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RESEARCH ARTICLE

Synthesis and Characterization of new Schiff base Derived from Benzothiazole with (Salicyldehyde and Saccharin) and Complexes for some Metal Ions (Co, Ni, Cd and Hg)

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Abstract

This research including preparation new derivatives for heterocyclic compounds are (1,3 benzothiazole), process synthesis in us research divided into two major pathways: First , synthesis 2- amino benzothiazole derivatives ethyl 2-aminobenzo[d]thiazole-6-carboxylate (HL).Second pathway ,reaction of salicyldehyde and saccharin with amine group of benzothiazole (HL) produced of Schiff's base compounds(HL_1, HL_2). The compound was characterized by FT-IR, UV-Vis and ^{1}H, ^{13C}-NMR spectra. The complexes of the bivalent ions (M^{+2} =Co, Ni, Cd and Hg) with Schiff bases derived to give ligands (HL_1, HL_2) were prepared and then reacted with metal salts in ethanol as a solvent in (1:2) ratio (M: L). the complexes which have the general formula [M (HL_n) $_{2Cl2}$] when (n=1, 2). Have been prepared and characterized by FT-IR, UV-Vis spectra, conductivity measurements, magnetic susceptibility. The proposed geometrical structures for all complexes were octahedral.

Keywords: *ligand, Benzothiazole, Salicyldehyde, Saccharin, Schiff bases, Complexes.*

Introduction

A heterocyclic compound is one which possesses a cyclic structure with at least two different kinds of hetero atoms in the ring. Nitrogen, Oxygen and Sulfur are the most common heterocyclic compounds are very widely distributed in nature and these are essential to life in various ways [1-3].

Thiazoles are heterocyclic organic compounds which have a five membered ring containing three carbons, one sulphur and one nitrogen atom. Many thiazole derivatives such as sulfathiazole, ritonavir, abafungin, bleomycine and tiazofurin are well known potent biologically active compounds [4-5]. While the Fused heterocyclic compounds are very important compounds partially because of their pharmacological properties which include wide applications in medicinal chemistry [6-8].

Recently, the development of antimicrobial and anticancer therapeutic agents has been paved the way to introduce both thiazole moieties and/or transition metal ions, which can avoid such side effects. Schiff base ligands play a central role as chelating ligands in transition metal coordination chemistry [9-11]. A bimetallic core is versatile at the active site of many metalloenzymes and plays an essential role in biological systems *via* the interplay of a pair of metal ions [12].

A large number of bimetallic Schiff base complexes of different structural types have been synthesized and characterized; these complexes vary in their new applications, of biological activities [13-14].

Experimental

Chemicals

All regents used were annular or chemically pure grade by (BHD), Merk and Fluka. Metal salts ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CdCl_2.H_2O$ and $HgCl_2$), 4-amino ethyl benzoate, glacial acetic acid, potassium thiocyanate, salicyladehyde, Saccharin, acetone, dimethyl sulphoxide, methanol.

Instruments

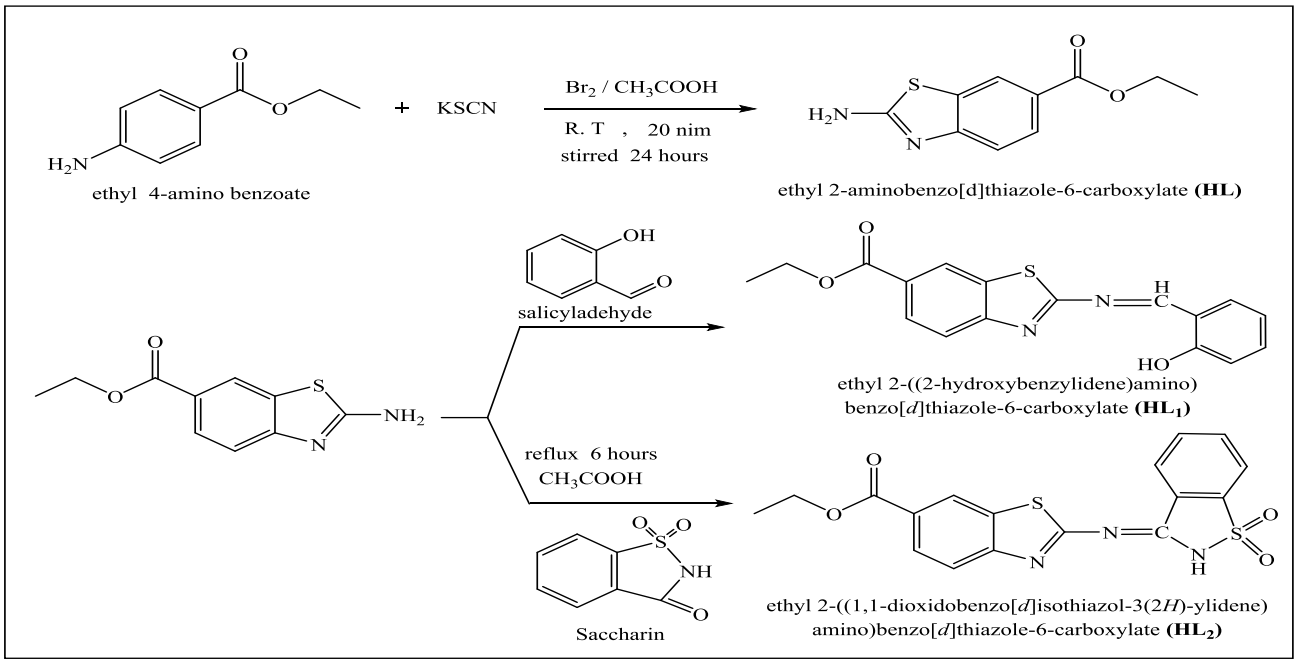
^{1}H and ^{13}C–NMR was recorded using Ultra Shield 300 MH_z Switzerl and at University of Isfahan (Iran). Melting point was recorded by using Stuart- melting point apparatus. FT-IR spectra were recorded as KBr disc using 3800 Shimadzu in the range of (4000-400) cm^{-1}. Electronic spectra were obtained 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 Philips PW. Digital Magnetic susceptibility measurements were obtained by balance magnetic susceptibility by model MSB-MKI.

Synthesis of ethyl 2-aminobenzo[d]thiazole-6-carboxylate (HL)

Ethyl 4-amino benzoate (6.66 g; 0.03 moles), glacial acetic acid (45 ml), and potassium thiocyanate (11.6 g; 0.12 moles) were stirred at room temperature for (20 minutes), and then bromine solution (1.5 ml; 0.03 moles) in glacial acetic acid was added over 20 minutes, during this addition, the temperature rise up to (35°C). The reaction mixture was stirred for 24 hours at room temperature, and then reaction mixture was poured into cold water (500 ml), made alkaline with 50% aqueous ammonia and precipitated solids were filtered out dried and recrystallized. The completion of the reaction was monitored on TLC by using silica gel-G coated plates by using ethyl acetate and petroleum ether (7:3) as the eluent. (m.p =241-245°C), Yield (75%).

