Synthesis and Characterization Number of new Dinuclear Complexes of Mn(II),Co(II),Ni(II), Cu(IIDerived from reaction of (6-bromo-2-aminothazole with 1-chloro-2-(2-Chloroethoxy)Ethan

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Abstract

Research includes the preparation and diagnosis of a number of new complexes of manganese (ll), cobalt (ll), nickel (ll) and copper (ll) and zinc (ll) with ligand which was obtained by condensation of 2-Mole (6-bromo-2-Aminobenzothazole) with 1-mole of 1-chloro-2- (2-chloro ethoxy) for ligand (L) and then was reaction with bilateral metals parity above-mentioned solvent methanol, the proportion (ligand: metal) (2: 1) to obtain complexes that have a formula CI_2 [M (L) (H_2O) $_2$] was someone ligand record and complex by elemental analysis (CHN) and IR spectroscopy and spectral and electronic spectroscopy NMR and through the search results show that ligand exhibits binary age ligand behavior associated with All metallic ions through the nitrogen atoms linked in a ring Althazole .pent above studies that figure is expected to spatial complexes ligand record four-brightness distorted depending on the test results that were obtained.

Introduction

The compounds 6-Bromo- 2-Aminobenzotheiazol of Althiazoles task conjunctivitis that received a large number of applications. These compounds attend several ways the most important way Hugerschoff synthesis [1] This is the way of the most widely used methods which include preparation Al thiaourea is derived from the interaction of a binary compensation Amin with Phenyl isothiaocyanat then treats derivative Al thiaourea output with bromine in a suitable solvent .

He (Mohammed) and his group [2] prepare and study the dual-core manganese complexes (II) nickel (II), copper (II) type [M_2 (L) CI_2 (H_2O) $_2$], Ni (II) = M and Cu (II) and Mn (II). as the user ligand quad age homogeneous complexes were diagnosed by spectroscopic measurements (1HNMR, VIS, UV, IR) as well as measuring the CHN and measure the ratio of the metal (M%). it was a distorted tetrahedral complexes Authority.Well attended (Khalaf) [3] and his various core complexes with the general formula [MCl_3 (AmoxH) M, Cl] as M = Zn (ll), Cd (ll) either M, = Ti (lll) Fe (lll), Amukcelin = AmoxH been analyzing these complexes analysis of metal and chlorides has emerged that ligand sync in five age where the three locations which are associated with the presence of three ions chlorides to give the order most likely a octahedral about ions Fe (lll), Cr (lll), Ti (lll) while constitute two sites the other two with the presence of two chloride ions form most likely a tetrahedral on bilateral ions Zn (ll), Cd (ll). These compounds will be with metals, transition metal complexes chelating color used in qualitative and quantitative exact diagnosis for many metal ions [4]. These compounds have also been used in the diagnosis and quantitative analysis and separation of compounds containing carbonyl group [5]. As that these compounds are also applications in the chemistry of drugs and pharmaceutical industries so as to possess biological effectiveness due to contain these compounds azomethein group, this is used as antidepressants for many diseases as they are operating anti-spasm and reducers, blood pressure [6]. as known, the Alaminates and complexes highlighted a wide range of pharmaceutical properties as an anti-inflammatory [7], and antivirals [8] as well as anti-fungal and bacteria [9,10]. And copper and its compounds are many uses, because some of the compounds used to heal wounds and sterilize drinking water and pollution treatment, and in the light of the evidence associated with the use of modern copper complexes with amino acids for cancer patients treated with radiation as material to be protective against radiation [11]

practical part

Equipped of all the materials used from my company Merck and BDH and without any additional purification processes.

1-Measurement of infrared spectroscopy (IR) spectra of radiation recorded IR ligands and complexes prepared and in the form of KBr tablets Between (400-4000) cm^{-1} and using a Shimadzu FTIR- Spectraphotometer and a Perkin Elmer FTIR-Spectraphotometer in the laboratory service of the College of Science / Tikrit University

2- UV-Visible spectra recorded spectra of ultraviolet radiation using a visual display cell (1cm) is made of quartz and the use of solvent (DMF) and concentration (10^{-3}m) in the laboratories of the Ibn Sina Company user device is shimadzu UV-240 (uvVisibe spectrophotometer) within the range [200-900] nm

3-Degrees Fusion Melting point was measured melting points and degrees of disintegration of ligands and complexes prepared using a device of the type Electro thermal 9300 in the laboratories of the Faculty of Science / Mustansiriya University.

