {}^4A_2g_{(F)}$and $^4T_1g_{(F)} \longrightarrow {}^4T_2g_{(F)}$transitions respectively[14].

[$Ni(HL)_2Cl_2$] d^8The spectrum of lawn green complex gave six bands at (44444)cm^{-1}, (38167)cm^{-1} attributed to (L.F), (24539)cm^{-1},attributed to (C.T), (15625)cm^{-1} ,(12484)cm^{-1} and (10869)cm^{-1}electronic transfer$^3A_2g \longrightarrow {}^3T_1g_{(P)}$, $^3A_2g \longrightarrow {}^3T_1g_{(F)}$, and $^3A_2g \longrightarrow {}^3T_2g_{(F)}$, transitions respectively, the(B^-) value found tobe (356.6)cm^{-1},while β was equal to (0.34) these are the characteristics for octahedralcomplexes of Ni(II)[14].

$[Cu(HL)_2Cl_2]d^9$The spectrum of turquoise complexgave fourbands at (44843)cm^{-1}, (38167)cm^{-1} attributed to (L.F), (23866)cm^{-1},attributed to (C.T), (12033)cm^{-1}electronic transfer$^2Eg_{(F)} \longrightarrow {}^2T_2g_{(F)}$whichwas a good agreement for distorted octahedral complex forCu(II) ion[16]

$[Pd(HL)_2Cl_2]$The spectrum of brown complexgave fourbands at (44444)cm^{-1}, (38167)cm^{-1} attributed to (L.F), (31847)cm^{-1},attributed to (C.T), (15384)cm^{-1}electronic transfer$^1A_1g_{(F)} \longrightarrow {}^1B_2g_{(F)}$which was a good agreement for square planar complex forPd(II) ion[14]

$[Cd(HL)_2Cl_2]$ and $[Hg(HL)_2Cl_2]$Shows only charge transfer of (M→L) in range (32051-32051)cm^{-1}respectively[14]

Conclusions:-

The ligand was characterized by elemental micro analysis C.H.N.S, FT-IR, UV-Vis and ^1H,^{13}C-NMR spectra. the metal complexes of this ligand were prepared and characterized by FT-IR, UV-Vis spectra, conductivity measurements, magnetic susceptibility and atomic absorption, the proposed

geometrical structure for all complexes were octahedral, when except palladium complex is have square planer.

Table (1) physical properties for free ligand and it's complexes

Comp. No.	M.Wt g/mole	Color	M.P ^{o}C or dec	Found, cal. %)		A_m in DMSO	μ_{eff} (B.M)	Suggested Formula
				M	Cl			
HL	285.32	White	242-245	---	---	3.4	---	---
$[Co(HL)Cl_2]$	700.47	Lavender	294 dec	8.41 (8.26)	10.12 (9.83)	16.4	4.75	Octahedral
$[Ni(HL)Cl_2]$	700.23	lawn green	278-290	8.39 (7.85)	10.13 (9.86)	17	2.71	Octahedral
$[Cu(HL)Cl_2]$	705.08	Turquoise	256dec	9.01 (8.93)	10.06 (9.65)	14	1.7	Distorted Octahedral
$[Pd(HL)Cl_2]$	747.96	Brown	>300	14.23 (13.97)	9.48 (9.32)	13.9	---	Square Planar
$[Cd(HL)Cl_2]$	753.95	White	>300	14.91 (14.53)	9.40 (9.27)	15.3	---	Octahedral
$[Hg(HL)Cl_2]$	842.02	White	186-189	23.82 (23.27)	8.42 (8.28)	10.3	---	Octahedral