Synthesis of Schiff base (HL_1, HL_2)

The Schiff base was prepared by mixing equimolar amounts of (HL) and salicyladehyde in ethanol give (HL_1), and with Saccharin give (HL_2), the mixture was refluxed for about (4 hours). Concentration of the solution was done to reduce it to one-half of its original volume and kept for overnight when deep yellow (HL_1) and green yellowish (HL_2) crystals were formed in the reaction mixture, which were filtered, washed thoroughly with same solvent and recrystallised with ethanol absolute .The Schiff base product obtained (m.p=182-185 °C, 141-143 ° C) produced in (80, 84%) yield was subjected to analysis (Scheme 1) [**14].**



Scheme 1: Preparation of (HL, HL_1, HL_2)

Synthesis Ligand (HL_1, HL_2) Complexes (15)

(0.001mole, 0.326g, 0.387g) of the ligands (HL_1, HL_2) was dissolved in (20ml) of methanol. A solution of (0.5mmole) metal salt ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CdCl_2.H_2O$ and $HgCl_2$) (0.119g, 0.118g, 0.1g and 0.135g) 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 and dried. Physical properties were given in Table (1).

Results and Discussion

Compound (HL)

IR spectrum (KBr) υ(cm^{-1}): 3340-3310 m(N–H $_{asy., sy}$), 1590 m(δN–H), 3095 m, 2900 m(C–$H_{Ar, aliph,}$), 1695 s(C=O), 1670m(C=$N_{thiozole}$), 1600-1470 m (C=C_{Ar}), 1285 m(C-O), 780 m(C-S) Fig:(1) showed the FTIR spectrum of (HL).

^{1}H, ^{13}C NMR spectra (DMSO-d^{6}) δ ppm: 1.30 (3H, m, CH_3), 4.27 (2H, m, CH_2), 7.37 (2H, s, NH_2), 7.39-8.29 (3H, m, $CH_{thiozole}$), ^{13}C NMR: 14.69 (CH_3), 60.79 (CH_2), 117.50-157.24(6CH-Ar), 166.08(C=O), 170.19 (SCN).

Ligand (HL_1)

IR spectrum (KBr) υ(cm^{-1}): 3305 br(O–H), 3100 m, 2900 m(C–$H_{Ar, aliph,}$), 1702 s(C=O), 1615,1650m(C=$N_{schiff\ bases, thiozole}$), 1550-1480 m (C=$C_{Ar}$), 1385 m(C-O), 805 m(C-S) Fig:(2) showed the FTIR spectrum of (HL_1).

UV-Visible spectrum in DMSO solution exhibited absorption band at (224nm, 44642cm^{-1}) which is due to (π→π*) transition, other band appeared at (298nm, 33557cm^{-1}) was expressed at the (n→π*) [16]. Fig :(3) showed the U.V spectrum of (HL_1).

^{1}H, ^{13}C NMR spectra (DMSO-d^{6}) δ ppm: 1.29 (3H, t, CH_3), 4.25 (2H, m, CH_2), 7.36 (2H, m, $CHAr_{thiozole}$), 7.80 – 7.83, 8.27 (4H, m, CH $_{phenyl}$), 7.89 (1H, s, N=CH), 12.23 (1H, s, OH), ^{13}C NMR: 14.70 (CH_3), 40.03 (CH_2), 117.51-131.59 (12CH-Ar), 157.25 (SCN), 166.09 (HC=N), 170.17 (C=O). Fig:(4, 5) showed the ^{1}H, ^{13}C-NMR spectrum of (HL_1).

Ligand (HL_2)

IR spectrum (KBr) υ(cm^{-1}): 3283 m(N–H), 3100 m, 2995 m(C–$H_{Ar, aliph,}$), 1705 s(C=O), 1625,1660m(C=$N_{schiff\ bases, thiozole}$), 1590-1470 m (C=$C_{Ar}$), 1290 m(C-O), 788 m(C-S),1095- 805 m (SO_2 $_{asy., sy}$) Fig:(6) showed the FTIR spectrum of (HL_2).

UV-Visible spectrum in DMSO solution exhibited absorption band at (222nm, 45045cm^{-1}) which is due to (π→π*) transition, other band appeared at (299nm, 33444cm^{-1}) was expressed at the (n→π*)[16]. Fig :(7) showed the U.V spectrum of (HL_2).

^{1}H, ^{13}C NMR spectra (DMSO-d^{6}) δ ppm: 1.29 (3H, m, CH_3), 4.26 (2H, m, CH_2), 7.04 (1H, s, NH), 7.37-8.29 (7H, m, CHAr), ^{13}C NMR: 14.71 (CH_3), 40.02 (CH_2), 117.38-124.51 (12CH-Ar), 163.96 (SCN), 166.05 (C=N), 170.22 (C=O). Fig :(8, 9) showed the ^{1}H, ^{13}C-NMR spectrum of (HL_2).

Complexes of the Ligand (HL_1 and HL_2)

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), complexes exhibit μeff (4.83, 4.91) , (2.83, 2.90) B.M respectively ,which can be a normal values for high spin octahedral complexes[18],Table (1) includes the physical properties for (HL, HL_1,HL_2) and its complexes.

FT-IR Spectra

HL_1- these spectra exhibited marked difference between bands belonging to the stretching vibration of υ(C=$N_{schiff\ bases}$) in the range between (1620-1635)cm^{-1} shifted higher frequencies by (5-20)cm^{-1} suggesting of the possibility of the coordination of ligand through the (C=$N_{schiff\ bases}$) group[14] while the band caused by υ(O-H) appeared between (3320-3360)cm^{-1} shifted to higher frequencies by (15-55) cm^{-1} which indicates to the coordination of ligand through the oxygen atom at the hydroxyl group [15] Metal- oxygen and metal-nitrogen bonds were confirmed by the presence of the stretching vibration of υ(M-O), (M-N)[16] around (421-463)cm^{-1}, (455-424)cm^{-1} respectively the spectra of complexes.

HL_2- these spectra exhibited marked difference between bands belonging to the stretching vibration of υ(C=$N_{thiozole}$) in the range between (1655-1643)cm^{-1} shifted lower frequencies by (5-17)cm^{-1} suggesting of the possibility of the coordination of ligand through the (C=$N_{thiozole}$) group[14] while the band caused by υ(N-H) appeared between (3240-3268) cm^{-1} shifted to lower frequencies by (43-15) cm^{-1} which indicates to the coordination of ligand through the nitrogen

atom at the (N-H) group[15] Metal- nitrogen bonds were confirmed by the presence of the stretching vibration of υ(M-N)[16] around (452-430) 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

[$Ni(HL_1)_2Cl_2$] d^8 The spectrum of Honey complex gave five bands at (44052)cm^{-1}, (33112)cm^{-1} attributed to (L.F), (20466)cm^{-1}, attributed to (C.T), (15625)cm^{-1} ,(14823)cm^{-1} electronic transfer $^3A_2g \longrightarrow {}^3T_1g_{(P)}$, and $^3A_2g \longrightarrow {}^3T_1g_{(F)}$, transitions respectively, the(B^-) value found to be (356.6)cm^{-1},while ß was equal to (0.34) these are the characteristics for octahedral complexes of Ni(II)[14].