4-Quantitative analysis to set the ratio of metal Metal analysis: using absorption technique flame Atomic absorption)) conducted measurements of the elements abncina Labs using a device [Atomic absorption] shimadzu model (AA-680)

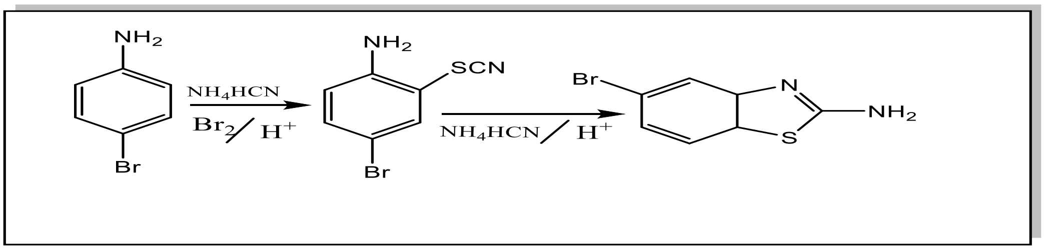
5- (CHN) Elemental Micro Analysis: appointed ratios each of carbon, hydrogen, nitrogen and sulfur ligand in the laboratories of the Department of Chemistry - Faculty of Science - University of Mustansiriya .as well conducted analyzes (CHN) of the complexes in the device of the type Eurovectro EA 3000 Italy in the laboratories of the Department of Chemistry / Al al-Bayt University in Jordan.

6-N.M.R. Spectra: measured spectra NMR 1H.N.M.R using a device of the type Bruker Ultra Shild 300MHz in a chemistry lab / University of each section of the Al al-Bayt in of Jordan.

Synthses ligand

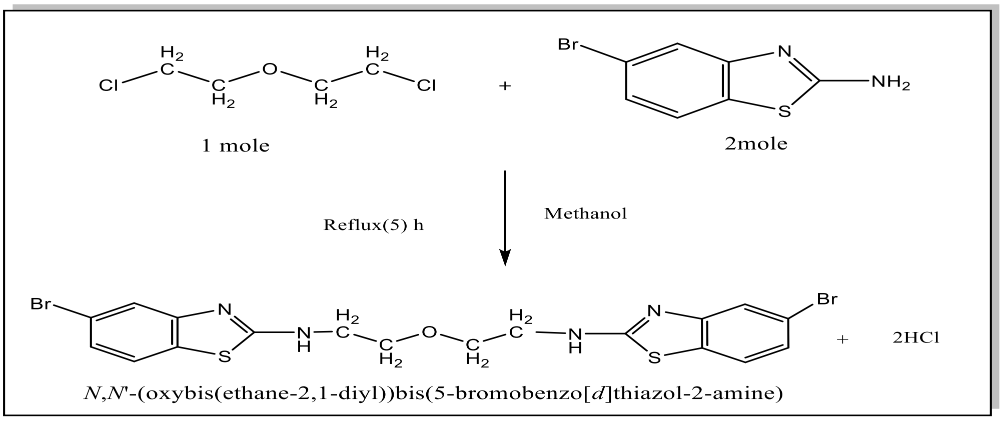
A-preparation 6-bromo-2-amino benzo thiazole [12]:

The first step involved in the preparation of the Secretary-thiazole group entry (-SCN) thiocyanogen way Site ortho-General aromatic compensator range seen in Bara location in the center of acidic and using liquid bromine dissolved in glacial acetic acid, and then comes a secondary interaction between the Secretary-group and thiocyanat, as they are closing the ring in the middle of an Acidic cooler between (0-5 c°) the composition is derived thiazole deposition in the vicinity of a base, according to the following equation.



(B) synthses ligand (L)

Attended ligand with the symbol (L) of the reaction (0.01mmol 1.42g) of dichloro diethyl ether dissolved in 10ml of absolute methanol in a circular flask capacity (100ml) Move the mixture until the solvent is complete, then added has (0:02 mmol 4.58g) of 6-bromo-2-aminobezothiazole)) dissolved in (10ml) of the absolute methanol and stir the mixture with a heat-escalation to the point 70 m 0 and after (10min) be precipitate Brown with High product up to (90%) and remained escalation process underway on the mix (5h) completion interaction then steamed mixture to ($\frac{1}{4}$) original Size and left for 24 hours consummation deposition process and then nominated the sediment washing withether several times and returned crystallized with ethanol, where formed Brown crystals needle form highly pure sludge weight and dry in electric oven degree (50-40 c°), according to the percentage and the following equation describes the interaction.