dec.=decomposition

Table (2): The characteristic infrared of ligand and its metal Complexes

Comp. No.	IR , (KBr, CsI), cm^{-1}								
	v(NH) 1 2	v(C=O) 1 2	v(C-H) aromatic	v(C=C)	v(C=N)	v(C=S)	v(C-N)	v(M-O)	v(M-S)
HL	3244 m 3124 m	1666 m 1716 vs	3066 m	1600 s 1546 s	1485 s	1346 s	1400 vs 1257 m		
$[Co(HL)Cl_2]$	3402 vs 3194 vs	1670 s 1700 s	3078 m	1604 m 1523 w	1477 m	1446 m	1396 s 1253 w	455 m	346 m
$[Ni(HL)Cl_2]$	3406 m 3194 m	1670 m 1697 m	3078 m	1600 s 1549 m	1477 m	1438 w	1392 vs 1253 w	447 w	353 m
$[Cu(HL)Cl_2]$	3402 vs 3192 vs	1666 m 1705 s	3072 m	1604 s	1481 m	1431 m	1381 vs 1249 w	439 s	361 s
$[Pd(HL)Cl_2]$	3406 s 3192 s	1666 m 1708 s	3066 w	1604 m 1543 m	1465 m	1346m	1381 vs 1253 w	435 m	٣٧١ s
$[Cd(HL)Cl_2]$	3390 vs 3190 vs	1666 s 1706 s	3074 m	1600 s 1550 m	1481 m	1442 m	1396 vs 1261 w	439 m	365 m
$[Hg(HL)Cl_2]$	3367 m 3181 m	1670 m 1702 s	3078 m	1593 w 1570 m	1473 m	1423 m	1393 vs 1267 m	432 s	347 m

s= strong , vs=very strong , w = weak , m=middle

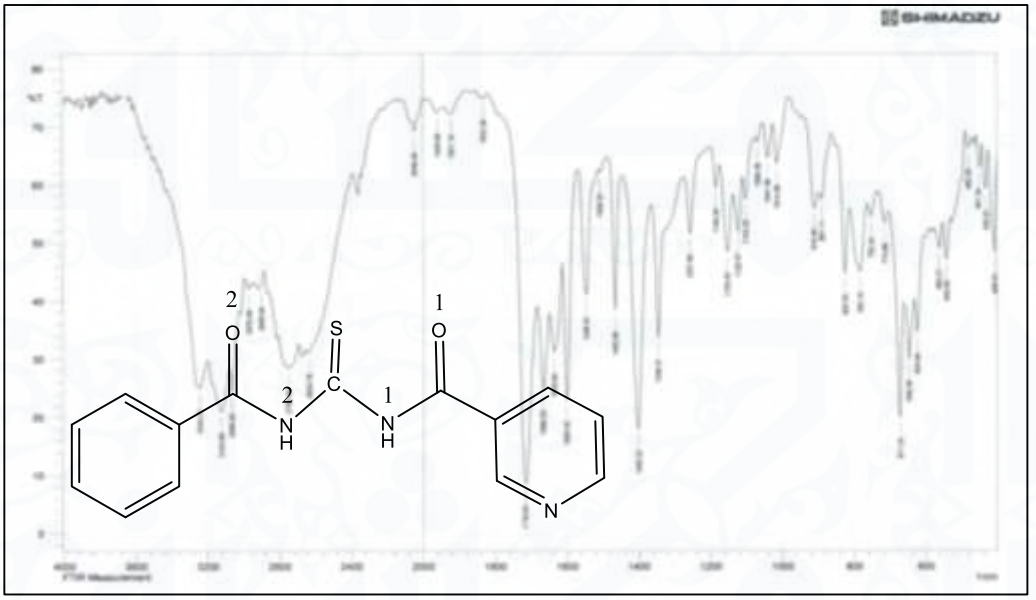


Fig.(1): Infrared spectrum of ligand (HL).

