

Synthesis and Spectral Studies of Heterocyclic Azo Dye Complexes with Y(III) and La(III) Ions.

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Abstract

Coupling reaction of 4-amino antipyrine with 2,6-dimethyl phenol gave bidentate azo ligand. The prepared ligand was identified by Microelemental Analysis, ¹HNMR, FT-IR and UV-Vis spectroscopic techniques. Treatment of the prepared ligand with the following metal ions (Y^{III} and La^{III}) in aqueous ethanol with a 1:3 M:L ratio and at optimum pH, yielded a series of neutral complexes of the general formula [M(L)₃]X₃ (X= Cl or NO₃). The prepared complexes were characterized using flame atomic absorption, (C.H.N) Analysis, FT-IR and UV-Vis spectroscopic methods as well as conductivity measurements. 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 absorptivity of the complex solutions were observed. From the obtained data the tetrahedral structure was suggested for all prepared complexes.

Keywords: - complexes, synthesis, pyrazole azo, azo dyes.

Introduction

Azo dyes are a class of compounds containing a N=N double bond and due to their ability to absorb visible light⁽¹⁾. For many years, the azo compounds have been the main class of dyes used in various application such as textile fibers dyeing, coloring of different materials and advanced organic synthesis⁽²⁾. The synthesis and dyeing properties of azo compounds are assigned in many papers^(3,4). It is well known that nitriles are widely used as intermediates in the synthesis of a large number of heterocyclic. Amino pyrazoles can be readily obtained by the reaction of nitriles with phenol derivatives⁽⁵⁾. Pyrazole are an important class of compound because of their biological and pharmacological activities⁽⁶⁾. Also, fused pyrazole moieties have a wide range of interesting properties such as anti-hyperglycemic analgesic, anti-inflammatory, anti-pyretic, anti-bacterial and sedative-hypnotic activities⁽⁷⁾. Azo Pyrazole derivatives and its metal complexes can be used as inkjet and process high dyeing power on fibers. They can also be used in subtractive photographic process

and for the production of color transparencies and color pictures and have many application⁽⁸⁾. The present paper reports the synthesized azo dye derived from 4-amino antipyrine 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 physicochemically.

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 ^1H NMR 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). In addition, melting points were obtained using (Stuart Melting Point Apparatus).

Materials and Reagents

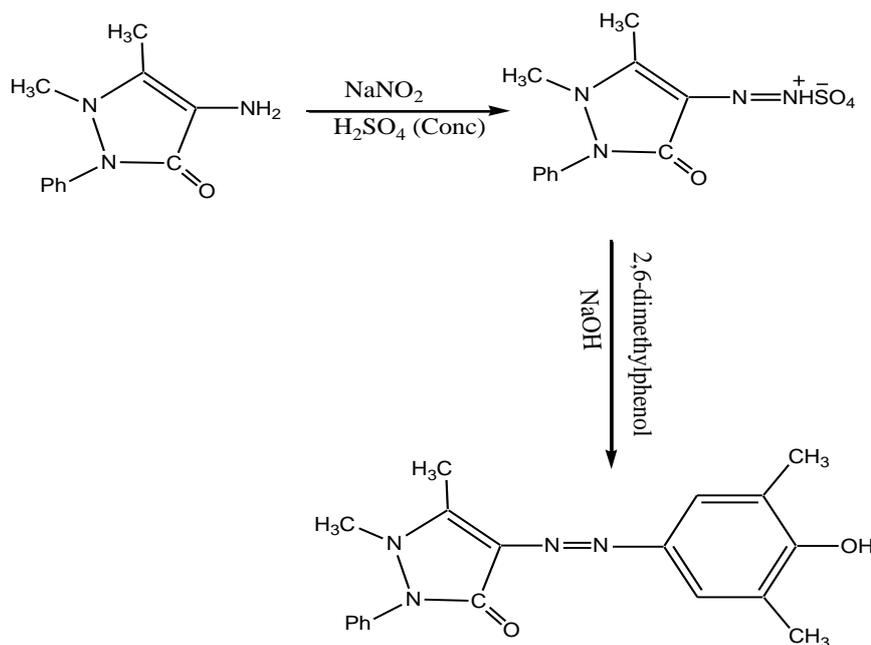
The following chemicals were used as received from suppliers; The following chemicals were used as received from suppliers; lanthanum chloride nonahydrate 98.8% and yttrium nitrate pentahydrate 99.9% (Merck), 4-amino antipyrine and 2,6-dimethyl phenol (B. D. H).