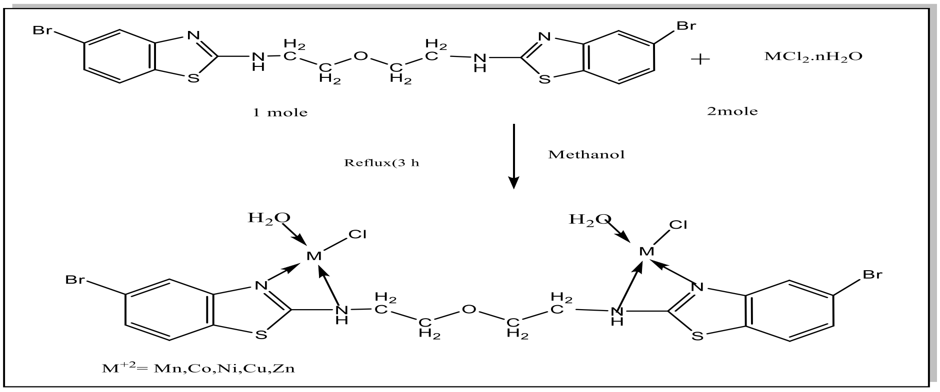


(2) synthses complexes

synthses complex ligand (L) with a metallic ion Cu (II)

Put (1mmol and 0.528 g) of ligand (L) record in (10ml) of methanol in a circular flask its size (100ml) with (2mmol and 0.34 g) of the aqueous copper chloride ($CuCI_2.2H_2O$) dissolved in (10ml) of ethanol shall be pink lotion dark Move mix with the escalation (Refluxe) for (3) hours we note be precipitate a pink color Light and evaporation of the solution to the ($\frac{1}{4}$) the original size and separation of the precipitate by filtration and washed with distilled water and dry in an electric oven degree (50 m) and weighed sludge according to the terms of percentage ratio was 85% product.

The same way as in a complex copper preparation (II) were prepared Other complexes, taking into account the difference in the escalation time and color (lotions when mixing and complexes after filtration) Note that the percentage molar combination and everyone complexes prepared (1: 2 metal- to ligand).



● Results and Discussion

Spectra UV - visible ligand [L].

It showed the UV spectrum - visible ligand free [L], six peaks of the three first at absorption wavelengths (215, 220 and 245) nm due to electronic transitions of type (π→π *). The last three summits At wavelengths (340, 365 and 370) nm due to electronic transitions of the type n→π *)) [13] for a group C = N successive ring with thiazole associated carbon stubs.

● spectra of radiology visible- ultraviolet of complexes

$[Mn_2(L)Cl_2(H_2O)]$, $[Co_2(L)Cl_2(H_2O)_2]$**,** $[Ni_2(L)Cl_2(H_2O)_2]$ $[Cu_2(L)Cl_2(H_2O)_2]$,

Showed the UV spectrum and visible complexes $[Mn_2 (L) Cl_2 (H_2O)]$ seven peaks of the first five absorb at wavelengths (210, 215, 233, and 260 and 275) nm in a row dating back to a nice transition ligand either sixth absorption peak of the wavelength (365) nm return to the gentle transfer of cargo at the seventh summit of the wavelength of 390 nanometers (ε max = 529 $Molar^{-1}.cm^{-1}$) return to overlap the top of the transfer medium intensity shipment Summit Jump-mail type (dd) (^4E, $^4A_{1(G)} \rightarrow {}^6A_1$). these results are consistent with the father of spectral studies received for complexes of manganese (II) tetrahedral [14] .show up UV spectrum and visible complex $[Co_2 (L) Cl_2 (H_2O)_2]$ seven absorption peaks first four When wavelongth (233) and (306) and (355) and (345) nm (εmax = 2125 and 2149 and in 1289 and 1248 $Molara^{-1}.cm^{-1}$) in a row dating back to a nice ligand the fifth summit when the wavelength of 360 nanometers (27777) cm -1 (εmax = 976 $Molar^{-1}.cm^{-1}$) return the shipment. As nice summits sixth and seventh at the wavelengths (716 and 764) nm (13966 and 13089) cm^{-1} (εmax = 19 and 17 $Molar^{-1} .cm^{-1}$), respectively, attributable to move mail (d-d) type (^4A (F) $\rightarrow {}^4T_1(P)$)) in conformity with the electronic spectra of complexes of cobalt (II) distorted tetrahedral [15] Showed the UV spectrum visible complexes $[Ni_2 (L) Cl_2 (H_2O)_2]$ Seven Peaks first five absorb at wavelengths (210, 235, 245, 285 and 290) Nm return to transitions ligand The sixth summit at a wavelength of 365 nm (εmax = 2472

Molar^{-1}.cm^{-1}), they return to the gentle transfer of the cargo, while the seventh summit at inspiring length (395) nm (εmax = 742 Molar^{-1}.cm^{-1}) goes back to move the electronic type (d-d) $^3T_1$ (F) →$^3T_1$ (P) [8] this is an indication that the geometry quad brightness Td [16] .show up UV spectrum visible complexes [Cu_2 (L) Cl_2 (H_2O) $_2$] seven peaks of the first five absorb at wavelengths (225, 230, 240 and 275 and 290) nm back to the nice ligand the sixth summit at wavelength 345 nm (ε max = 1134 Molar^{-1}.cm $^{-1}$) return to the gentle transfer of the shipment.The seventh summit at the wavelength (450) (εmax = 123 Molar^{-1}.cm^{-1}) nm attributable to move mail (d-d) type ($^2E \rightarrow ^2B_2$) and the result of the nature of the influence of Jean - Taylor consistent with previous spectroscopic studies of complexes copper (II) distorted tetrahedral [17] [18].