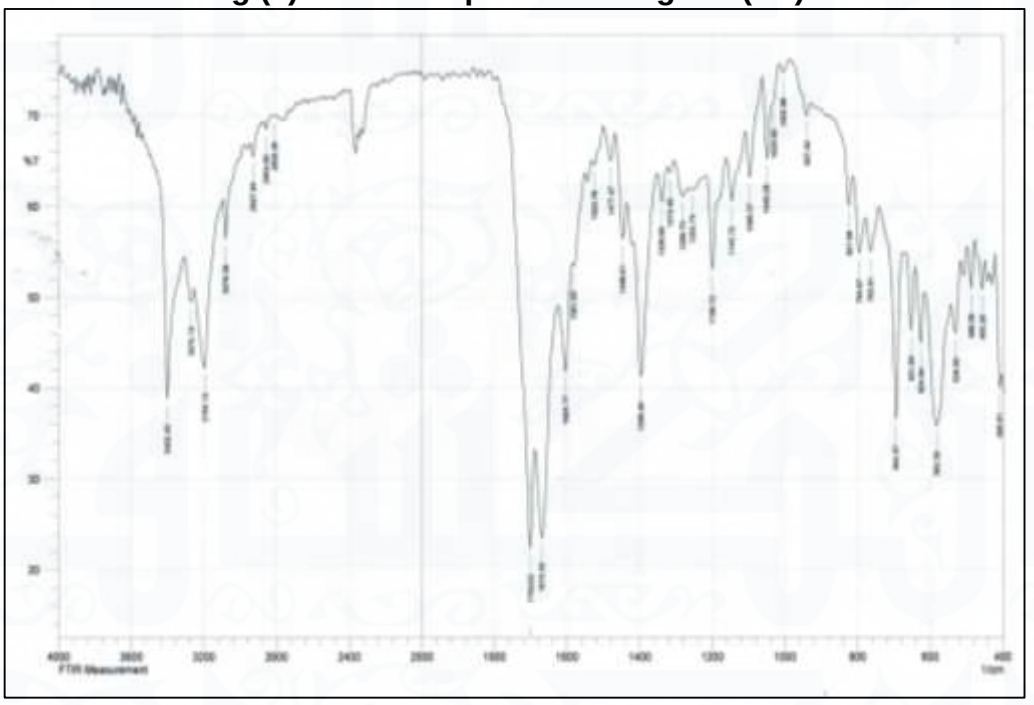


Fig.(2): Infrared spectrum of complex $[Co(HL)_2Cl_2]$

Fig.(3): Infrared spectrum of complex $[Pd(HL)_2Cl_2]$

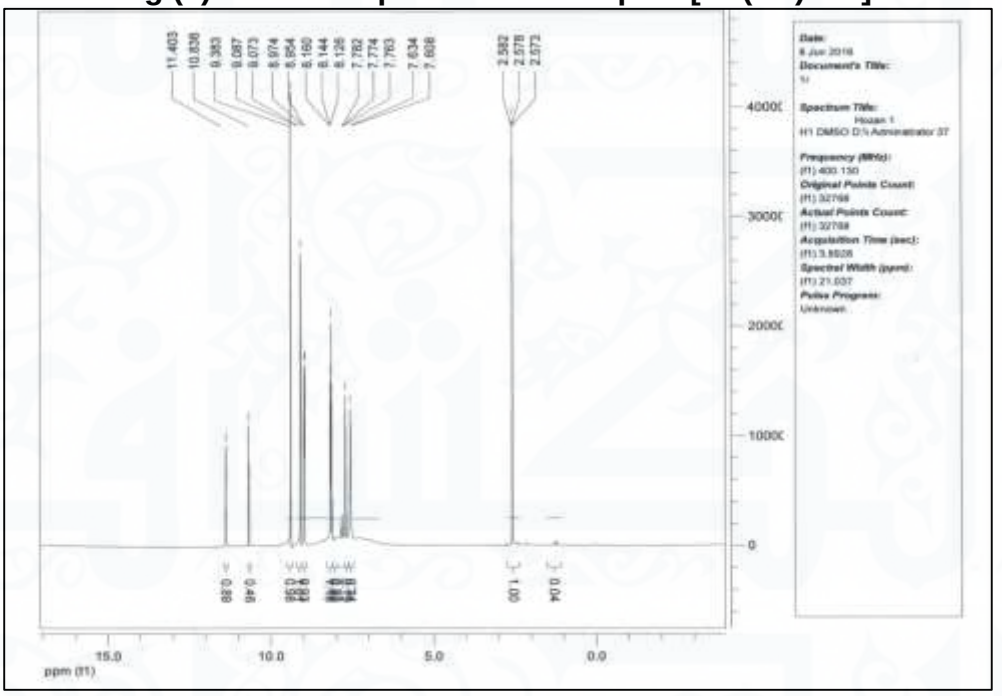


Fig.(4): ^{1}H-NMR spectrum of ligand (HL).

