Synthesis and Characterization of Heterocyclic Azo Dye Complexes with Selected Metal Ions

تحضير وتشخيص معقدات صبغة آزو غير متجانسة الحلقة مع بعض الأيونات الفلزية المنتخبة.

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Abstract

Coupling reaction of 4-amino antipyrene with 2,6-dimethyl phenol gave bidentate azo ligand. The prepared ligand was identified by Microelemental Analysis, ^{1}HNMR, FT-IR and UV-Vis spectroscopic techniques. Treatment of the prepared ligand with the following metal ions (Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, and Hg^{II}) in aqueous ethanol with a 1:2 M:L ratio and at optimum pH, yielded a series of neutral complexes of the general formula $[M(L)_2Cl_2]$. The prepared complexes were characterized using flame atomic absorption, (C.H.N) Analysis, FT-IR and UV-Vis spectroscopic methods as well as magnetic susceptibility and conductivity measurements. Chloride ion content was also evaluated by (Mohr method). The nature of the complexes formed were studied following the mole ratio and continuous variation methods, Beer's law obeyed over a concentration range (1×10^{-4} - 3×10^{-4} M). High molar absorbtivity of the complex solutions were observed. The stability constant of the complexes have also been studied.

Keywords: - complexes, synthesis, spectral studies, azo dyes.

الخلاصة

حضرت الليكاند 4-(4- انتبيرين ازو)- 2،6-ثنائي مثيل فينول من تفاعل ازدواج 4- امينو انتبيرين مع (2،6-ثنائي مثيل فينول). شخص الليكاند المحضر بوساطة أطياف الرنين النووي المغناطيسي والأشعة تحت الحمراء وفوق البنفسجية- المرئية والتحليل الدقيق للعناصر(C.H.N) . تمت مفاعلة الليكاند مع بعض ألايونات ألفلزية المنتخبه (Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, and Hg^{II}) في وسط ايثانول ـ ماء وبنسبة فلز: ليكاند (2:1) وفي الدالة الحامضية المثلى، وخضعت محاليل هذه المعقدات لقانون لامبرت ـبير ضمن مدى التراكيز   (1×10^{-4} - 3×10^{-4} M)   وتم الحصول على سلسلة من المعقدات ذات الصيغة العامة $[M(L)_2Cl_2]$.

شخصت هذه المعقدات باستخدام تقنية الامتصاص الذري اللهبي، أطياف الأشعة تحت الحمراء والأشعة فوق البنفسجية – المرئية والتحليل الدقيق للعناصر(C.H.N)، فضلا عن قياسات التوصيلية الكهربائية والحساسية المغناطيسية،كما تم تقدير محتوى الكلور باستخدام طريقة مور .درست تراكيب المعقدات باستخدام طريقتي النسب المولية والمتغيرات المستمرة ،كما تم حساب استقرارية المعقدات المحضرة .

Introduction

Azo compounds are a very important class of chemical compounds receiving attention in scientific research. They are highly colored and have been used as dyes and pigments[1]. Azo dyes that have the chromophore of -N=N- unit in their molecular structure and over 15% of the textile dyes are lost in wastewater stream during dyeing operation. These azo dyes are known to be largely non-biodegradable in aerobic conditions[2]. Since dyes are photo chemically active, there have been various approaches to destruct them efficiently using solar light, especially visible light[3]. Heterocyclic amines have been put to much use in disperse dyes chemistry which it has been claimed was the first area to foster the industrial exploitation[4].The development of new structures of azo dyes has been a subject of interest and many novel structure of these dyes, useful in the commercial application to polyester, polyamide or poly acrylic as well as their blends with other

fibers[5,6]. Dyes usually have a complex aromatic molecular structure, which makes them stable and biodegradation[7].Metal complexes of azo compounds containing hetroaryl ring systems find various application[8]. These types of molecules have several advantages, for example the azo group is

photocromic, redox responsive and pH-sensitive [9-11]. In this work, we synthesized azo dye derived from 4-amino antipyrene as diazo component and 2,6-dimethyl phenol as coupling agent. The complex of this ligand with some metal ions has also been studied and characterized physciochemically.

Experimental
Instrumentation

UV-Vis spectra were recorded on a (Shimadzu UV- 160A) Ultra Violet-Visible Spectrophotometer. IR- spectra were taken on a (Shimadzu, FT-IR- 8400S) Fourier Transform Infrared Spectrophotometer (4000- 400) cm^{-1} with samples prepared as KBr discs. Atomic absorption was obtained using a (Shimadzu A.A-160A) Atomic Absorption/Flame Emission Spectrophotometer. The ^{1}HNMR spectra were obtained on a (Brucker- 300 MHz Ultra Shield) University of Al- al- Bayt using DMSO as a solvent and (TMS) as a reference. Microelemental analysis (C.H.N) were performed in Al- al- Bayt University- Jordan using (Euro vector EA 3000A Elemental Analyser). Conductivities were measured for 10^{-3}M of complexes in ethanol at 25°C using (Philips PW- Digital Conductimeter).

Magnetic susceptibilties were performed by using (Brucker Magnet B.M.6) instrument at 25C^o . In addition, melting points were obtained using (Stuart Melting Point Apparatus).

Materials and Reagents

The following chemicals were used as received from suppliers; cobaltous chloride hexahydrate 98.8%, nickel chloride hexahydrate 99.9%, copper chloride dihydrate 98%, zinc chloride 98.8%, cadmium chloride monohydrate 99.9%, mercury chloride 98% (Merck), 4-amino antipyrene and 2,6-dimethyl phenol (B. D. H).
The pH of the medium (4-8) was adjusted with ammonium acetate –ammonia – glacial acetic acid buffer solution.

Solutions were made of the ligand (1×10^{-5}-1×10^{-3} M) in absolute ethanol and same concentration range of metals salts in buffer solutions.