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⁽⁹⁾ (0.508g, 1mmole) of 4-amino antipyrine 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, 3mmole) was added gradually with stirring to the 0.121g and 0.135g of $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{LaCl}_3 \cdot 9\text{H}_2\text{O}$ 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 coupling 2,6-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 ^1H NMR, FT-IR, (C.H.N) and UV-Vis spectroscopic technique.

The ^1H NMR spectrum of the ligand in DMSO (Fig-1) shows multiplet signals at ($\delta=7.332-7.577$ ppm) refers to aromatic protons ⁽¹⁰⁾. On the other hand, the signal at ($\delta= 6.447$ ppm) due to proton of phenol. The $\delta(\text{CH}_3)$ of pyrazole shown in ($\delta= 2.633$ ppm). The signal at ($\delta= 3.319$ ppm) due to $\delta(\text{N}-\text{CH}_3)$ of pyrazole. Whereas, the signal at ($\delta=2.23$ ppm) is assigned to $\delta(\text{CH}_3)$ groups of phenol and the signal peak at ($\delta=2.50$ ppm) referred to $\text{DMSO}-d_6$ ⁽¹¹⁾.

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 $\pi-\pi^*$ transition of the aromatic rings. The third peak (λ_{max}) was observed at the (371nm) was referred to the $\pi-\pi^*$ transition of intermolecular charge-transfer taken place from benzene through the azo group ($-\text{N}=\text{N}$) ⁽¹²⁾.

Interaction of the metal ions (Y^{III} and La^{III}) 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 red.

The interaction of the metal ion with the ligand manifests itself in the absorption spectra by the appearance of a peak at 442 nm and 463 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 Y^{III} 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 (4-9) and the absorbance-pH curves for each metal ion measured at certain (λ_{max}) were plotted. (Fig-4) showed 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 (1:3) 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.

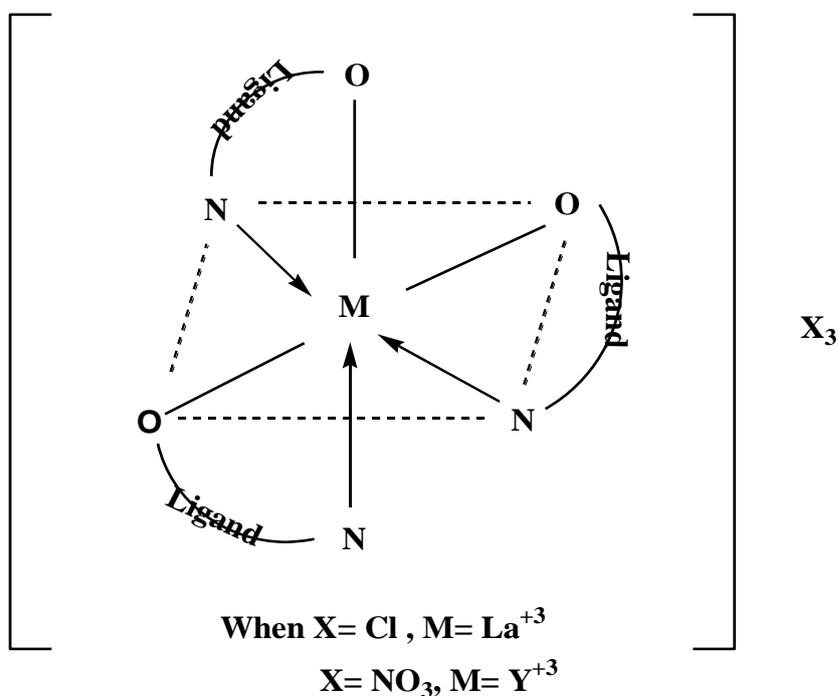
The solid complexes have been prepared by direct reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions at the optimum pH and in a (M:L) ratio of (1:3). The (C.H.N) and metal contents of these complexes were in good agreements with the calculated values.

The molar conductance of the complexes as (10^{-3} M) in ethanol indicating their electrolytic type⁽¹³⁾, 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.