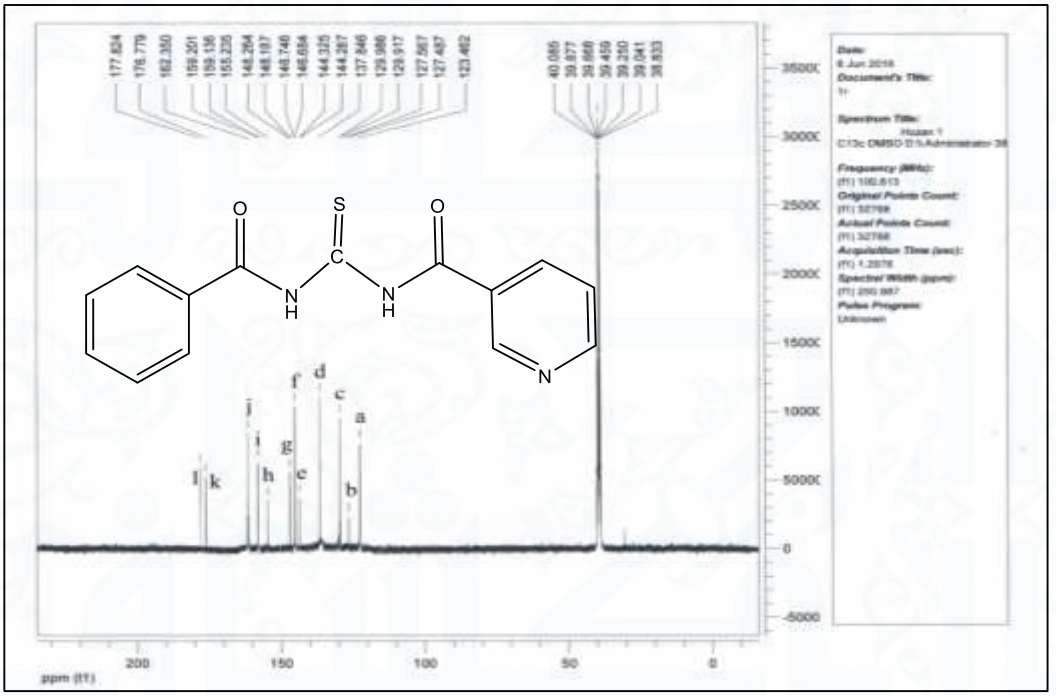


Fig.(5): ^{13}C-NMR spectrum of ligand (HL).

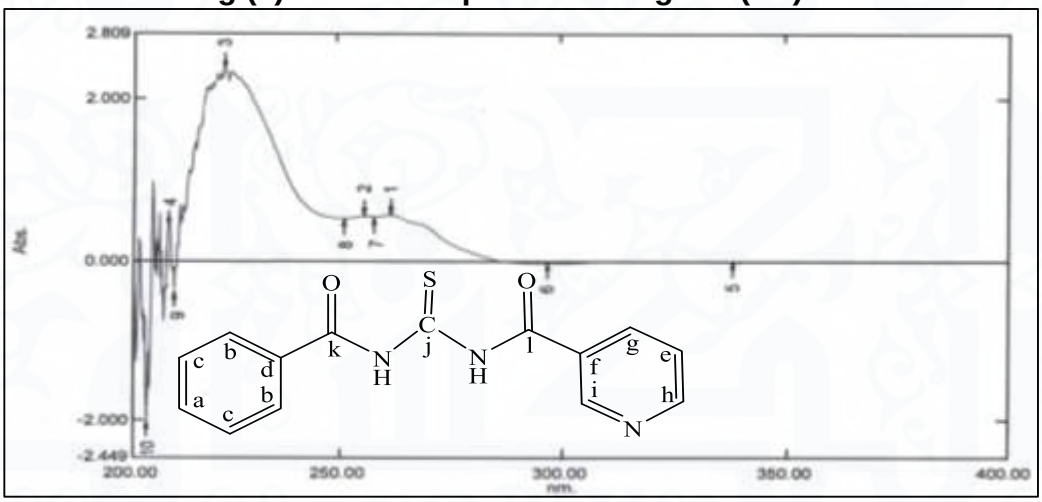


Fig.(6): U.V spectrum of ligand (HL)