Preparation of the Ligand

The ligand was synthesis according to the general method[12] (0.508g, 1mmole) of 4-amino antipyrene was dissolved in a mixture of (2ml) sulphuric acid, (10 ml) ethanol and (10 ml) distilled water, and diazotized at 5°C with sodium nitrite solution. The diazo solution was added dropwise with stirring to a cooled ethanolic solution of (0.304g, 1mmole) of 2,6-dimethyl phenol. (25 ml) of (1M) sodium hydroxide solution was added to the dark colored mixture. The precipitate was filtered off and washed several times with (1:1) ethanol: water, mixture then left to dry. The reaction is shown in scheme (1), while (Table-1) describes the physical properties and elemental analysis.
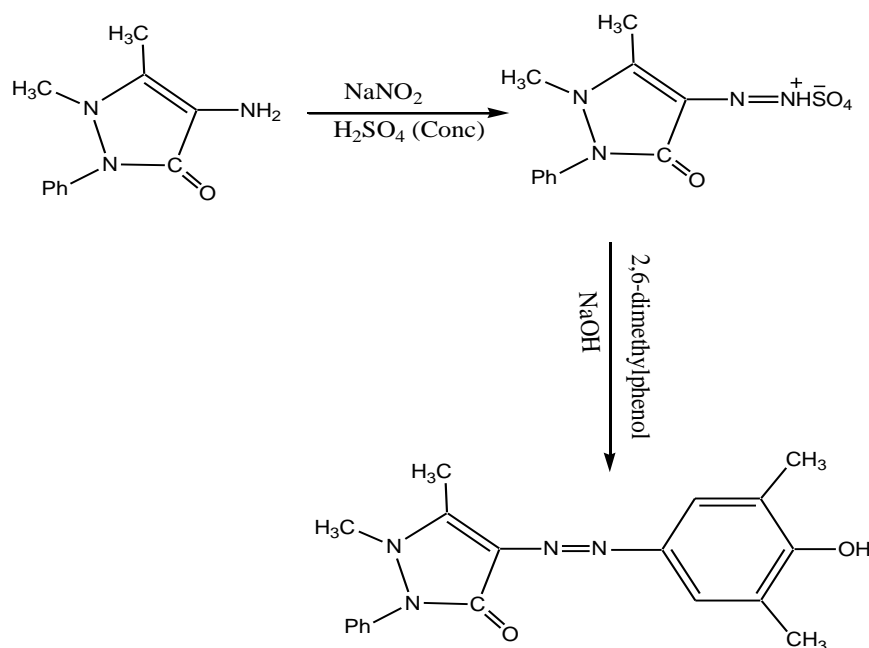
Scheme (1): Preparation of the Ligand.

Preparation of Metal Complexes (general procedure)

An ethanolic solution of the ligand (0.336g,2mmole) was added gradually with stirring to the 0.118g, 0.118g, 0.085g, 0.068g,0.10g and 0.135g (1mmole) of $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2.H_2O$ and $HgCl_2$ respectively dissolved in the buffer solution of the required pH. The mixture was cooled until dark color precipitate was formed, filtered and washed several times with (1: 1) water: ethanol then with acetone.

Results and Discussion

The ligand was prepared by coupling2,6-dimethyl phenol with the appropriate diazotate in alkaline solution. The ligand sparingly soluble in water but soluble in organic solvents, stable toward air and moisture.

The synthesized ligand was characterized by ^{1}HNMR, FT-IR,(C.H.N) and UV-Vis spectroscopic technique.

The ^{1}HNMR spectrum of the ligand in DMSO (Fig-1) shows multiplet signals at (δ=7.332-7.577 ppm) refers to aromatic protons [13] .On the other hand, the signal at (δ= 6.447 ppm) due to proton of phenol. The $\delta(CH_3)$ of pyrazole shown in (δ= 2.633 ppm).The signal at (δ= 3.319 ppm) due to $\delta(N-CH_3)$ of pyrazole. Whereas, the signal at (δ=2.23 ppm) is assigned to $\delta(CH_3)$ groups of phenol and the signal peak at(δ=2.50 ppm referred to DMSO-d6[14] .

The UV- Vis spectrum of an ethanolic solution of the ligand (10^{-3} M) display mainly three peaks, the first and second peaks were observed at (247nm) and   (342 nm) were assigned to the moderate energy π- π^* transition of the aromatic rings. The third peak (λ_{max}) was observed at the (371nm) was referred to the π- π^* transition of intermolecular   charge- transfer taken place from benzene through the azo group   (-N=N) [15] .

Interaction of the metal ions (Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, and Hg^{II}) with the prepared   ligand has been studied in solution; an aqueous- ethanolic solution were always performed over wide molar concentration and acidity range. The colors of these mixed solutions were varied from brown or yellow to red.

The interaction of the metal ion with the ligand manifests itself in the absorption spectra by the appearance of a peak in the range (420- 508 nm). A great bathochromic shift in the visible region was detected in the complex solutions spectra with respect to that of the free ligand. The high shift

in the (λ_{max}) gave a good indication for complex formation. (Fig-2) showed a comparison between the spectra of the ligand and Zn^{II} mixed solution.

From the wide studied range of molar concentration (10^{-5}-10^{-3} M) of the mixed solutions, only concentrations of (10-4 M) obey Lambert- Beer's law and showed intense color. A calibration curve was plotted on absorbance against molar concentration in the range (1×10^{-4} - 3×10^{-4} M). Best fit straight lines were obtained (Fig-3) with correlation factor R> 0.998.

The optimum concentration was chosen for complex solution gave rise to a constant (λ_{max}) at different pH.

The influence of pH was also studied at pH range (4- 8) and the absorbance- pH curves for each metal ion measured at certain (λ_{max}) were plotted. (Fig-4) showed a selective pH- absorbance curves. The plateaus of the curves represent the completion of the reaction and consequently represent the optimum pH.