● IR spectroscopy

In this study, measuring the vibrational spectra of ligand within the range (400-4000) cm^{-1} as well prepared for the complexes in the range (200-4000) cm $^{-1}$, where a nice note (FT-IR) of Article initial 6-bromo-2-amino-prepared Benzothazole the emergence packs a strong absorption at the wavelength (3275) and (3450) cm $^{-1}$, which date back to stretch bond υ (NH) symmetric and asymmetric that demonstrate the presence of Secretary-range freely, [19] and when measuring the spectra of ligand note the emergence of a single package that back to stretch bond υ (NH). Radiation spectrum also showed infrared package when (3074) cm $^{-1}$ back to stretch bond υ (CH) aromatic.As well to the two packages at (2942 and 2837) cm $^{-1}$, which date back to stretch bond υ (CH) aliphatic as well as the emergence of packages when the numbers (in 1159) cm $^{-1}$ and (1158) cm $^{-1}$, which date back to stretch bond C-O-C [20]. also showed the infrared spectrum of ligand record pack when the wavelength of 1630 cm $^{-1}$, which date back to the group amin [21], table (3) in measuring the spectra of complexes note the disappearance of the absorption of total packages (C = N) which emphasizes metals link in ligand by amin group (C = N), [22] also showed infrared spectrum of ligand prepared (L) absorption packages in region (1424) cm^{-1} attributable to the stretching group (CN) associated with the loop [23] and when you configure complexes note that the complexes L appeared in the higher frequencies different from the frequency (CN) in Allicand packs absorption complexes prepared confined between (1435-1460) cm^{-1}, which confirms metals link in ligand by a group (CN) associated with the loop [24], the spectra of radiation showed IR ligand record (L) absorption in the region packages (811) cm^{-1} [12] due to the stretching group (CS) as shown in the table (3) when you configure complexes observed is very slight change in the location of these packages than it was in ligand indicating no correlation metallic ion with sulfur atom of this group. Radiation spectrum also showed infrared stretching Group (M-N) in the area between (441-455) cm^{-1}, confirmed correlation of the metal through the nitrogen atom [23]. When measuring the infrared spectrum of the complexes prepared noon absorption bond (M-Cl) within the range (280-330) cm^{-1} in packs absorption of weak, medium or strong at times, as shown in the table (3) This is consistent with the published research in this field[24].

●Magnetic measurements

These rules have shown a complex cobalt (II) with ligand(H_2L_2) magnetically torque of \$ (5.65) BM [16] has shown a complex of nickel (II) with ligand (H_2L_2) determined the amount magnetically(3.57) BM and this is within the range of complexes of nickel (II) high quad twisting surfaces [16]. As for a complex copper (II) appears determined amount of magnetic (2.52) BM so they Baramagnatic as there is a single electron as expected for ion copper (II) [17]. Some research has indicated that there is a difference in the value of the magnetic moment of the complexes of copper (II) quad consistency. As the complexes with tetrahedral structure gives the magnetic moments values equal to (2.0-2.20 B.M) [18]. While complexes of copper (II) with box structure level magnetic moments give up values (1.80-1.90 B.M) [18,19]

● spectrum resonance nuclear magnetic NMR H.N.M.R for ligand (L_1).

It showed spectrum^{1}H.N.M.R for ligand (L) in a binary solvent unprecedented sulfoxide (DMSO-d6) (Figure 5) A set of signals at the location H = 2.50-3.42ppm) (δ corresponds to four protons have been inferred from the chemical displacement of this signal and integration values her back to the total aliphatic (CH2).

Spectrum also showed several combined signals within the range H = 7.00-9.02p.p.m) δ) corresponding to six protons have been inferred from the displacement of these chemical signals and thus back to protons to two rings aromatic.

Spectrum also showed a mono signal at the site H = 10.99p.p.m) (δ correspond to a single proton, as inferred from the chemical displacement of this signal and this back to protons group (NH).

● **careful analysis of the elements**

Was measured by a careful analysis of the elements for some ligands and complexes prepared were the results of these analyzes are included in Schedule (1) When comparing the obtained values it practically with those values calculated theoretically observed convergence among them, which confirms the correctness ratios molar (L: M) used in the preparation of these complexes, which Our measurements confirm spectral, which supports the validity of the proposed formulas of the complexes.