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-3). The IR spectrum of the ligand (Fig-6) exhibited broad band at 3286 cm^{-1} was assigned to the stretching vibration of $\nu(\text{OH})$ group⁽¹⁴⁾. 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 1651 cm^{-1} in the ligand spectrum ascribed to the $\nu(\text{C}=\text{O})$ stretching vibration^(15,16), suffered a great change to lower frequency was observed on complexation (Fig-7) with metal ion. Band characteristic of the azo bridge vibration at 1471 cm^{-1} , on complexes shifted to higher frequency with change in shape was observed indication the engagement of this group in the coordination with the metal ion^(17,18).

The characteristic band in the ligand spectrum at 1377 cm^{-1} which was assigned to the $(-\text{C}=\text{N}-\text{N}=\text{C}-)$ stretching⁽¹⁹⁾, 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 $(456-580)\text{ cm}^{-1}$ are tentatively assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ (Metal-Ligand) stretching bands⁽²⁰⁻²²⁾.

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



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

Compounds	Color	M.P °C	Yield %	Analysis Calc. (Found)			
				M%	C%	H%	N%
Ligand	Orange	280	86	-	67.85 (67.12)	5.95 (4.89)	16.66 (15.35)
[Y(L) ₃]NO ₃	Brown	>360	73	6.93 (5.87)	53.31 (52.64)	4.67 (3.89)	13.09 (12.73)
[La(L) ₃]Cl ₃	Deep	>360	84	11.08	54.56	4.78	13.40
	Brown			(10.34)	(54.06)	(3.78)	(12.56)

Table (2):- Conditions for the Preparation of the Complexes, UV-Vis 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.cm².mol⁻¹) In Absolute ethanol
Ligand	-	-	-	371	1.870	1870	-
[Y(L) ₃]NO ₃	6.5	2	1:3	442	2.036	2036	123
[La(L) ₃]Cl ₃	7	2.5	1:3	463	1.965	1965	125

Table (3):- 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.	1471 s.	1377 sh.	-	-
[Y(L) ₃]NO ₃	3280 br.	1581 sh.	1489 s.	1336 sho.	580 w.	456 w.
[La(L) ₃]Cl ₃	3275 br.	1631 sh.	1492 s.	1369 m.	532 w.	455 w.