The composition of the complexes formed in solution has been established by mole ratio and job methods. In both cases the results reveal (1:2) metal to ligand ratio. A chosen plots of were represented in (Fig- 5). (Table- 2) summarize the results obtained as conditions for the preparation of the complexes.

The apparent stability constant(K)of the(1:2) metal: ligand complex were evaluated spectroscopically using the following equations:

$$K = \frac{1-\alpha}{4\alpha^3 c^2} \qquad\qquad \alpha = \frac{A_m - A_s}{A_m}$$

Where c = the concentration of the complex solution in mole/ L α = degree of dissociation, As = the absorption of solution containing a stoichiometric amount of ligand and metal ion and Am= the absorption of solution containing the same amount of metal and excess of ligand.

The As and Am measured at (λ_{max}) of solution. The values of (As, Am, α, K and log K) were tabulated in (Table- 3). The high values of K may reflect the high stability of the prepared complexes [16].

The solid complexes have been prepared by direct reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions at the optimum pH and in a (M:L) ratio of (1:2). The (C.H.N) and metal contents of these complexes were in good agreements with the calculated values.

The molar conductance of the complexes as (10^{-3} M) in ethanol indicating their non-electrolytic nature[17], the data were recorded in (Table- 2). The UV- Vis spectra of the prepared complexes dissolved in ethanol (10^{-3} M) have been measured and the data obtained were included in (Table- 2). Again the large bathochromic shift of the (λ_{max}) assigned to (π- π^*) transition of the ligand suggesting the involvement of the ligand in the bond formation with the metal ion.

The effective magnetic moments (Table-2) of the complexes lie in the range (1.83-4.35) B.M. This value refers to a paramagnetic (high spin) which has been reported for most octahedral geometry. In case of Zn^{II}, Cd^{II}, and Hg^{II} complexes because of filled-d orbital, therefore the magnetic moments (μ=0) are diamagnetic [18].

In order to study the binding mode of the ligand with the metal ions, a comparison have been made for the FT. IR spectra of the free ligand and the prepared complexes and the data was tabulated in (Table-4). The IR spectrum of the ligand (Fig-6) exhibited broad band at 3286 cm^{-1} was assigned to the stretching vibration of υ(OH) group[19]. Since no change in this band was noticed, the possibility that coordination occur via the donation atom in this group was excluded. Strong band at 1651cm^{-1} in the ligand spectrum ascribed to the υ(C=O) stretching vibration[20,21], suffered a great change to lower frequency was observed on complexation with metal ion.

Band characteristic of the azo bridge vibration at 1471cm^{-1}, on complexes (Fig-7) shifted to higher frequency with change in shape was observed indication the engagement of this group in the coordination with the metal ion[22,23]. The characteristic band in the ligand spectrum at 1377 cm^{-1} which was assigned to the (-C=N-N=C-) stretching [24], suffered a great change in the intensity and

in position to lower frequency was also observed in the spectra of all complexes. The absence of new band at (447-590) cm^{-1} are tentatively assigned to υ(M-O) and υ(M-N) (Metal-Ligand) stretching bands[25-27] .

The ^{1}HNMR spectra in DMSO (Fig-8) for one of the prepared complexes have been measured for reason of comparison. Change was observed in the shape and position of multiplet signals belong to the aromatic protons (δ= 7.071-8.295 ppm). These signals were observed in the ligand spectrum at (δ=7.332-7.577 ppm). The (OH) signal of the phenol was shifted to higher frequency (δ=6.832 ppm), this was recorder at (δ= 6.447 ppm) for the free ligand. On the other hand, the signals at (δ= 3.406 ppm), (δ= 2.960 ppm) and (δ= 2.616 ppm) refer to δ(N-CH$_3$), δ(CH$_3$) of pyrazole and δ(CH$_3$) groups of phenol, were also undergo shift to lower region (higher frequency).

According to the results obtained an octahedral structure has been suggested to these complexes.
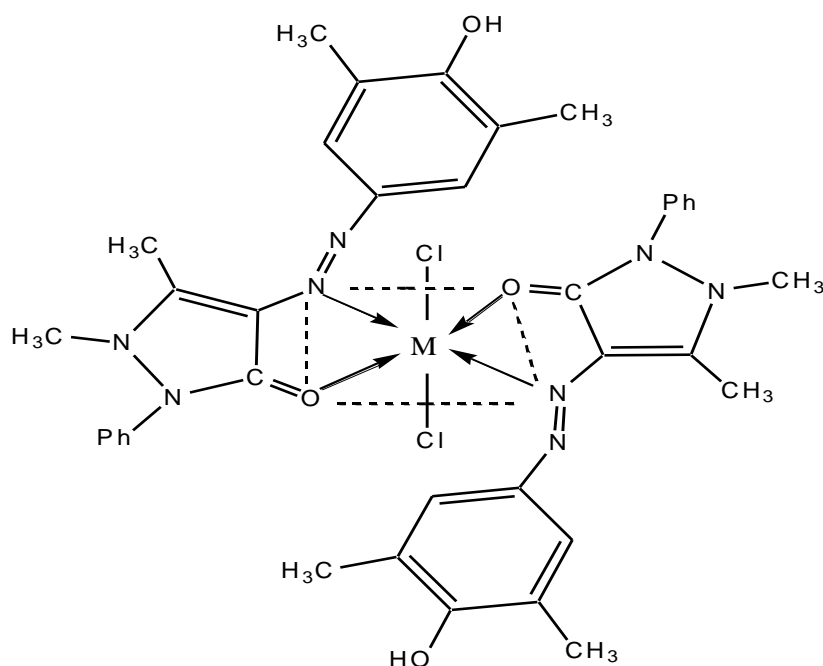
References