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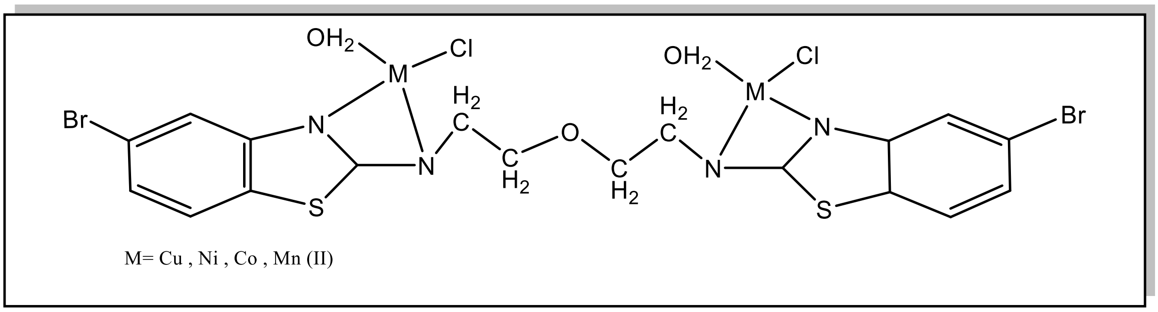
Geometry is expected to lecture complexes (1)



M= Cu , Ni , Co , Mn (II)

Table 1 shows the ligand record and complexes physical properties

componds	m.pC°	M.wt	Color	(Cala%)	(Found%)			
				C	H	N	S	Metal
L	193-196	528.06	brown	38.40 (40.92)	2.90 (3.05)	9.99 (10.61)	11.78 (12.41)	
$[Cu_2(L)Cl_2(H_2O)_2]$	253-256	762.07	Light pink	28.30 (28.36)	2.05 (2.64)	6.14 (7.35)	7.18 (8.41)	15.22(16.67)
$[Co_2(L)Cl_2(H_2O)_2]$	287-291	753.12	Dark brown	27.99 (28.71)	2.06 (2.68)	6.20 (7.44)	7.50 (8.51)	14.24(15.65)
$[Mn_2(L)Cl_2(H_2O)_2]$	310-312	745.11	purple	28.36 (29.06)	2.16 (2.71)	6.13 (7.52)	6.87 (8.61)	13.98(14.75)
$[Ni_2(L)Cl_2(H_2O)_2]$	283-285	753.88	nutty	27.52 (28.73)	2.09 (2.68)	6.56 (7.44)	6.94 (8.52)	14.54(15.60)

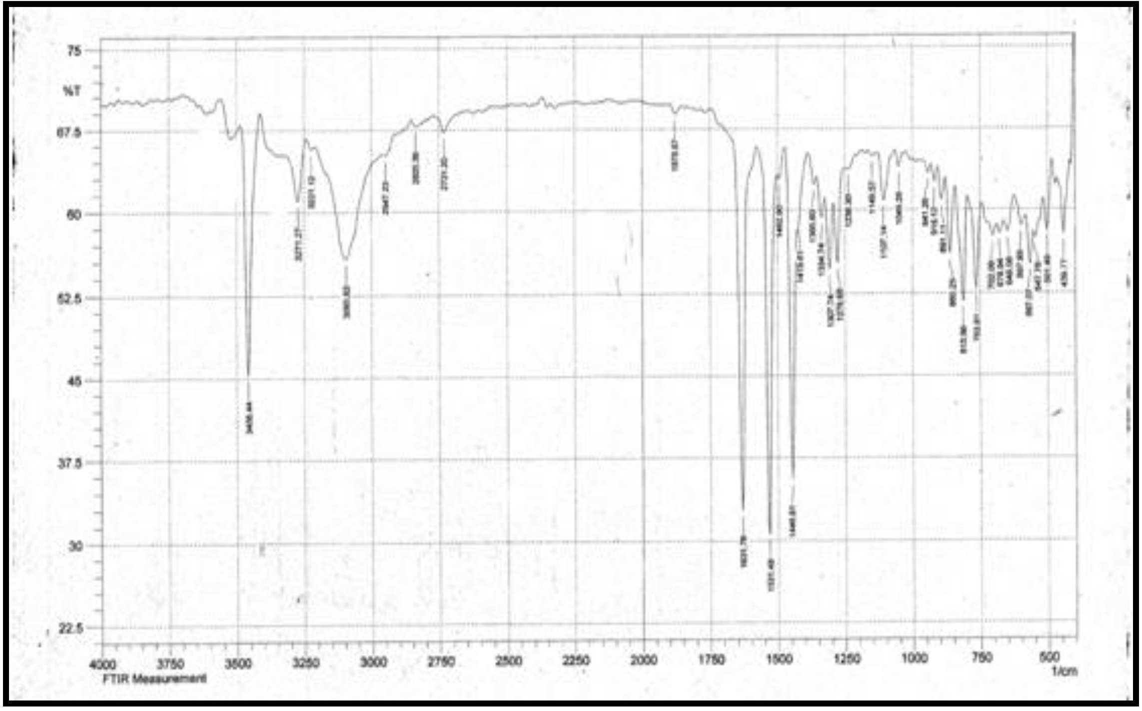
Table 2 shows the electronic transfer and geometric shapes projected