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

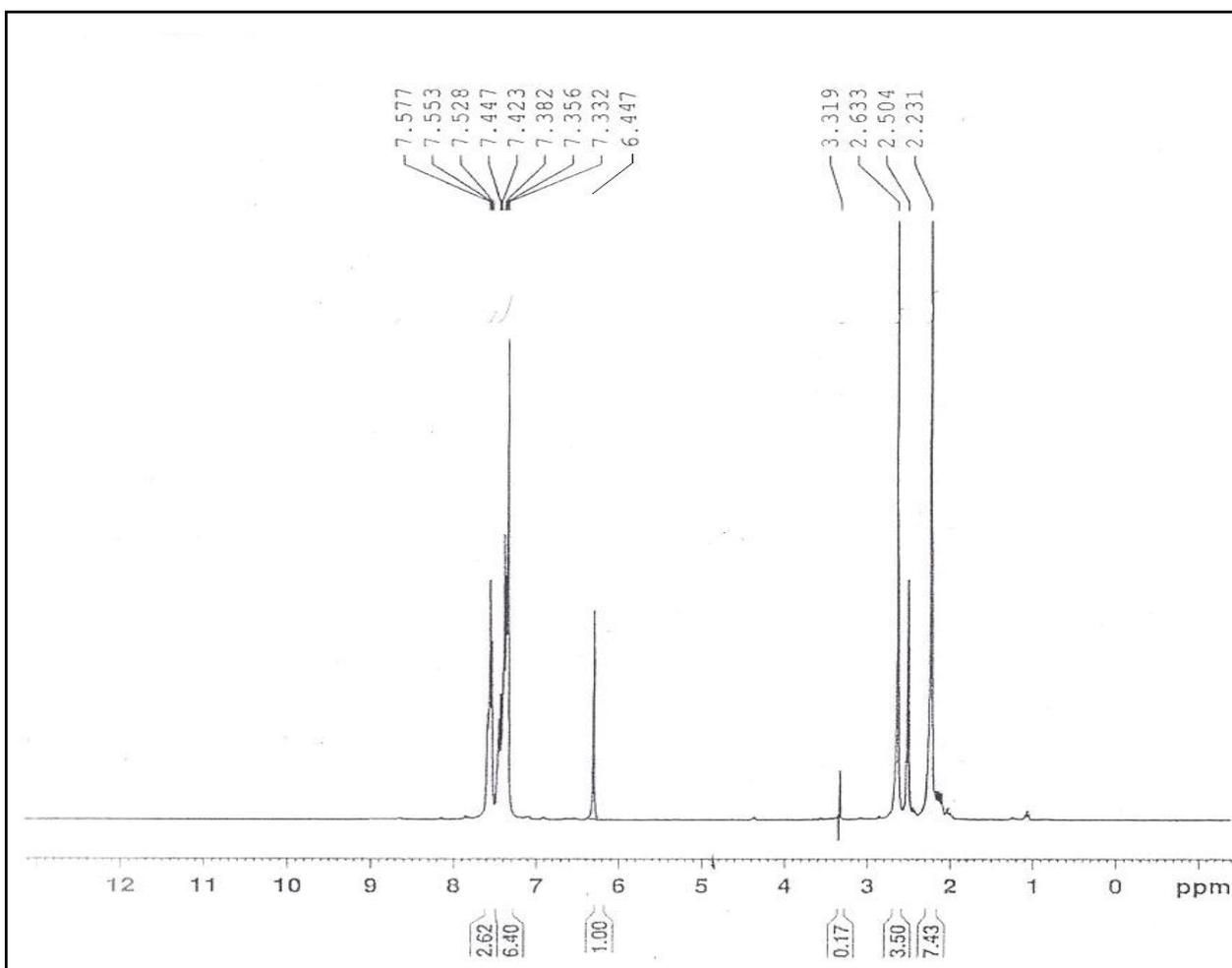


Fig.(1):- ¹H NMR Spectrum of the Ligand.