1. B.Kirkan and R.Gup; ***Turk.J.Chem***; 52(2008)9-17.
2. G.L.Baughman and E.J. Weber; ***Environ.Sci.Technol***; 28(1994)267.
3. H.Park and W.Choi; ***Journal of Photochemistry and Photobiology***; 159(2003). 241-247.
4. H.R.Maradiya***; Turk. J. Chem***; 25(2001)441-450.
5. V.H.Patel, M.P.Patel and R.G.Patel; ***J.Serb.Chem.Soc***; 67(2002)727-734.
6. H.R.Maradiya and V.S.Patel; ***J.Serb.Chem.Soc***; 66(2001)87-93.
7. Y.Z.Fu and T.Viraraghavan; ***Bioresoure Technol***; 29(2001)251-262.
8. F.Karipcin and E. Kabalcilar; ***Acta.Chim.Slov***; 54(2007)242-247.
9. M.Y.Abdeal, I.M.M.Kenawy and M.A.H.Hafez; ***J.App.Poly.Sci***; 77(2000) 3044-3048.
10. T.Mathur, U.S.Ray, J.C.Liou, J.S.Wu, T.H.Lu and C.Sinha; ***Polyhedron***; 24 (2005)739-746.
11. F.Huang,Y.Wu,D.Gu and F.Gan; ***Dyes and Pigments***;66(2005)77-82.
12. M. Panda,C.Das,C.Hung and S.Goswami ; ***J. Chem. Sci*** ;119(2007)3-9.
13. R.Carballo, A.Castineiras, B.Covelo, J.Niclos and E.Vazguez-Lopez; ***Polyhedron***; 20(2001)2415-2420.
14. P.Bartta; ***J.Chem.Sci***; 118(2006)171-177.
15. M.R.Mahmoud, A.M.Hamman and S.A.Ibrahim; ***Z.Phy.Chem***; 265(1994)203.
16. H.W.Cao and J.F.Zhao; ***Cro.Chem. Acta***; 76(2003)1-6.

17. W.J.Geary; *Coord. Chem .Rev;* 7(1971)110.
18. R.C.Khuble and R.P.Singh; *Indian.J.Chem*; 22A (1982)214.
19. E.Yildiz and H.Boztepe; *Turk.J.Chem*; 26(2002)897-903.
20. Y.SI, Q.Hu, Z.Huang, G.Yang and J.Yin;*Turk.J. Chem*; 29(2005)135-140.
21. A.A.Osowole, G.A.Kolawole and O.E.Fagade; *Int.J.Chem*; 15(2005)237.
22. S.Pal and C.Sinho; *Proc. Ind.Acad. Sci;* 113(2001)173-182.
23. F.Karipcin and E.Kabalcilar; *Acta.Chim.Slov;* 54(2007)242-247.
24. K.S.Abou-Melha and H.Faruk; *J.Iran.Chem.Soc;* 5(2008)122-134.
25. F.A.El-Saied, R.M.El-Bahnasawy, A.K.Abdel-Azeem and A.K.El-Sawaf; *Polyhedron*; 13(1994)1781.
26. V.K.Sharma and S.K.Sengupta; *Metal-Organic and Nano-Metal Chemistry*; 23(1993)401.
27. T.D.Thangadurai and K.Natarajan; *Indian.J.Chem*; 41(2002)741.

Table (1):- Physical Properties and Elemental Analysis of the Complexes.

Compounds	Color	M.P$^\circ$C	Yield %	Analysis Calc. (Found)				
				Cl%	M%	C%	H%	N%
Ligand	Orange	280	86	-	-	67.85 (67.12)	5.95 (4.89)	16.66 (15.35)
[Co(L)$_2$Cl$_2$]	Brown	>360	77	8.85 (7.92)	7.35 (6.88)	56.85 (55.78)	4.98 (4.12)	13.96 (12.77)
[Ni(L)$_2$Cl$_2$]	Deep Brown	>360	82	8.86 (8.03)	7.32 (6.58)	56.88 (56.34)	4.99 (4.07)	13.97 (12.84)
[Cu(L)$_2$Cl$_2$]	Brown	>360	81	8.79 (7.85)	7.93 (6.94)	56.50 (55.27)	4.95 (3.85)	13.87 (12.63)
[Zn(L)$_2$Cl$_2$]	Yellowish Orange	>360	88	8.78 (7.64)	8.04 (7.72)	56.43 (56.11)	4.95 (3.97)	13.86 (12.73)
[Cd(L)$_2$Cl$_2$]	Yellow	>360	85	8.30 (7.55)	13.09 (12.56)	53.33 (52.85)	4.67 (4.06)	13.09 (12.48)
[Hg(L)$_2$Cl$_2$]	Red	>360	83	7.53 (6.77)	21.20 (20.75)	48.35 (47.88)	4.24 (3.88)	11.87 (10.66)

Table (2):- Conditionsfor the Preparation of the Complexes and UV-Vis, Magnetic Susceptibility and Conductance Measurements Data.

Compounds	Optimum pH	Optimum Molar Conc. x 10^{-4}	M:L Ratio	(λ_{max}) nm	ABS	ε_{max} (L.mol^{-1}.cm^{-1})	Λ_m(S.cm^2.mol^{-1}) In Absolute ethanol	μ_{eff} (B.M)
Ligand	-	-	-	371	1.870	1870	-	-
[Co(L)$_2$Cl$_2$]	6	2	1:2	462	0.951	951	27.70	4.35
[Ni(L)$_2$Cl$_2$]	6.5	2	1:2	459	0.811	811	28.50	3.08
[Cu(L)$_2$ Cl$_2$]	6.5	2.5	1:2	508	0.163	163	14.20	1.83
[Zn(L)$_2$Cl$_2$]	6.5	2	1:2	420	1.314	1314	29.40	Dia
[Cd(L)$_2$Cl$_2$]	6	2	1:2	466	1.364	1364	14.85	Dia
[Hg(L)$_2$Cl$_2$]	6	2	1:2	462	0.884	884	11.66	Dia

Table (3):- Stability Constant of the Prepared Complexes.