$Co(HL_2)_2Cl_2$] d^7 The spectrum of the brown complex gave five bands at (44444)cm^{-1}, (33112)cm^{-1} attributed to (L.F), (24323)cm^{-1}, attributed to (C.T), (16181)cm^{-1} and (14858)cm^{-1} electronic transfer $^4T_1g_{(F)} \longrightarrow {}^4T_2g_{(P)}$ and $^4T_1g_{(F)} \longrightarrow {}^4A_2g_{(F)}$ transitions respectively[14].

[$Cd(HL_1)_2Cl_2$] and [$Hg(HL_1)_2Cl_2$] Shows only charge transfer of (M→L) in range (32067-32072)cm^{-1}, [$Cd(HL_2)_2Cl_2$] and [$Hg(HL_2)_2Cl_2$] and (32051-32062)cm^{-1} respectively [14].

Conclusions

The ligand was characterized by 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 and magnetic susceptibility, the proposed geometrical structure for all complexes were octahedral.

Table 1: Physical properties for (HL, HL_1, and HL2) and its complexes

Comp. No.	M.Wt g/mole	Color	M.P °C or dec	A_m in DMSO	μ_{eff} (B.M)	Suggested Formula
HL	222.26	yellow	241-245	—	—	—
HL_1	326.37	yellow	182-185	—	—	—
HL_2	387.43	green yellowish	141-143	—	—	—
[$Co(HL_1)_2Cl_2$]	780.56	Turquoise	282-284	17.5	4.83	Octahedral
[$Ni(HL_1)_2Cl_2$]	780.32	Honey	241-243	16.8	2.83	Octahedral
[$Cd(HL_1)_2Cl_2$]	834.04	yellow	289 dec	13	—	Octahedral
[$Hg(HL_1)_2Cl_2$]	922.21	yellow	216-218	15.9	—	Octahedral
[$Co(HL_2)_2Cl_2$]	902.67	brown	245 dec	12.8	4.91	Octahedral
[$Ni(HL_2)_2Cl_2$]	902.43	lawn green	226-229	18.3	2.90	Octahedral
[$Cd(HL_2)_2Cl_2$]	956.15	yellow	275-278	11.3	—	Octahedral
[$Hg(HL_2)_2Cl_2$]	1044.33	yellow	>300	10.5	—	Octahedral

dec. = decomposition

Table 2: the characteristic infrared of ligand and its metal Complexes

Comp. No.	IR , (KBr), cm^{-1}								
	$\nu(NH_2)$ vasy., vsy ν(NH)	ν(C=O)	ν(C-H) aromatic aliphatic	ν(C=N) Schiff thiozole	ν(C-O)	ν(C-S)	ν(M-O)	ν(M-N)	Notes
HL	3310 m 3340 m ----	1695 s	3095 m 2900 m	---- 1670 m	1285 m	780 m	----	----	δNH_2 1590 m
HL_1	---- ----	1702 s	3100 m 2900 m	1615 m 1650 m	1385 m	805 m	----	----	ν(OH) 3305 br
HL_2	---- 3283 m	1705 s	3100 m 2992 m	1625 m 1660 m	1290 m	788 m	----	----	
[$Co(HL_1)_2Cl_2$]	---- ----	1711 s	3100 m 2906 m	1632 m 1654 m	1289 m	791 w	455 m	446 m	ν(OH) 3318 br
[$Ni(HL_1)_2Cl_2$]	---- ----	1693 s	3101 m 2988 m	1633 s 1657 m	1382 m	811 m	447 w	413 m	ν(OH) 3360 s

$[Cd(HL_1)_2Cl_2]$	---- ----	1708 s	3079 s 2924 w	1638 m 1650 m	1377 w	808 s	459 s	447 w	ν(OH) 3355 s
$[Hg(HL_1)_2Cl_2]$	---- ----	1702 s	3100 m 2900 m	1615 m 1650 m	1385 m	805 m	435 m	421 s	ν(OH) 3327 s
$[Co(HL_2)_2Cl_2]$	---- 3264 m	1710 s	3095 m 2986 m	1629 m 1649 m	1288 m	780 m	----	456 m	
$[Ni(HL_2)_2Cl_2]$	---- 3269 s	1708 m	3100 m 2990 w	1627 m 1642 m	1282 s	784 m	----	447 m	
$[Cd(HL_2)_2Cl_2]$	---- 3246 m	1710 s	3095 m 2992 m	1629 w 1654 m	1288 m	763 m	----	454 w	
$[Hg(HL_2)_2Cl_2]$	---- 3256 m	1708 s	3095 m 2990 m	1627 m 1654 m	1293 w	773 m	----	465 m	

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

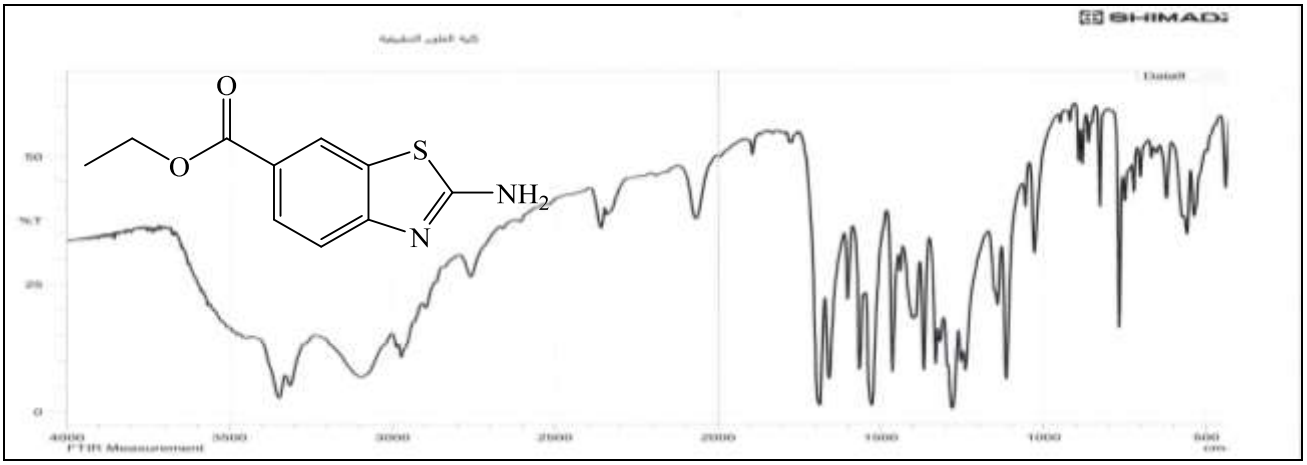


Fig.1: Infrared spectrum of Compound (HL).