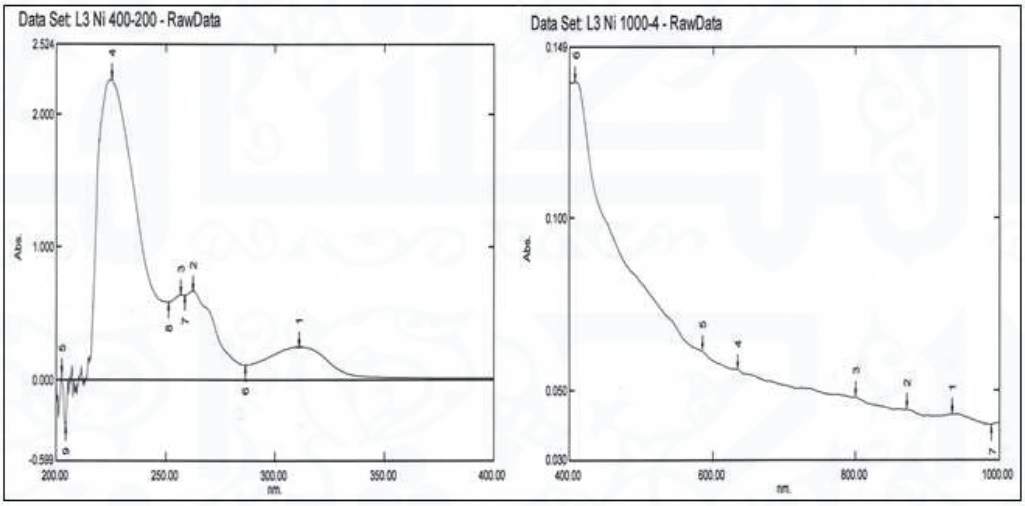


Fig.(٧): U.V spectrum of of complex $[Ni(HL)_2Cl_2]$

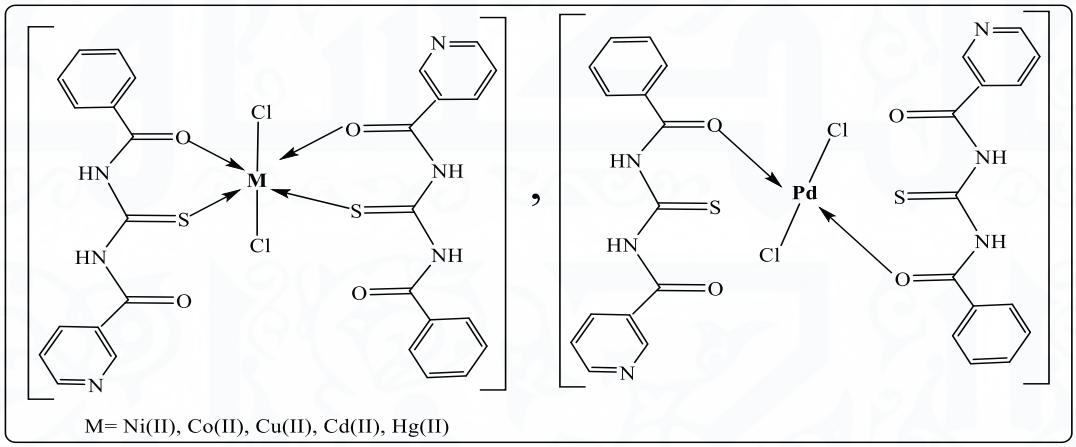


Fig.(8): The proposed chemical structure of complexes

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