Complexes	A_s	A_m	α	k	Log k
[Co(L)$_2$Cl$_2$]	0.161	0.221	0.271	2.29×10^8	8.359
[Ni(L)$_2$Cl$_2$]	0.086	0.121	0.289	1.84×10^8	8.264
[Cu(L)$_2$Cl$_2$]	0.162	0.291	0.443	1.11×10^8	8.045
[Zn(L)$_2$Cl$_2$]	0.183	0.277	0.339	1.06×10^8	8.025
[Cd(L)$_2$Cl$_2$]	0.277	0.412	0.327	7.75×10^8	8.889
[Hg(L)$_2$Cl$_2$]	0.386	0.558	0.308	3.15×10^8	8.498

Table (4):- The Main Frequencies of the Ligand and Their Complexes (cm^{-1}).

Compounds	ν (OH)	ν(C=O)	ν(-N=N-)	ν (-C=N-N=C-)	ν (M-O)	ν (M-N)
Ligand	3286 br.	1651 v.s.	1481 s.	1377 sh.	-	-
[Co(L)$_2$Cl$_2$]	3280 br.	1581 sh.	1489 s.	1346 sho.	590 w.	466 w.
[Ni(L)$_2$Cl$_2$]	3279 br.	1624 s.	1485 s.	1334 sho.	582 w.	455 w.
[Cu(L)$_2$Cl$_2$]	3275 br.	1631 sh.	1492 s.	1369 m.	532 w.	455 w.
[Zn(L)$_2$Cl$_2$]	3286 br.	1612 s.	1489 s.	1366 sho.	551 w.	459 w.
[Cd(L)$_2$Cl$_2$]	3277 br.	1640 sh.	1485 s.	1327 sho.	574 w.	493 w.
[Hg(L)$_2$Cl$_2$]	3281 br.	1639 sh.	1481s.	1369 sho.	520 w.	447 w.

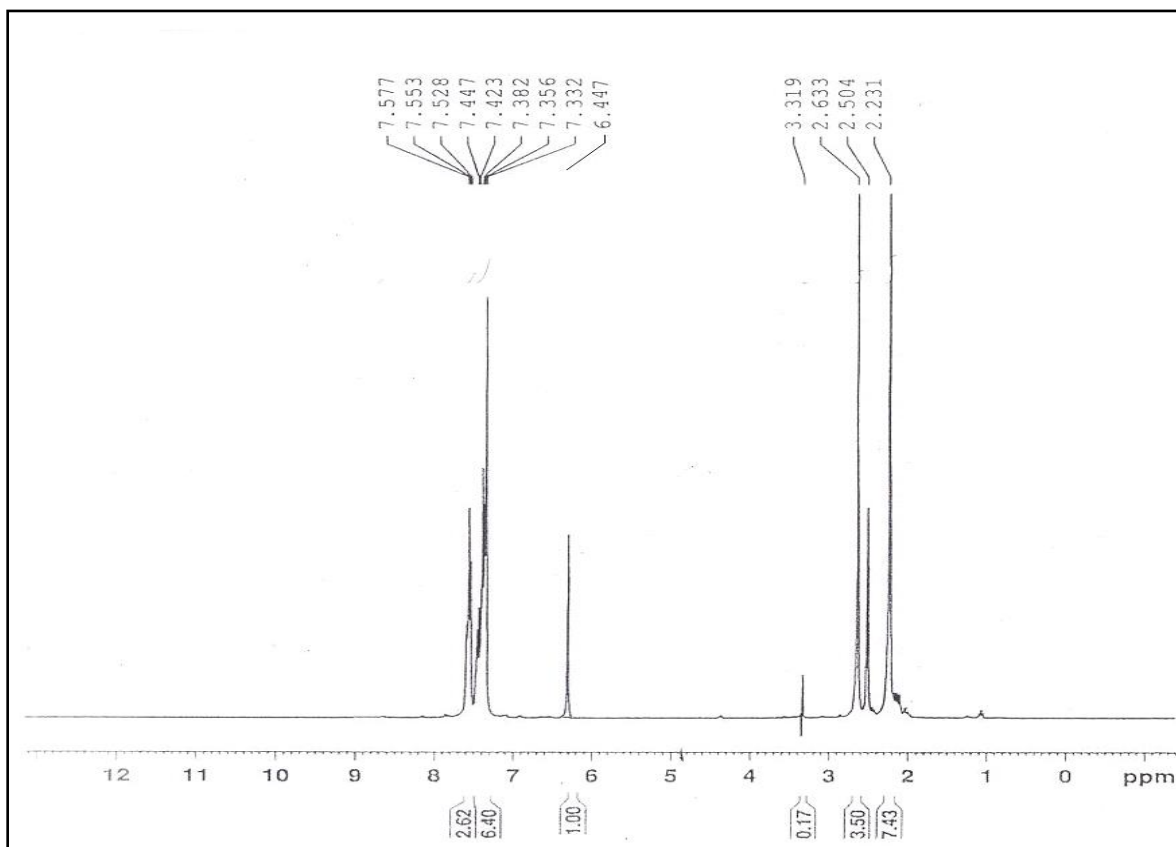br = broad, s= strong, , sh = sharp, sho = shoulder, w = weak