Comp. No.	**Complexes**	**Band absorption**		**C . T L.F**	**Assignments**	**Structure**
		cm^{-1}	**Nm**			
1	**$[Cu_2(L)Cl_2(H_2O)_2]$**	44444 43478 41666 36363 34468 28985 22222	225 230 240 275 290 345 450	L.F L.F L.F L.F C.T L.F	$^2E \rightarrow ^2B_2$	Td
2	**$[Co_2(L)Cl_2(H_2O)_2]$**	42918 32679 28169 27777	233 306 355 360	L.F L.F L.F C.T	$E,^4A_{1(G)} \rightarrow ^6(A_1)$	Td
3	**$[Mn_2(L)Cl_2(H_2O)_2]$**	47619 46511 42918 38461 36363 27397	210 215 233 260 275 365	L.F L.F L.F L.F L.F C.T	$^4T_1(P) \rightarrow ^6A_1$	Td
4	**$[Ni_2(L)Cl_2(H_2O)_2]$**	47619 42553 40816 35087 25316	210 235 245 285 395	L.F L.F L.F L.F C.T	$^3T_1\ (F) \rightarrow ^3T_1\ (P)$	Td
dc$_4$	$[Ni(L_2H)(H_2O)_2Cl_2]$	10752 17921 24390	930 558 410	32625	$^3A_2g\ (F) \rightarrow ^3T_2g(F)$ $^3A_2g(F) \rightarrow ^3T_1g\ (F)$ $^3A_2g(F) \rightarrow ^3T_1g\ (P)$	O.h

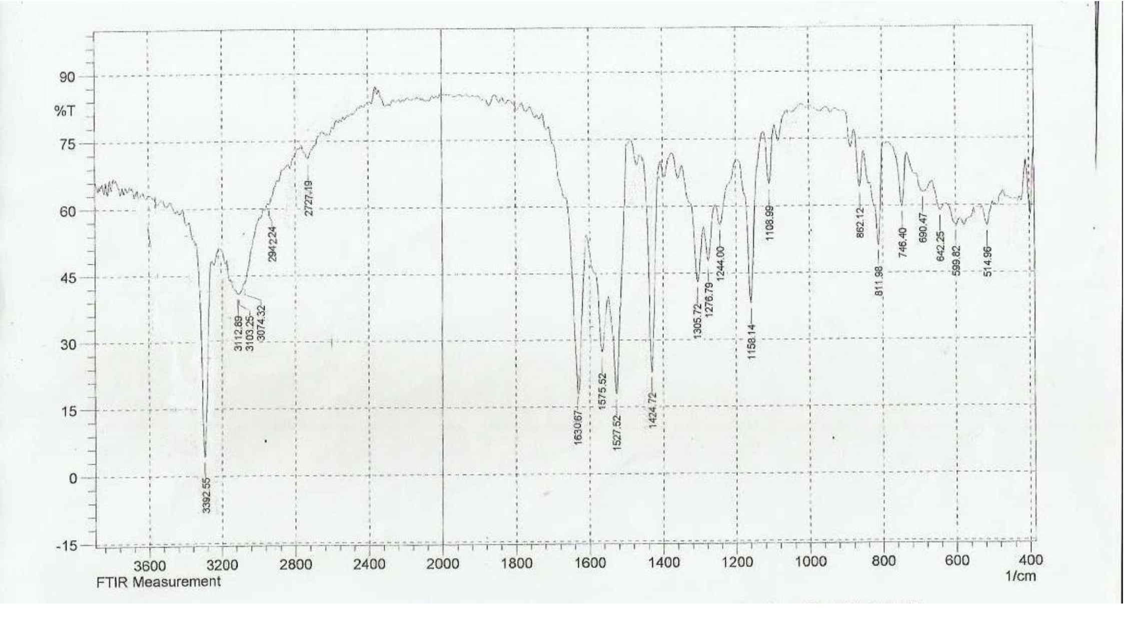
Table 3 illustrates some of the important frequencies IR spectroscopy (cm^{-1}) in ligands and complexes.