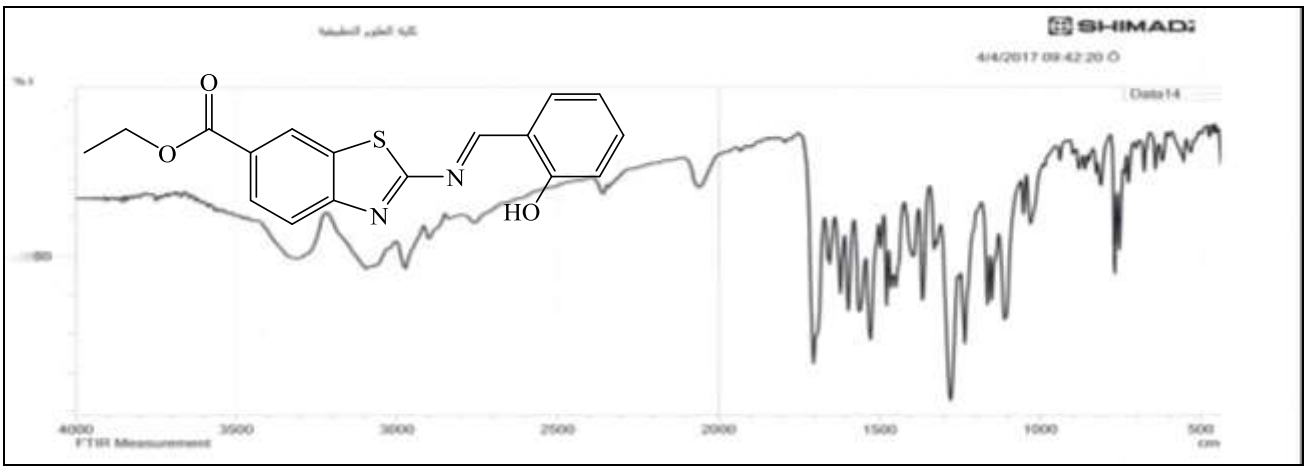


Fig.2: Infrared spectrum of ligand (HL_1).

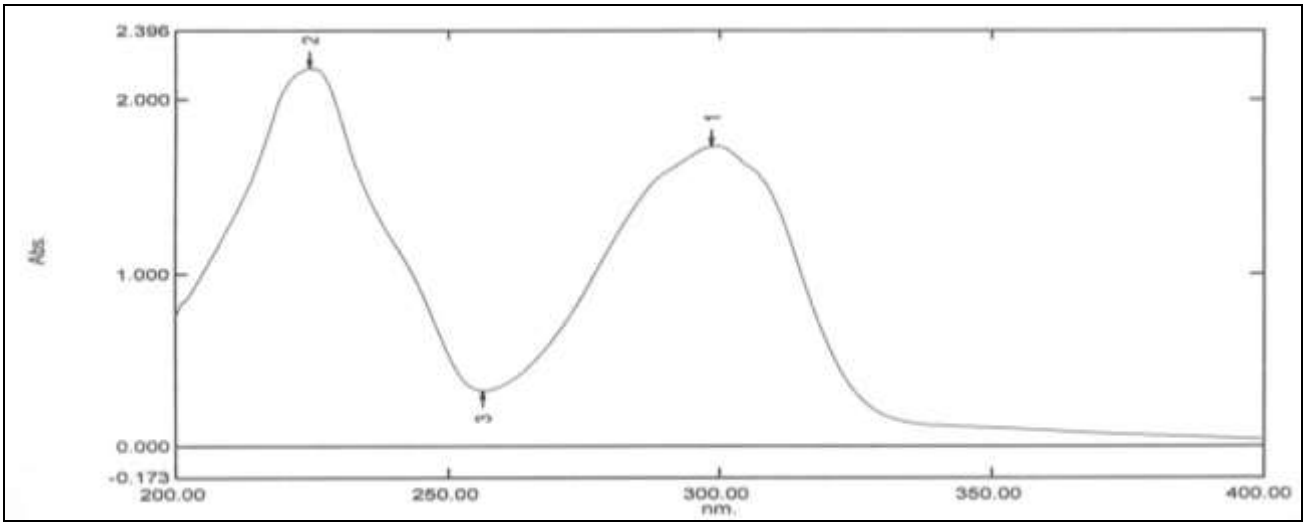


Fig.3: U.V spectrum of ligand (HL_1)

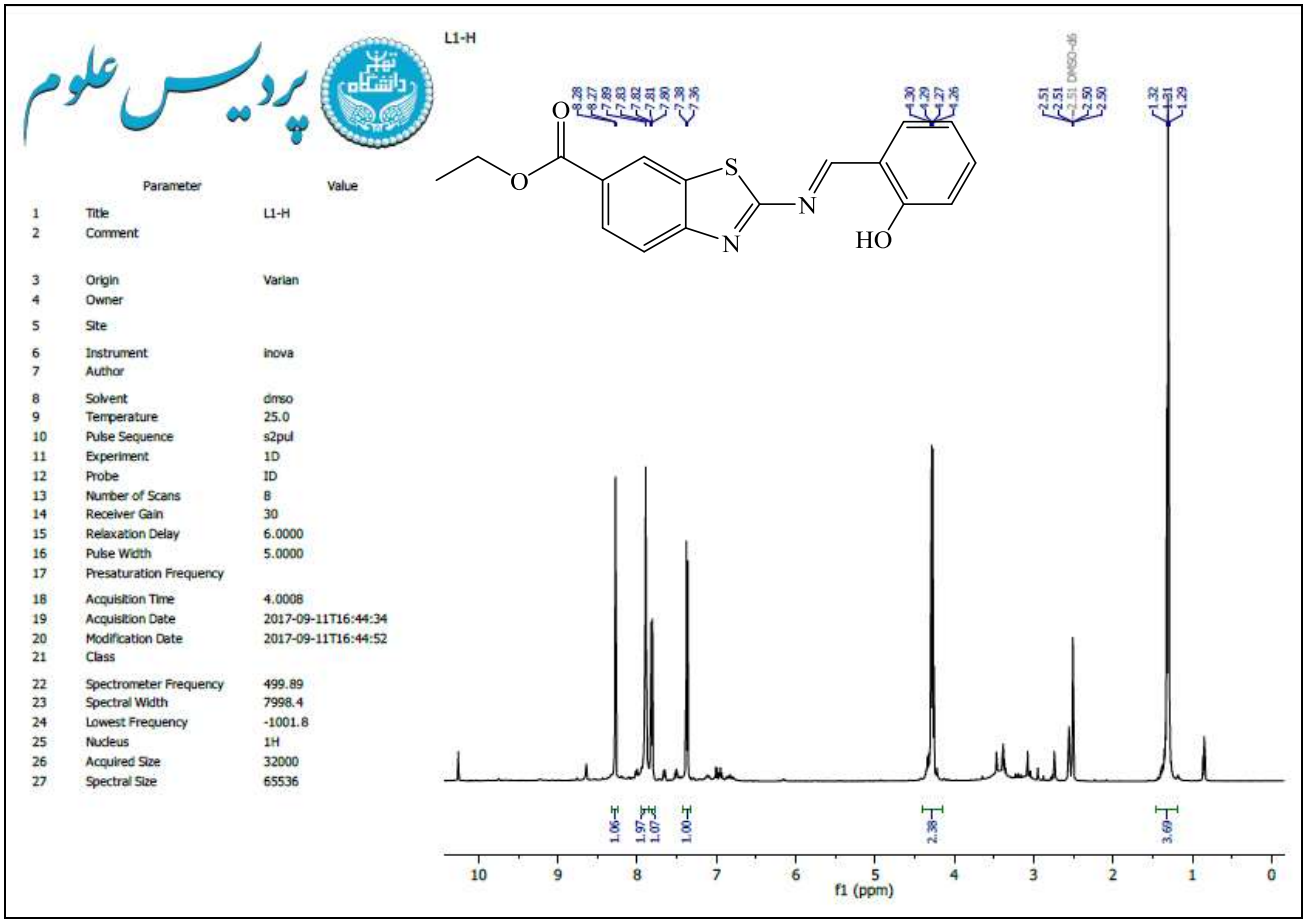


Fig.4: ^{1}H-NMR spectrum of ligand (HL_1)