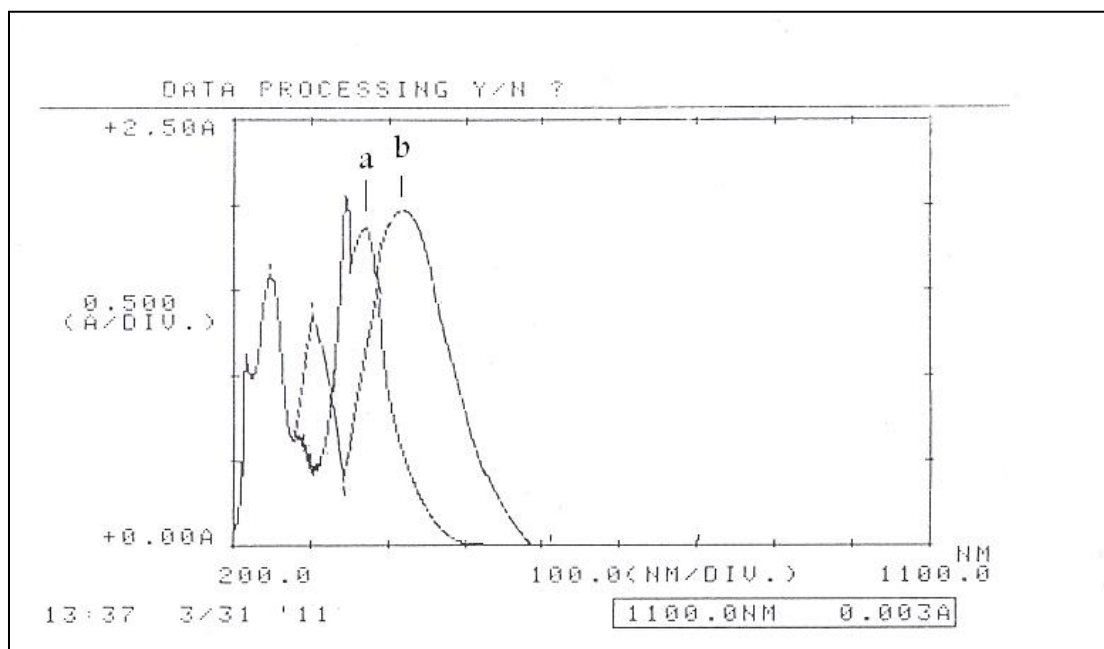Fig.(1):- ^{1}HNMR Spectrum of the Ligand.

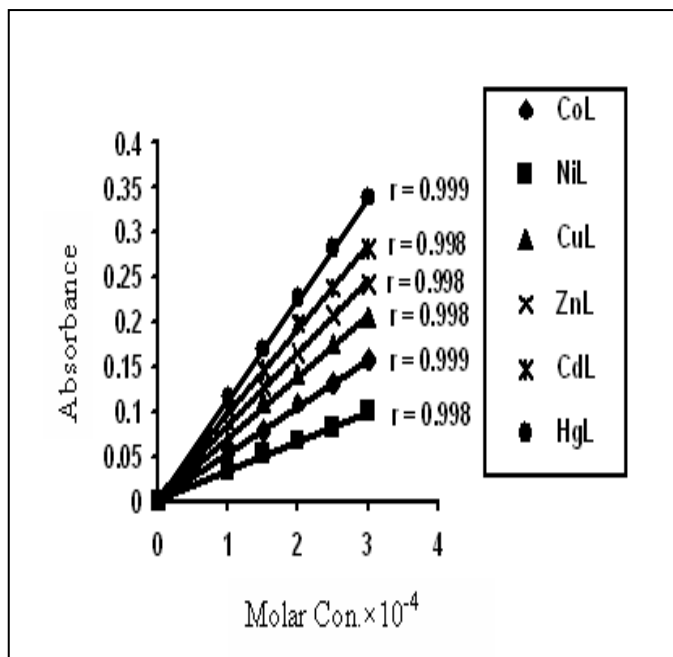Fig.(2): -UV-Vis spectra of a- free Ligand Solution b- Zn^{II}- L Mixed Solution.

Fig.(3):- Linear Relation Between Molar
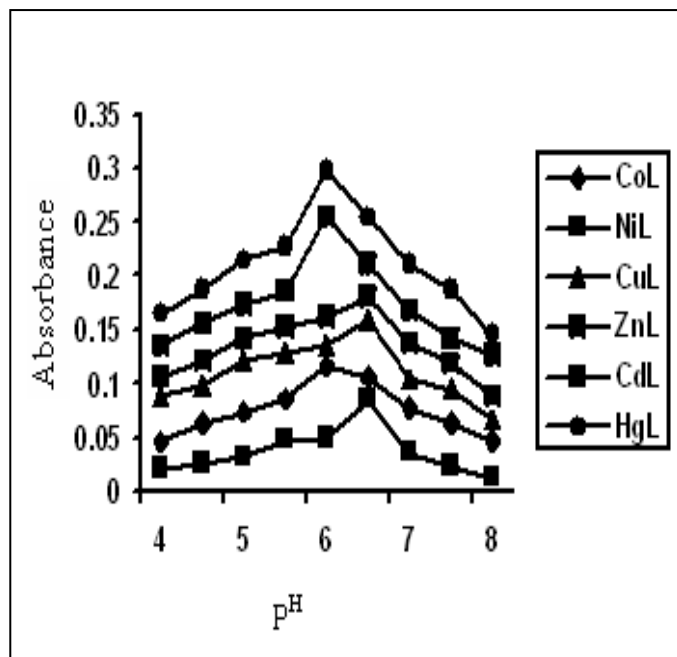Concentration and Absorbance.