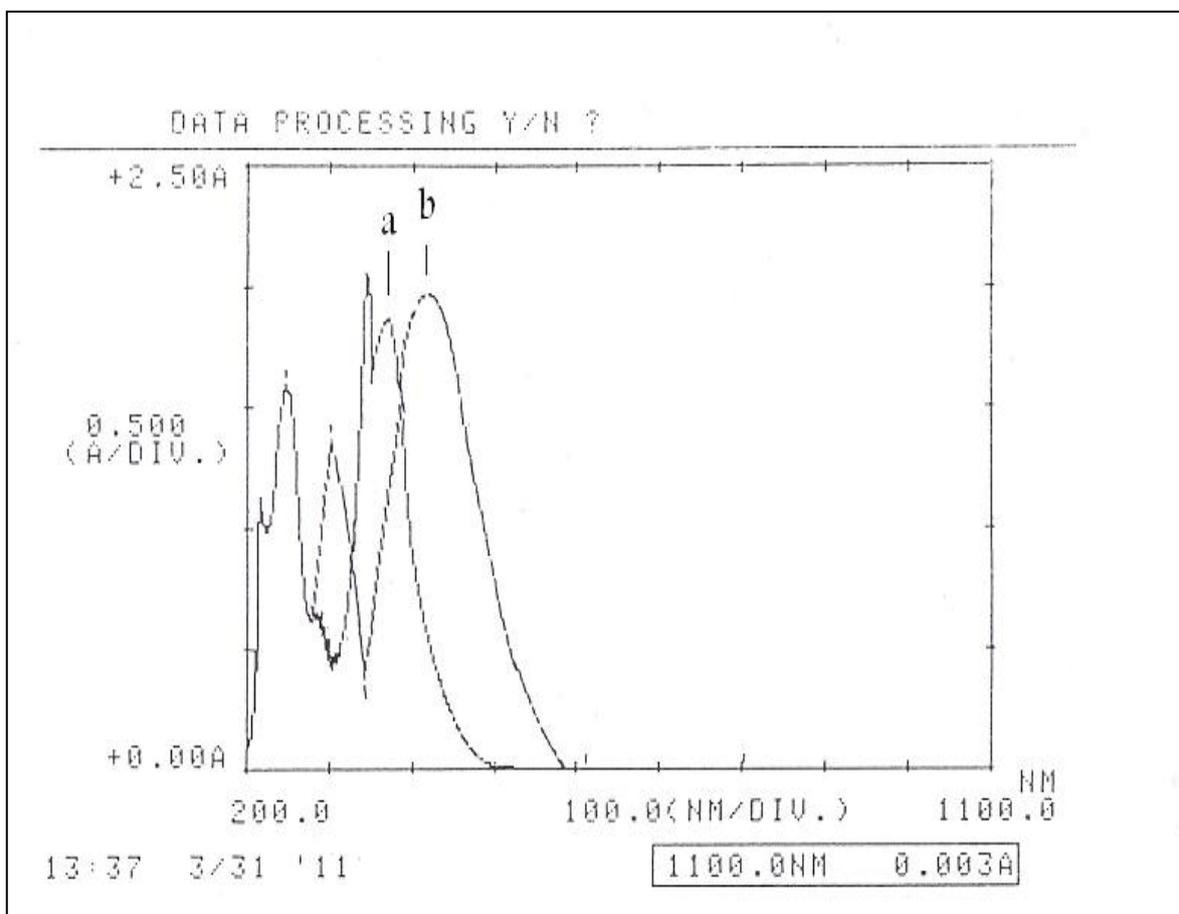


Fig.(2): -UV-Vis spectra of a- free Ligand Solution b- Y^{III} - L Mixed Solution.

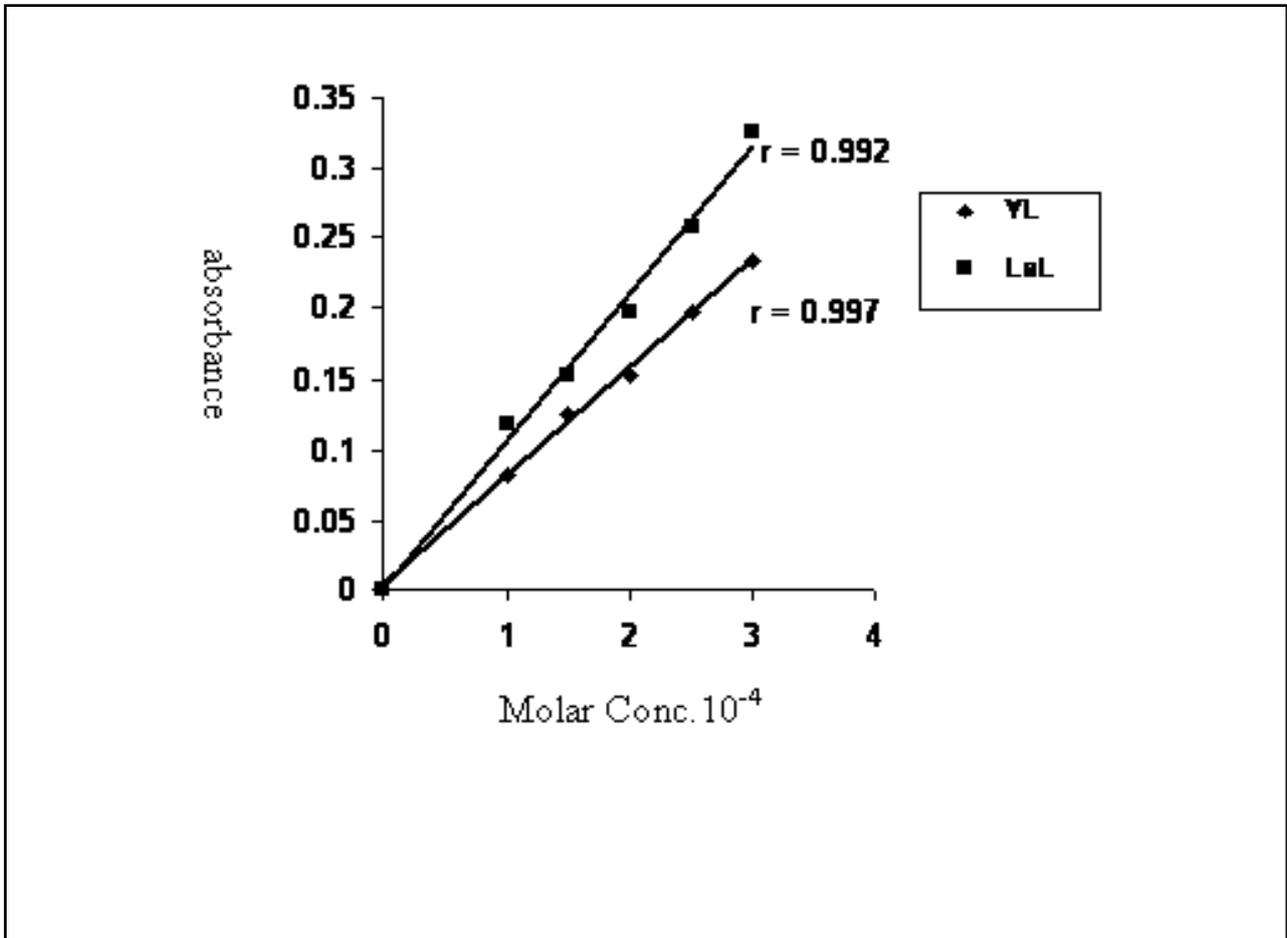


Fig.(3):- Linear Reaction Between Molar Concentration and Absorbance.