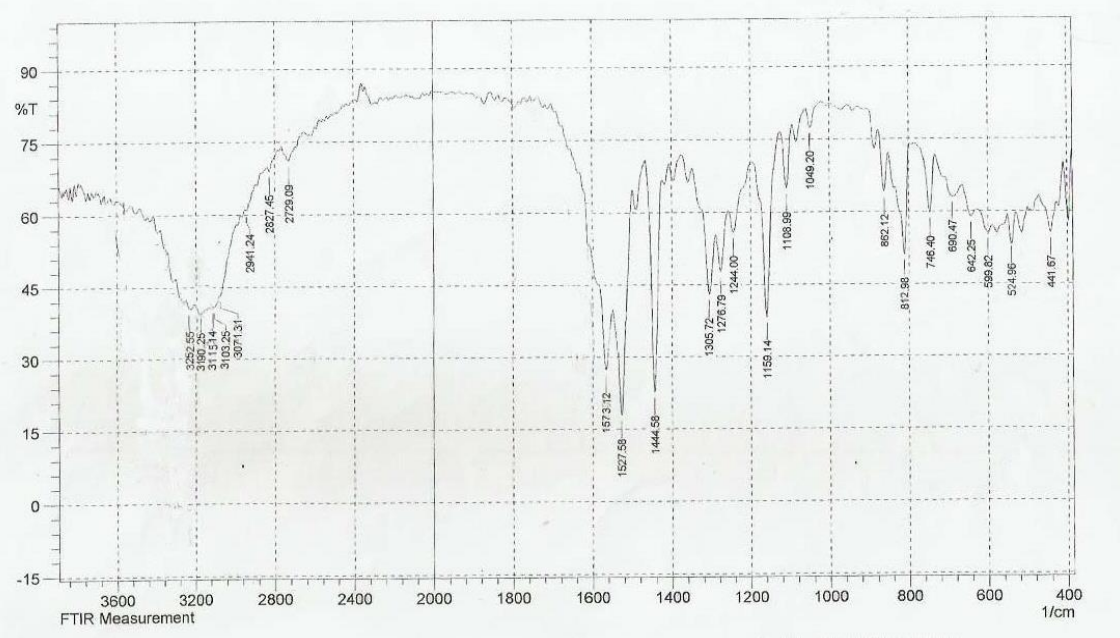
Compounds	V(C=N) Thiazole	V(C-S)	V(C=C)	V(M-N)	V(M-Cl)	V(C-N)	V(NH$_2$) V(NH)
A$_1$	1629	812	1525	………	….	1426	3275 3450 S
L	1630	811	1527	………	….	1424	3392
$[Cu_2(L)Cl_2(H_2O)_2]$	………	813	1527	441	271	1444	…..
$[Co_2(L)Cl_2(H_2O)_2]$	………	814	1623	445	298	1446	…..
$[Mn_2(L)Cl_2(H_2O)_2]$	……….	815	1626	449	312	1448	…..
$[Ni_2(L)Cl_2(H_2O)_2]$	……….	815	1628	446	314	1447	…..

Figure 2 infrared spectrum of the lecture material

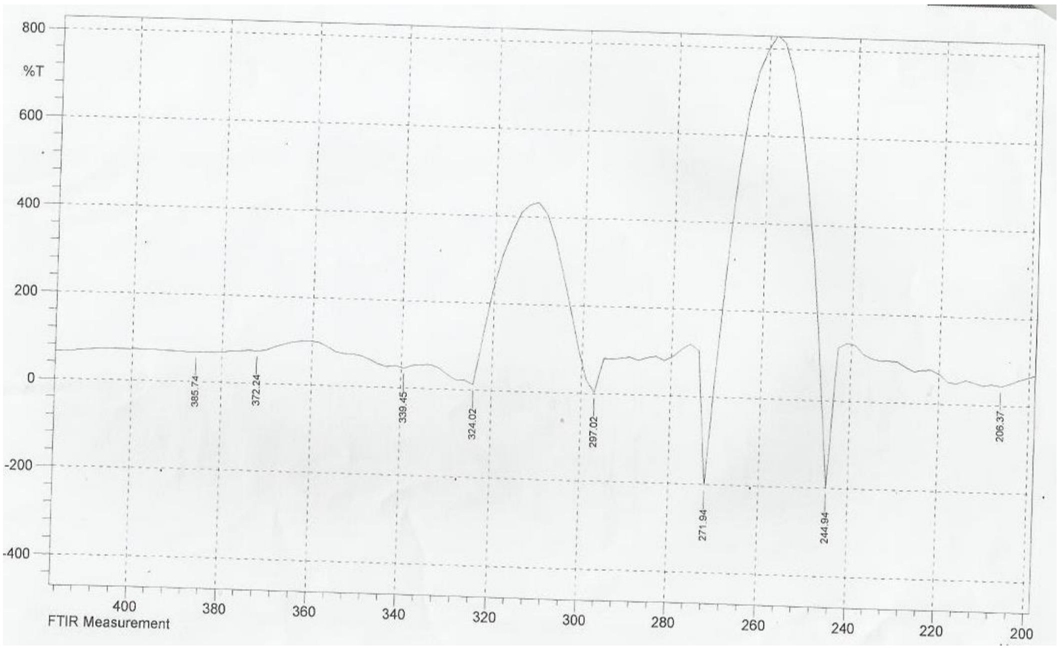


Shaped radiation spectrum (3) IR ligand record (L)