Fig.(4):- Effect of pH on Absorbance
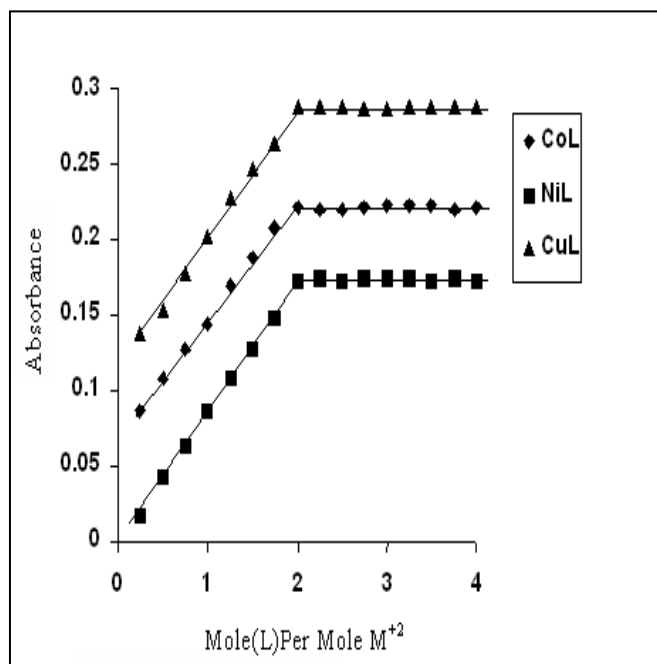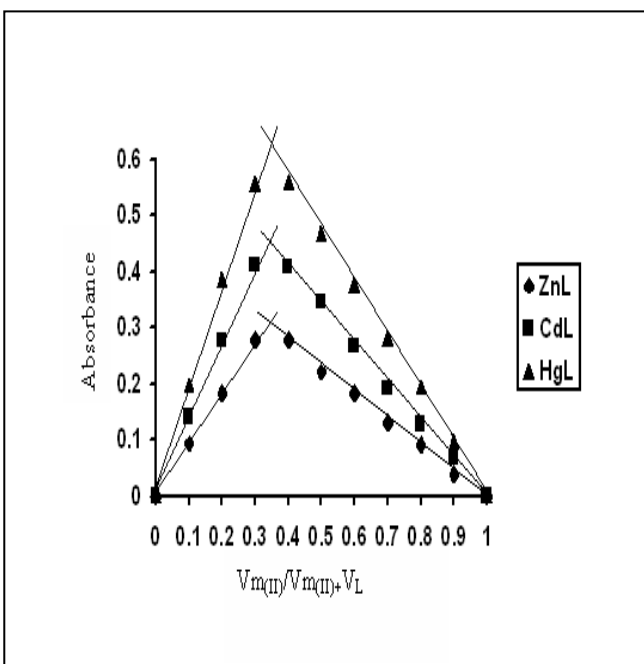(λ_{max}) for Complexes.

Fig.(5):- Mole Ratio and Job Methods for Complexes Solutions.

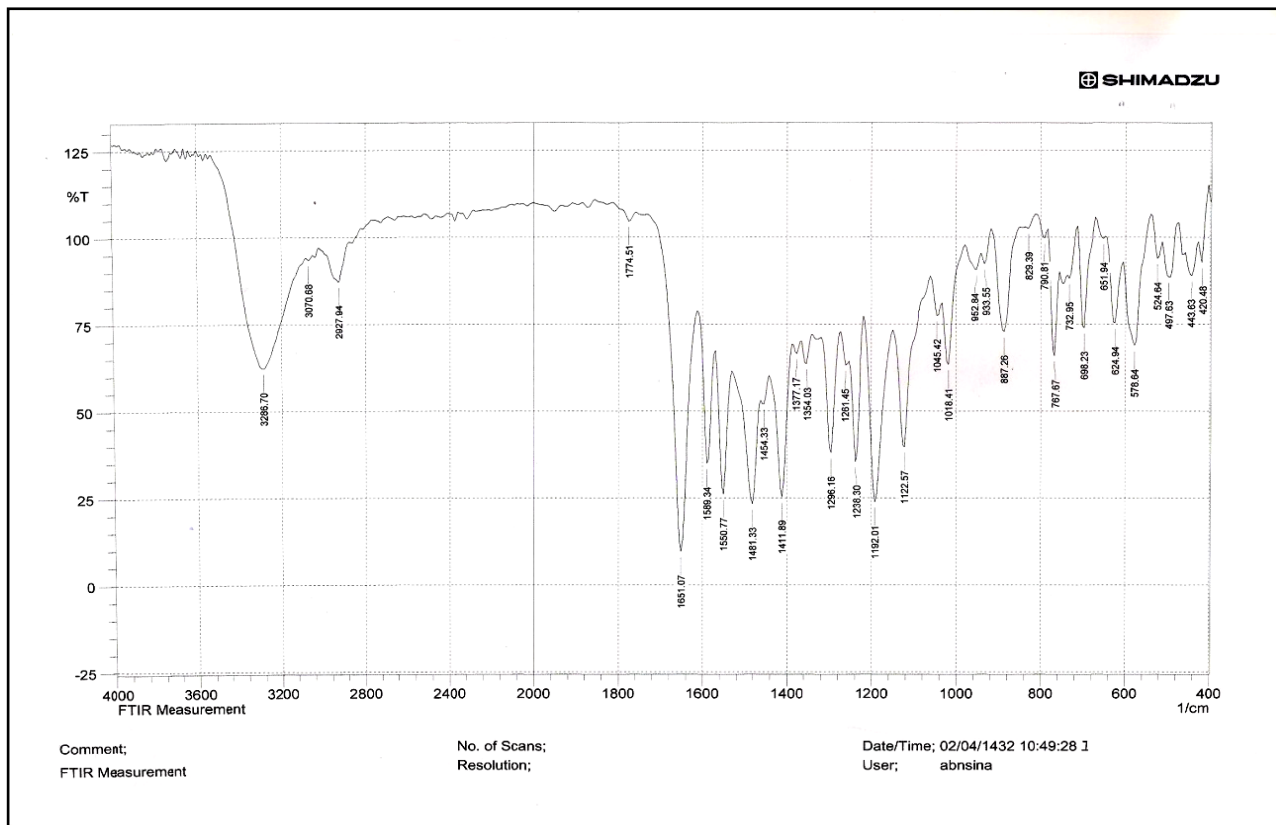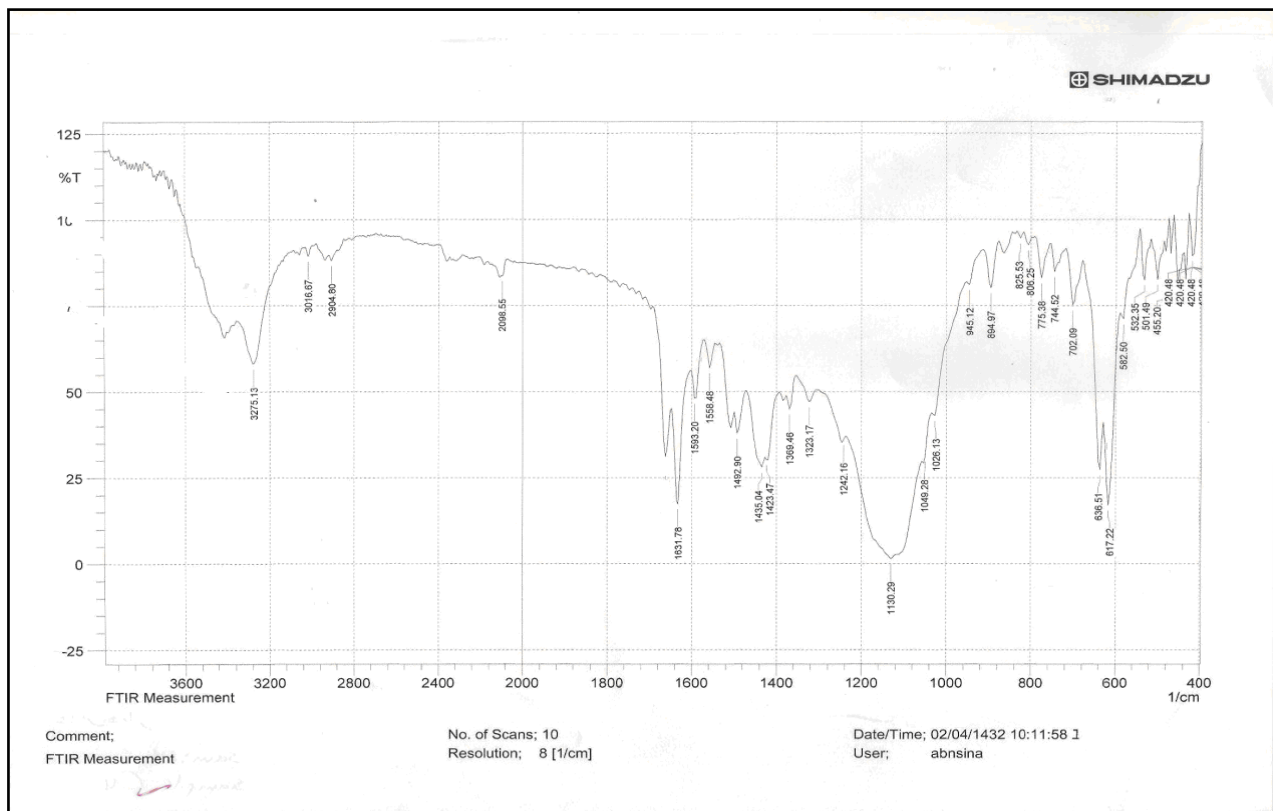Fig.(6):- FT-IR Spectrum of the Ligand.