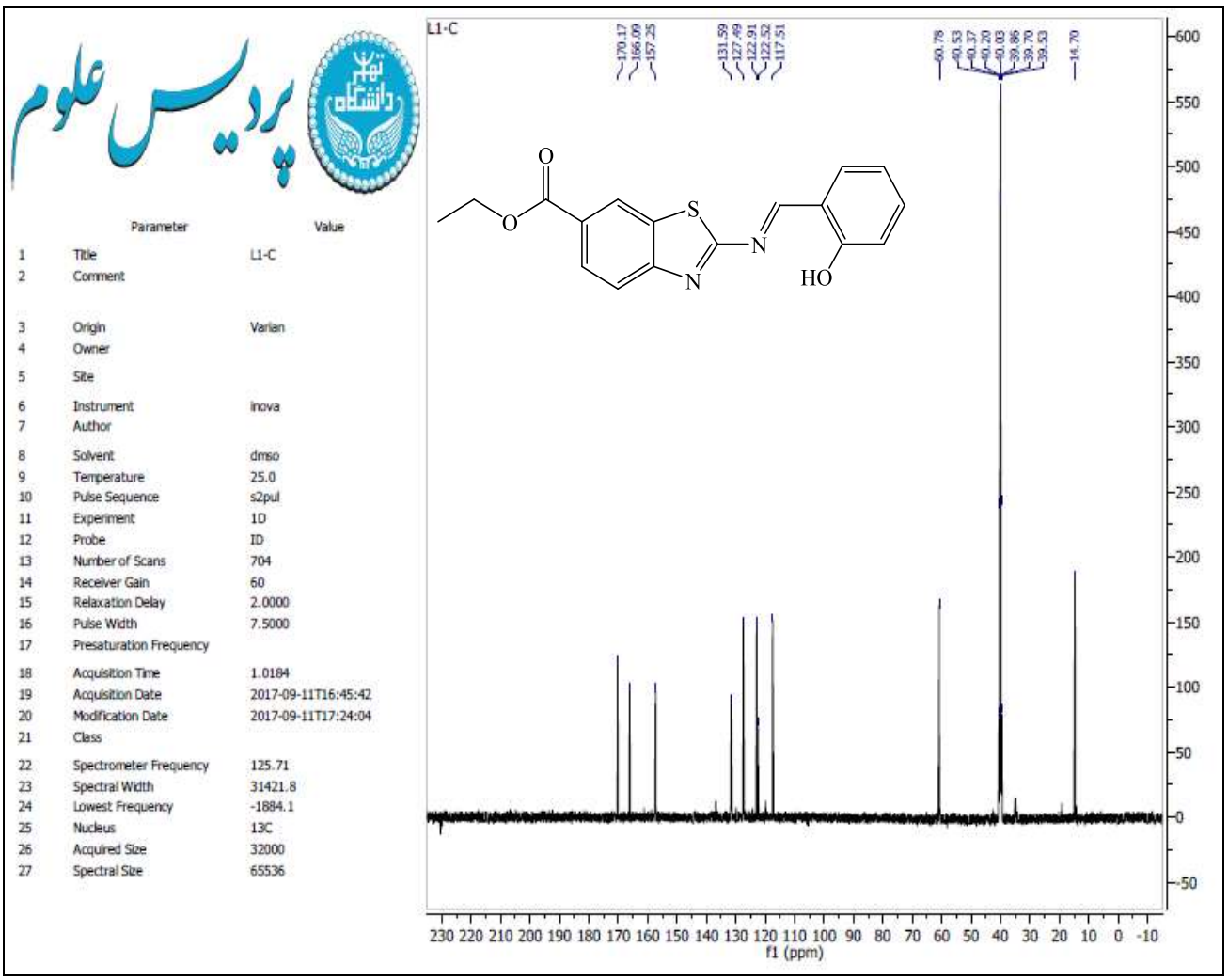


Fig.5: ^{13}C-NMR spectrum of ligand (HL_1)

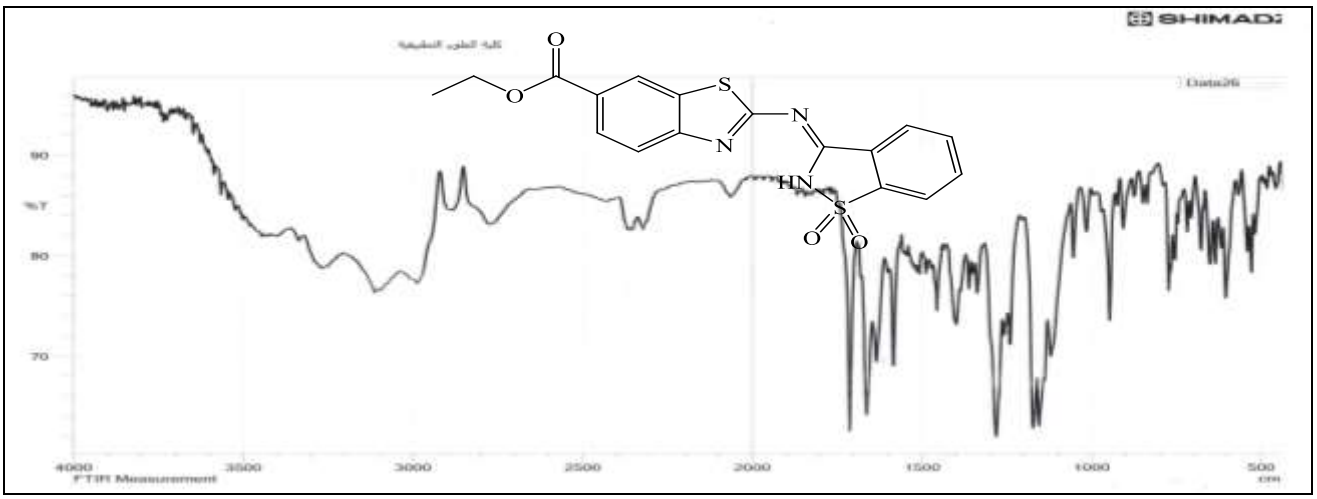


Fig.6: Infrared spectrum of ligand (HL_2)