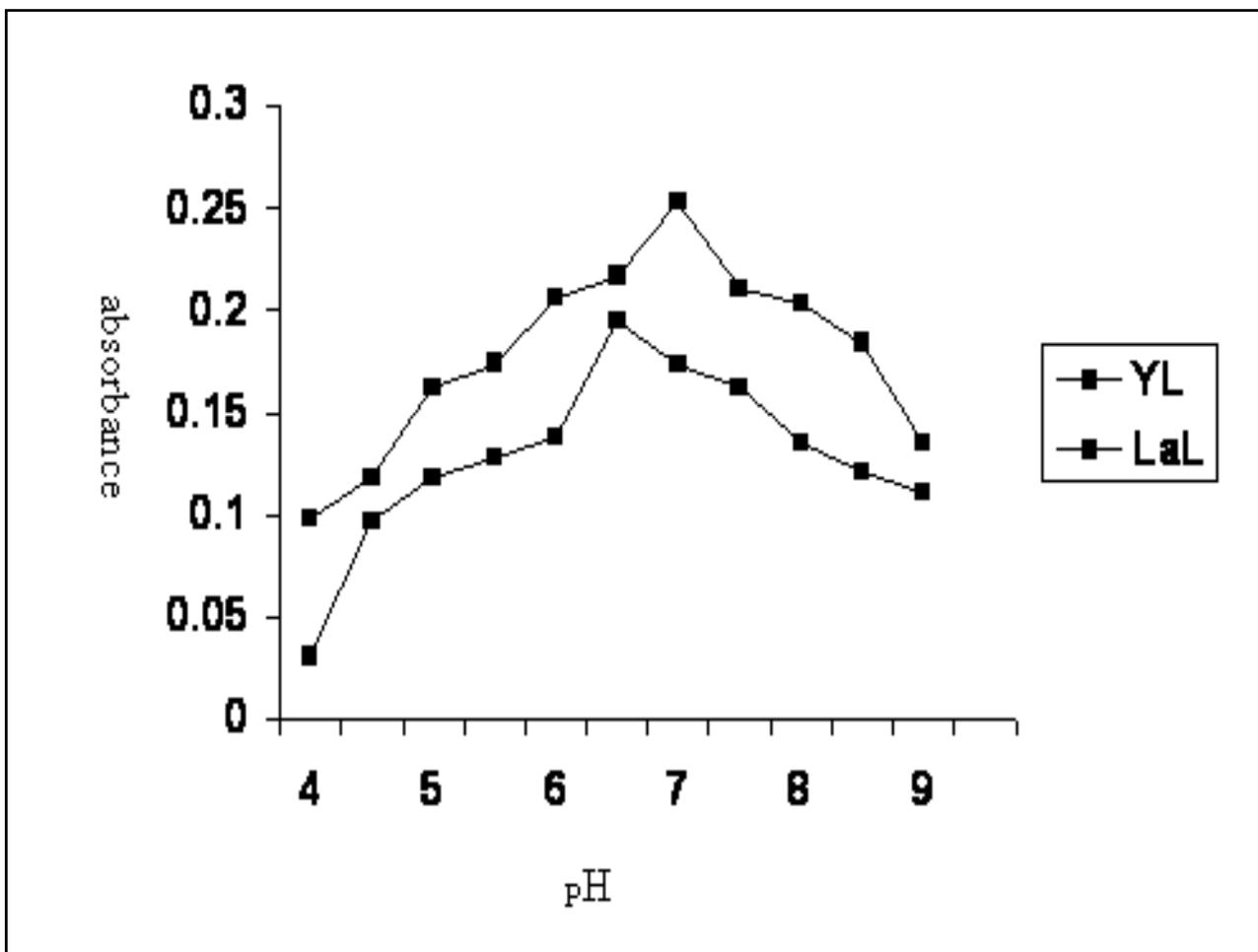


Fig.(4):- Effect of pH on Absorbance (λ_{\max}) for Complexes.