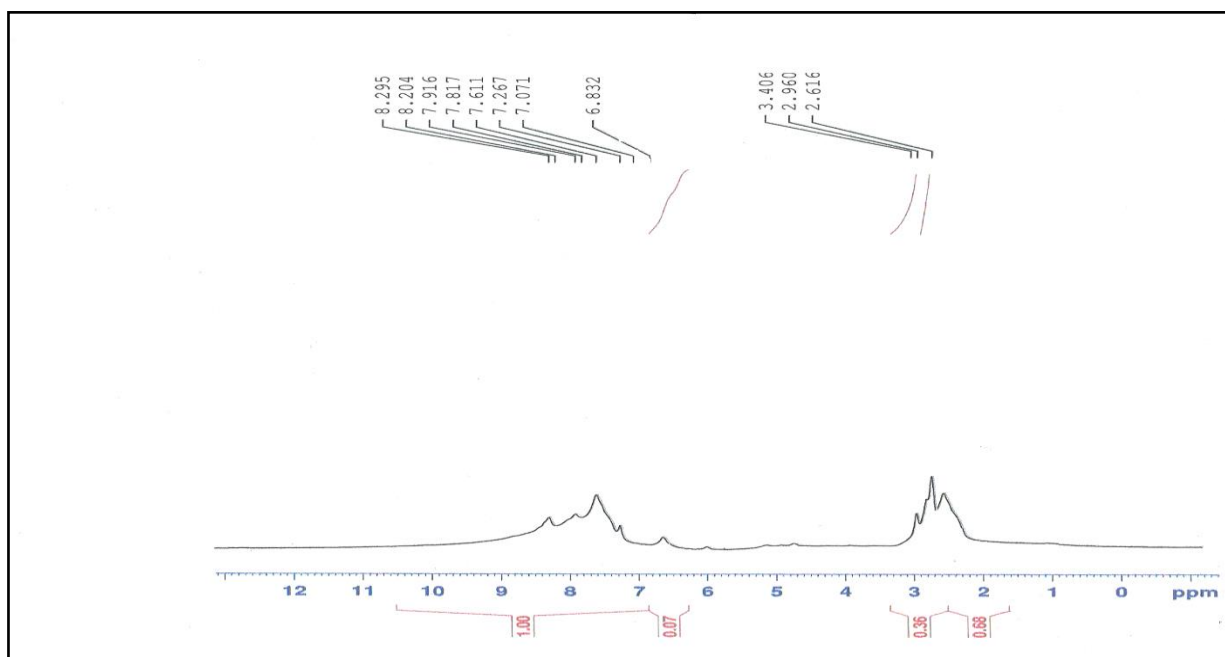Fig.(7):- FT-IR Spectrum of the [Cu(L)$_2$Cl$_2$] Complex.

Fig.(8):- ^{1}HNMR Spectrum of the [Co(L)$_2$Cl$_2$] Complex.