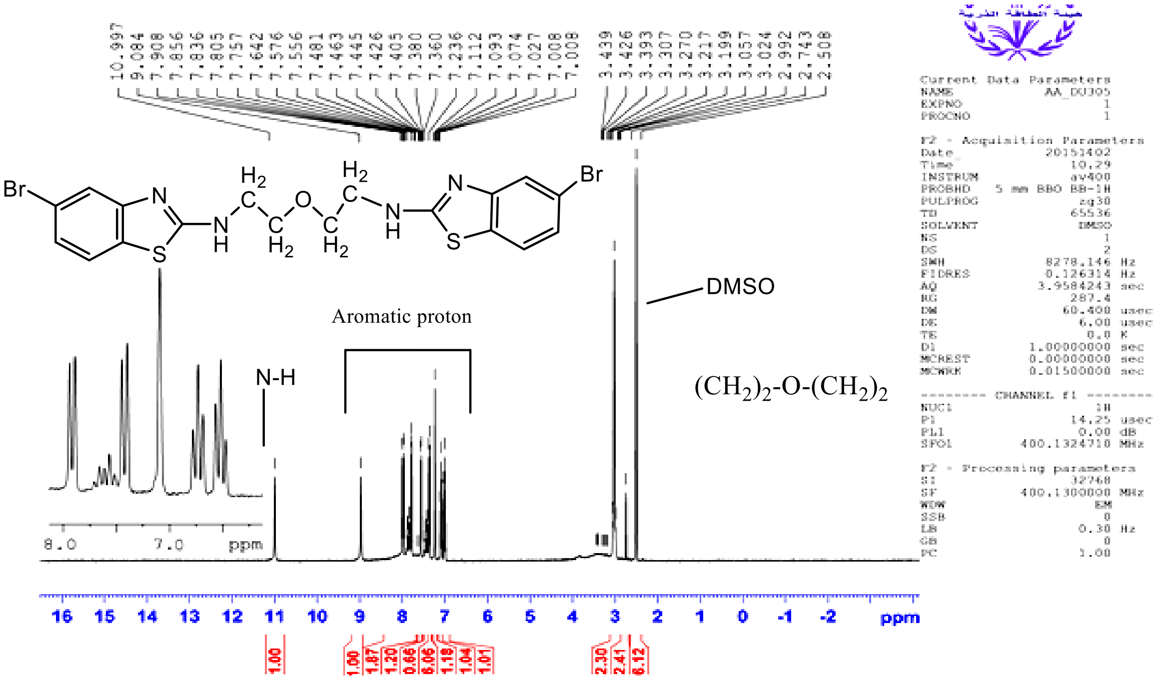




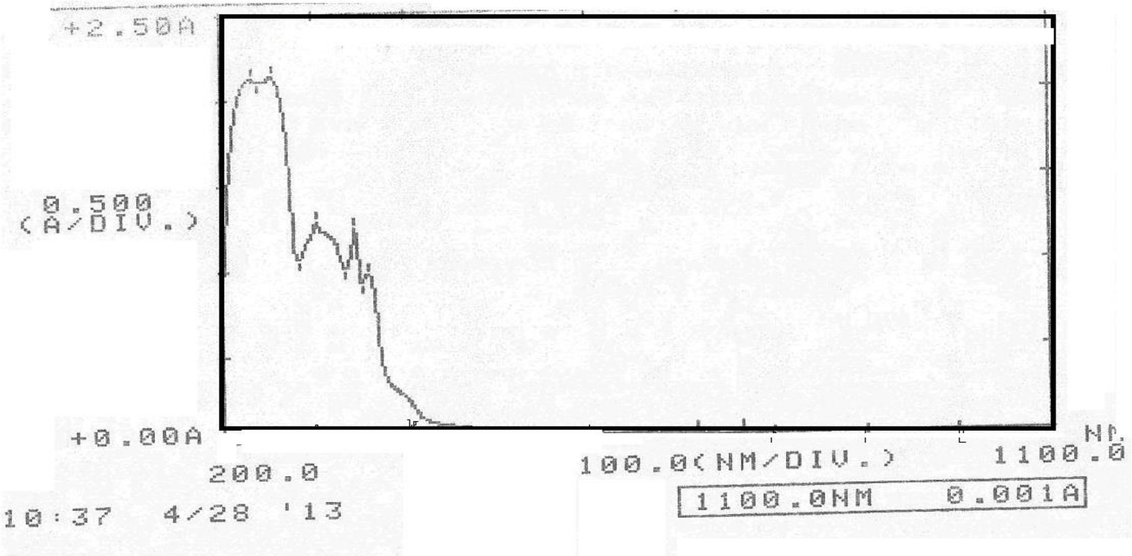
Form (4) infrared spectrum of complex copper [Cu $_2$ (CL) Cl_2 $(H_2O)_2$],



Form (5) IR spectrum within the range of 200-400 cm- copper complex $[Cu_2$ (L) Cl_2 $(H_2O)_2]$,



Form (5) NMR spectrum of ligand record (L)



Form (7): UV spectrum - visible to the complex [Co_2 (L) Cl_2 $(H_2O)_2$]