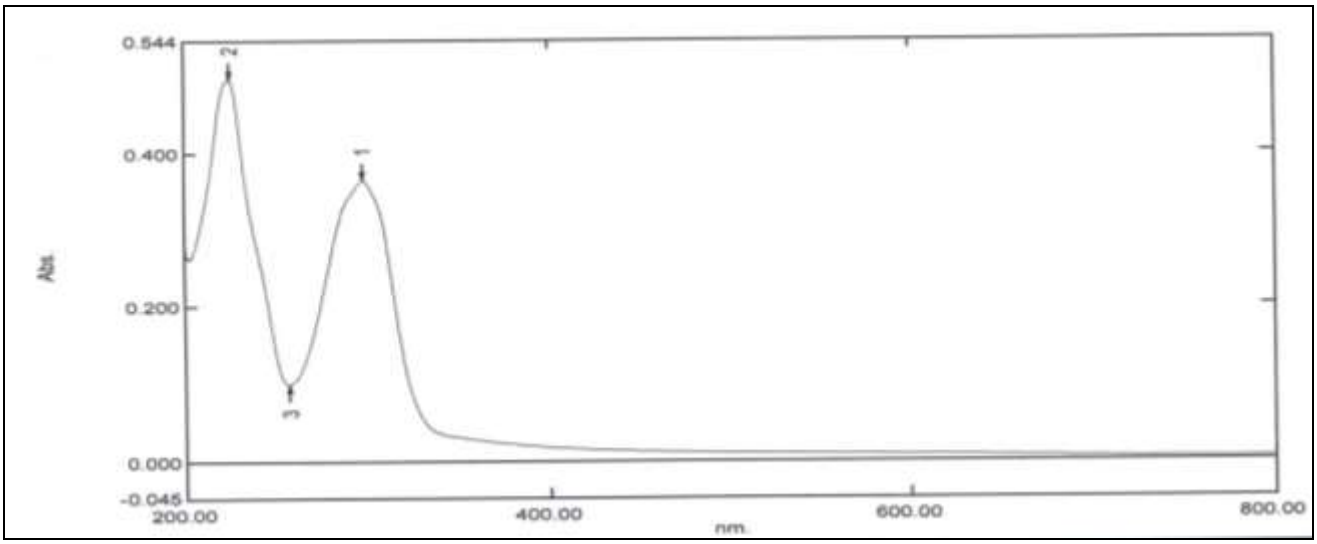


Fig.7: U.V spectrum of ligand (HL_2)

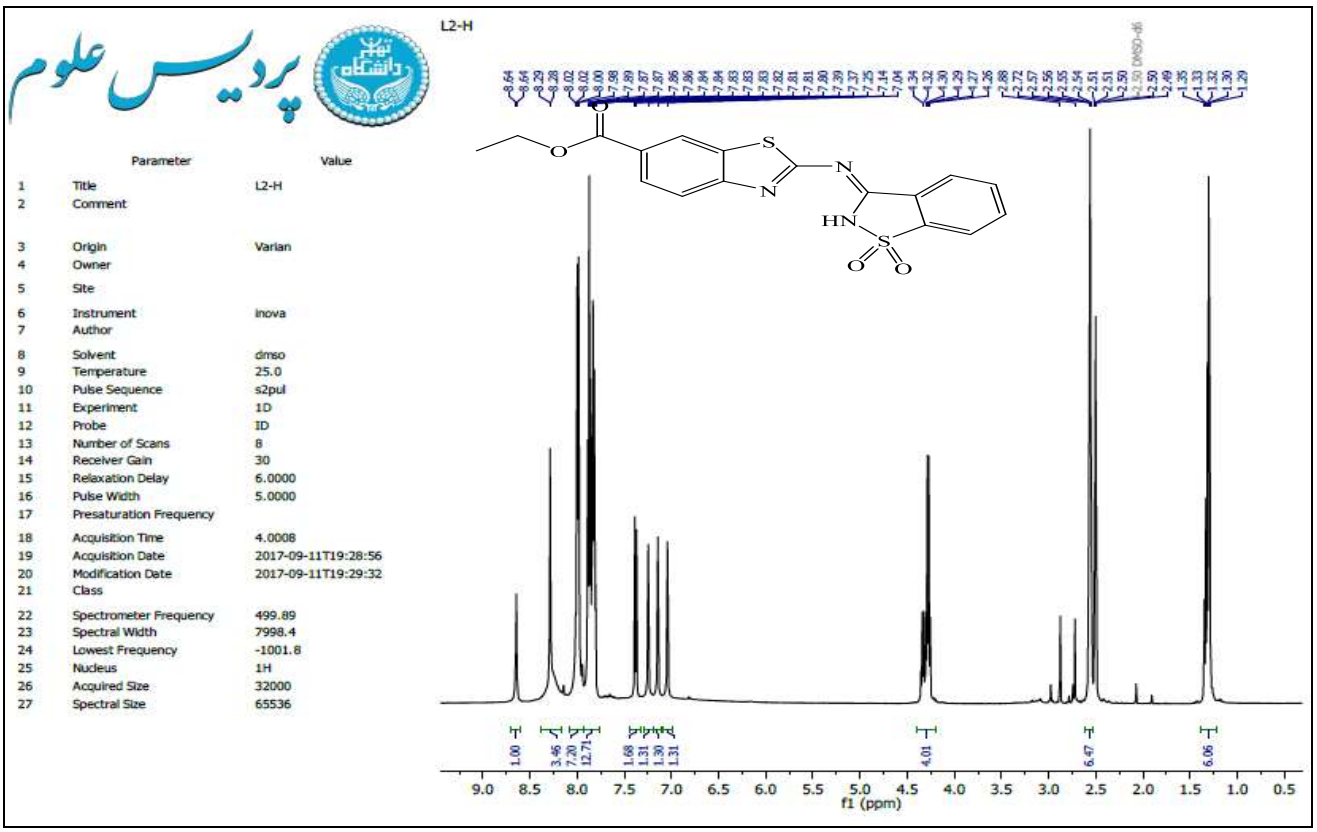


Fig.8: ^{1}H-NMR spectrum of ligand (HL_2).