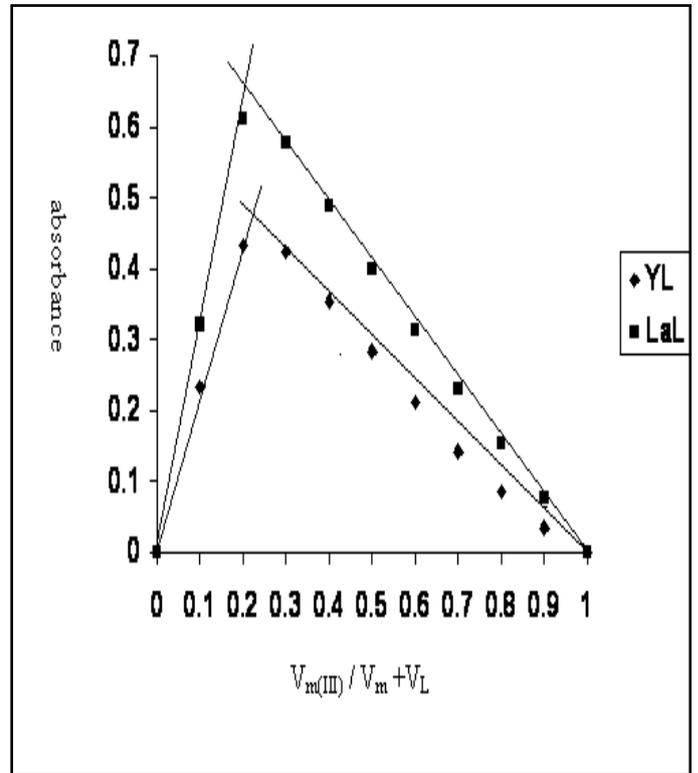
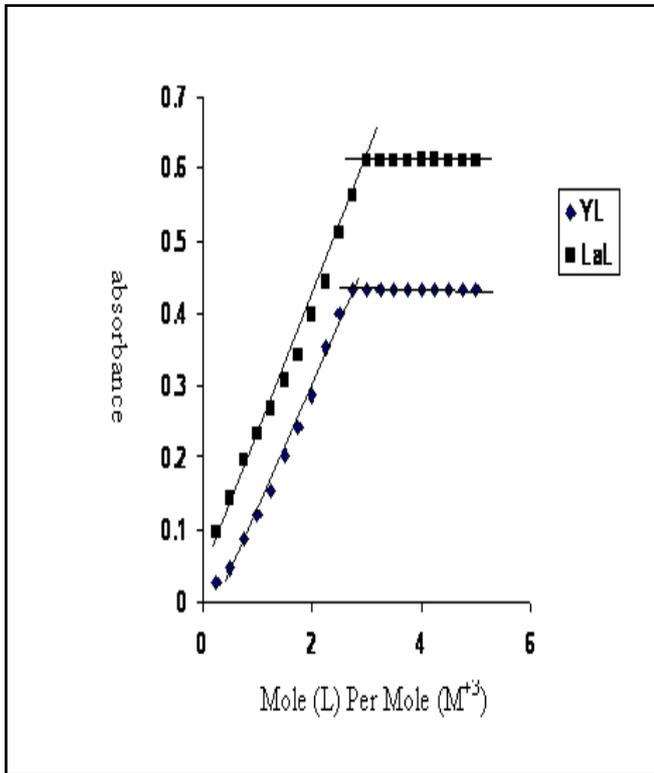


Fig.(5):- Mole Ratio and Job Methods for Complexes Solutions.