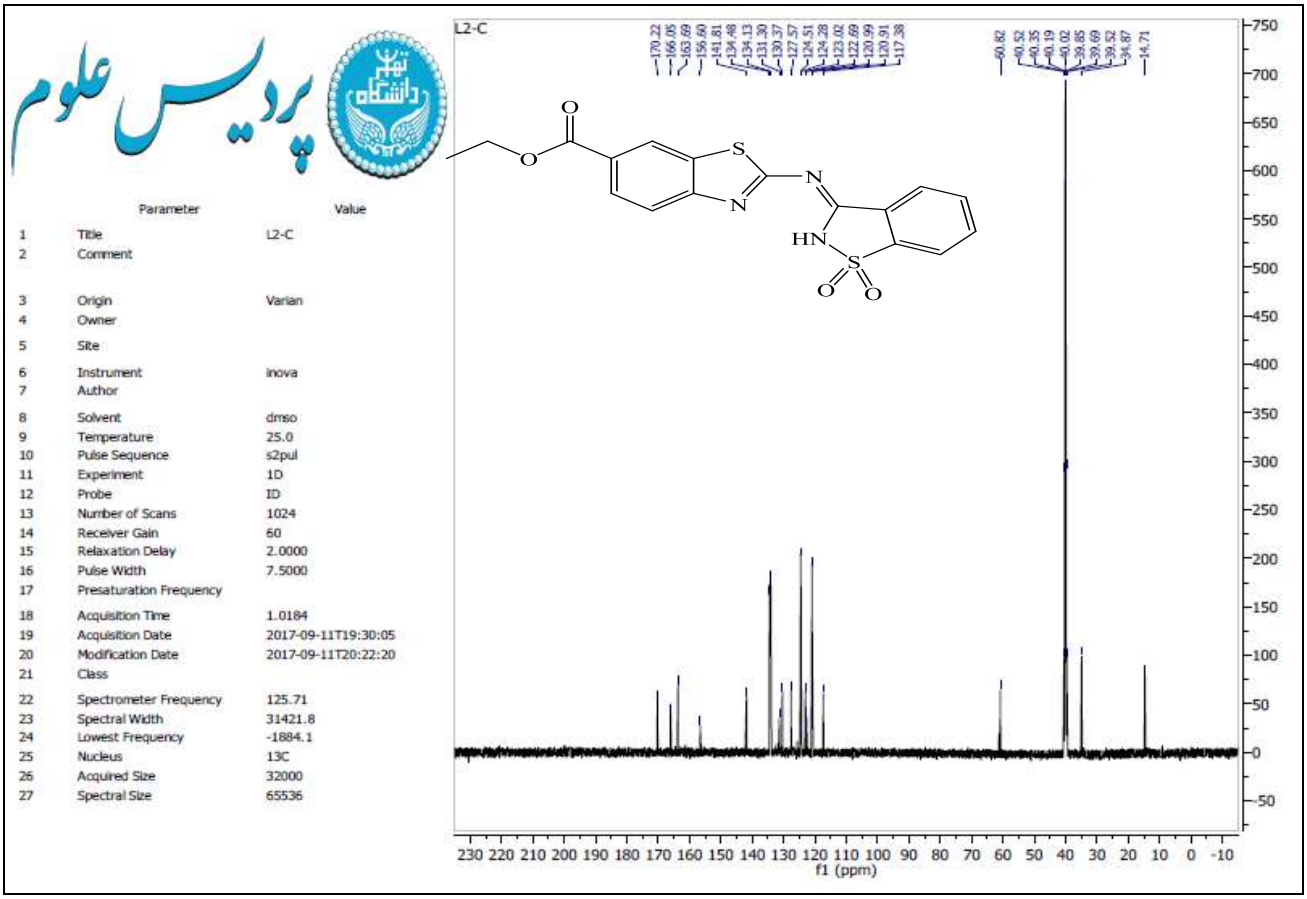


Fig.9: ^{13}C-NMR spectrum of ligand (HL_2)

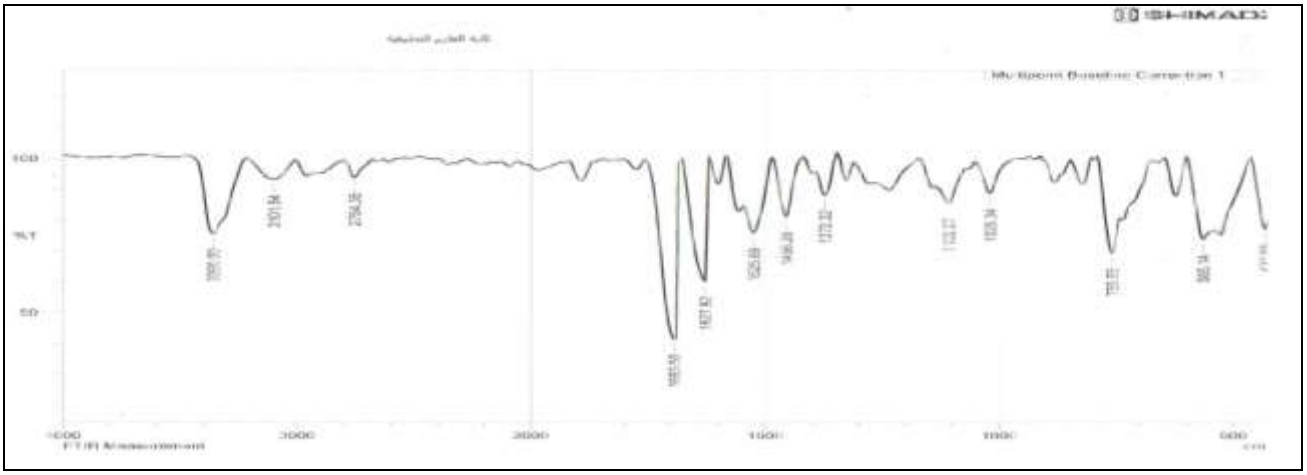


Fig.10: Infrared spectrum of complex [Ni $(HL_1)_2Cl_2$]

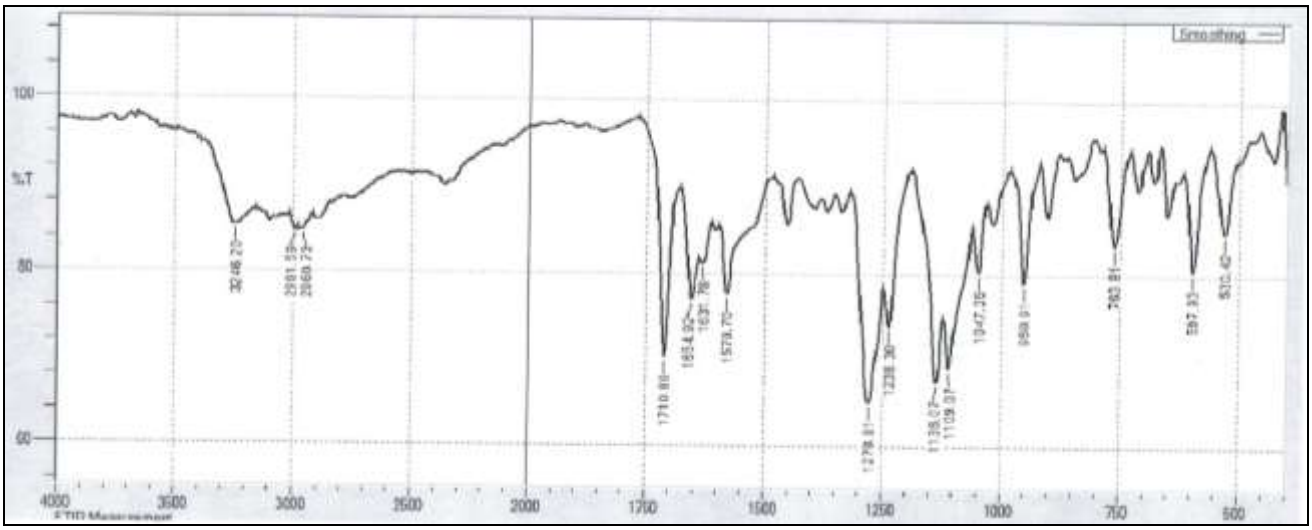


Fig. 11: Infrared spectrum of complex [Cd $(HL_2)_2Cl_2$]