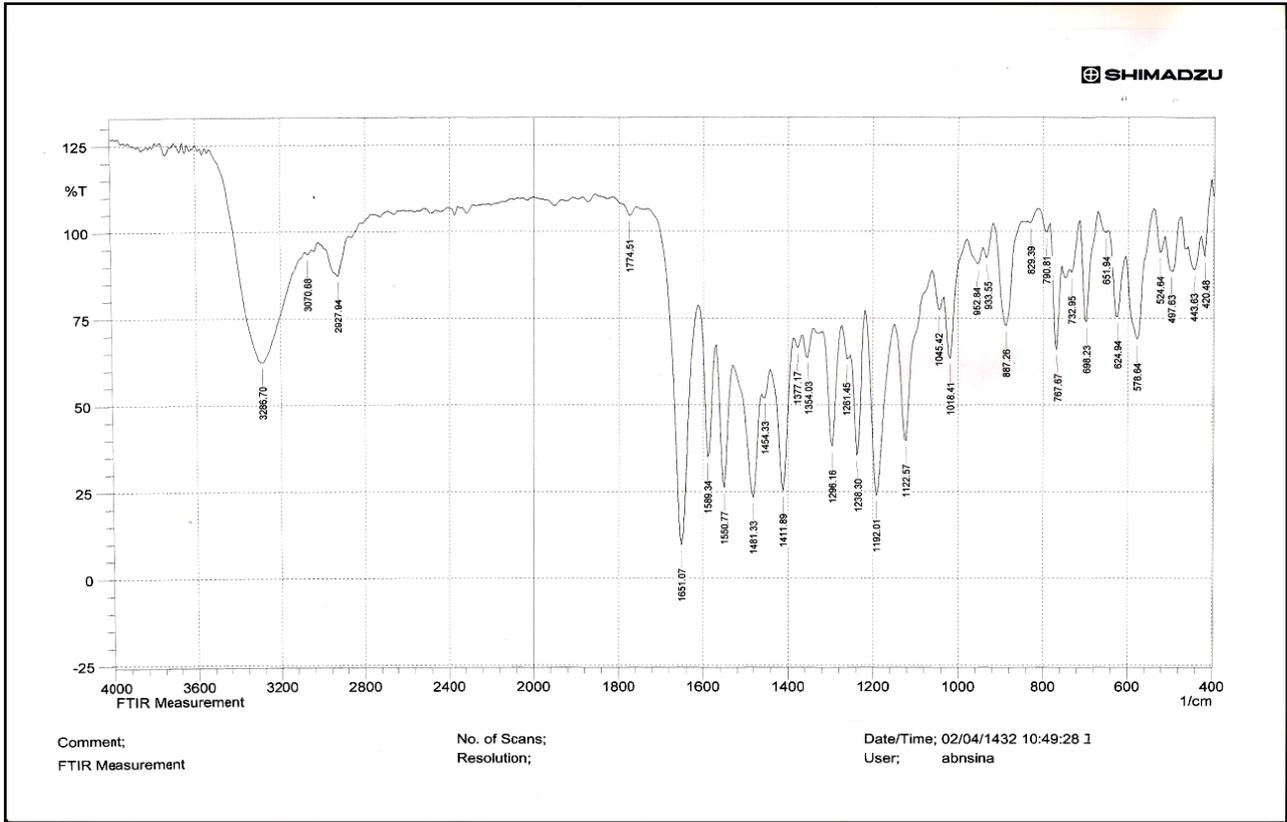


Fig.(6):- FT-IR Spectrum of the Ligand.

تحضير ودراسة طيفية لمعقدات صبغة آزو غير متجانسة الحلقة مع أيونات اليتيريوم اللانثانيوم الثلاثية الشحنة.

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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 أطيف الرنين النووي المغناطيسي والأشعة تحت الحمراء وفوق البنفسجية- المرئية والتحليل الدقيق للعناصر (C.H.N). تمت مفاعلة الليكاند مع أيونات اليتيريوم واللانثانيوم الثلاثية الشحنة في وسط ايثانول - ماء وبنسبة فلز: ليكاند (3:1) وفي الدالة الحامضية المثلى، وخضعت محاليل هذه المعقدات لقانون لامبرت -بيرر ضمن مدى التراكيز (3×10^{-4} M - 1×10^{-4}) وتم الحصول على سلسلة من المعقدات ذات الصيغة العامة $[M(L)_3]X_3$ (X= Cl or NO₃). شخصت هذه المعقدات باستخدام تقنية الامتصاص الذري اللهبى، أطيف الأشعة تحت الحمراء والأشعة فوق البنفسجية - المرئية والتحليل الدقيق للعناصر (C.H.N)، فضلا عن قياسات التوصيلية الكهربائية. درست تراكيب المعقدات باستخدام طريقتي النسب المولية والمتغيرات المستمرة. ومن النتائج المحصول عليها تم اقتراح الشكل ثماني السطوح للمعقدات المحضرة.