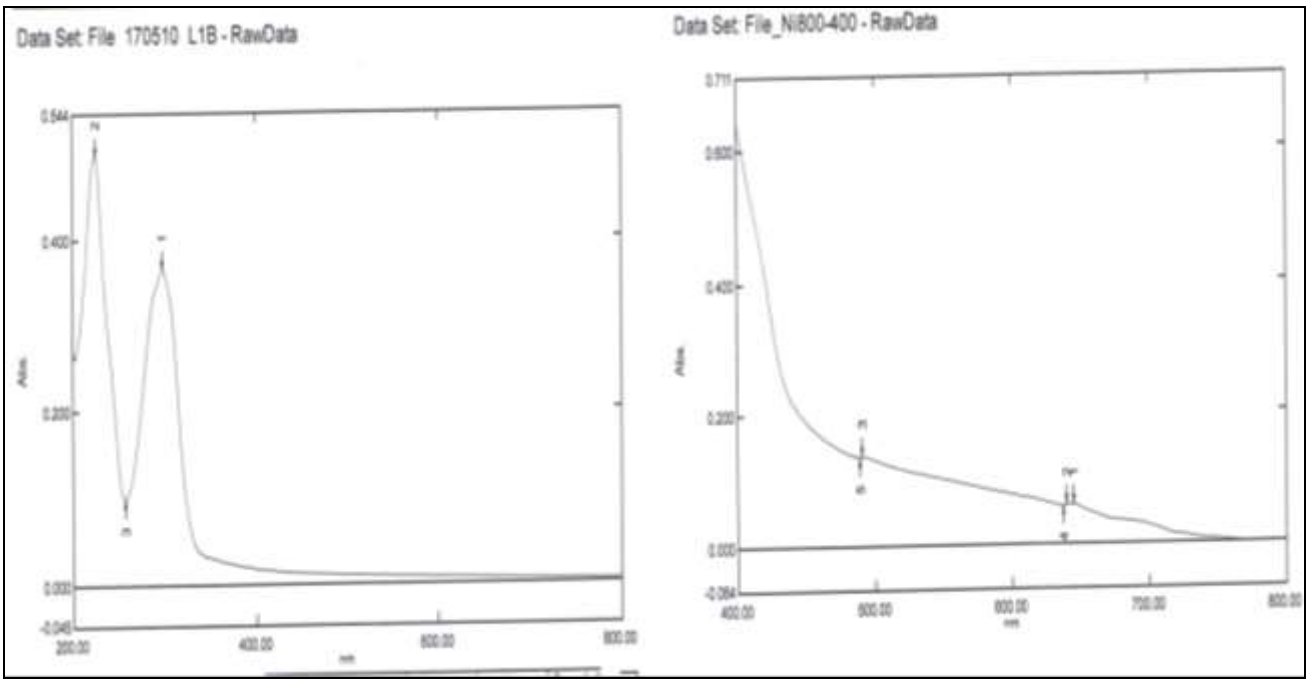


Fig.12: U.V spectrum of complex [Ni $(HL_1)_2Cl_2$]

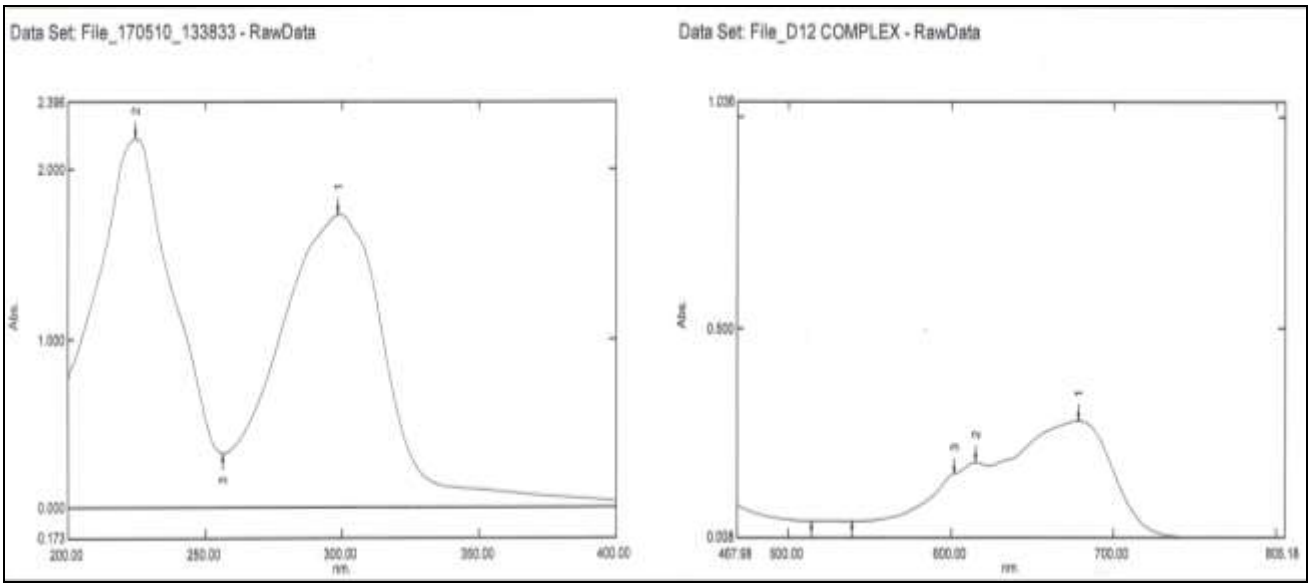


Fig.13: U.V spectrum of complex [Co $(HL_2)_2Cl_2$]

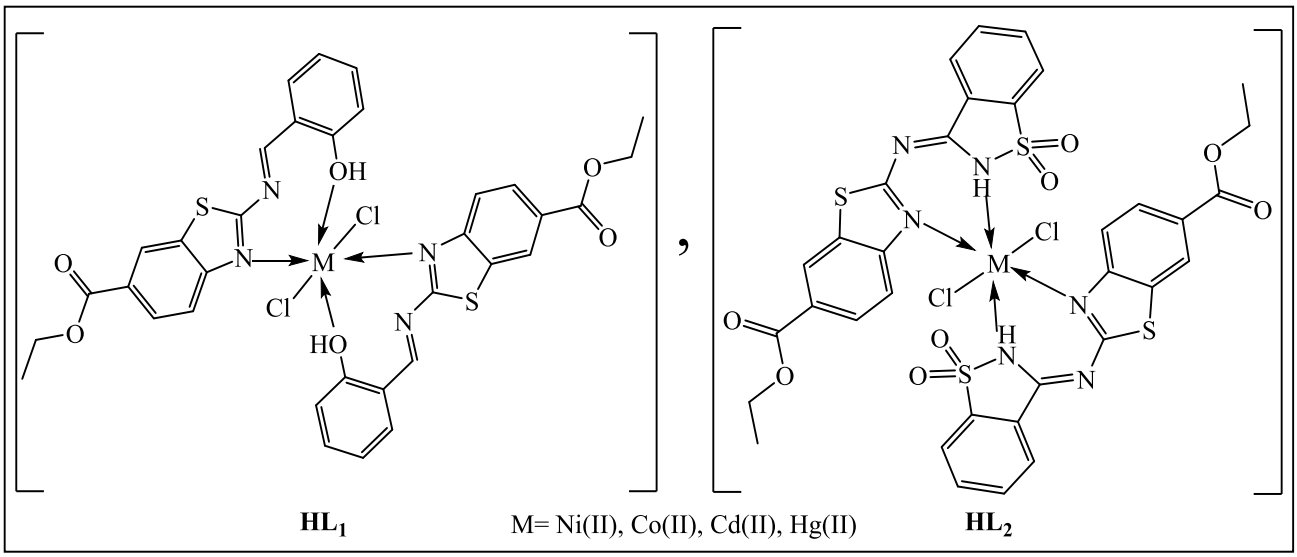


Fig.14: The proposed chemical structure of complexes

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