

Synthesis, Characterization and Spectral Studies of Y(III), La(III) and Rh(III) Complexes with 2,4-dimethyl-6-(4-nitro-phenylazo)-Phenol .

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Abstract

Transition metal complexes of Y(III), La(III) and Rh(III) with azo dye 2,4-dimethyl-6-(4-nitro-phenylazo)-phenol derived from 4-nitroaniline and 2,4-dimethylphenol were synthesized. Characterization of these compounds has been done on the basis of elemental analysis, electronic data, FT-IR, UV-Vis and ¹HNMR, 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}). High molar absorptivity of the complex solutions were observed. From the analytical data, the stoichiometry of the complexes has been found to be 1:3 (Metal:ligand). On the basis of Physicochemical data octahedral geometries were assigned for the complexes.

Key words: complexes, transition metals, spectral studies, azo dyes.

Introduction

Synthetic dyes produced in large quantities are extensively used in paper printing, textile dyeing, pharmaceutical, food, color photography, cosmetics, textile and other industries[1-3]. For many years the azo compounds have been the main class of dyes used in various applications such as textile fibers dyeing and coloring of different materials and advanced organic synthesis [4-7]. Several bidentate azo dyes in which the phenolic-OH group and azo nitrogen are present in such a way that they form six membered ring with metal ions are published [8]. The vast applications of azo dyes have inspired the modern chemists to prepare new metal chalets by reacting with new poly dentate azo dyes with different transitional and non-transitional metal ions[9]. Recently metal complex dyes have also attracted increasing attention due to their increasing electronic and geometrical features in connection with their application for molecular memory storage[10]. This work presents the synthesis of an azo dye derived from 4-nitro aniline as diazo component and 2,3-dimethylphenol as coupling agent. Complexes of this ligand (L) with Y(III), La(III) and Rh(III) have also been studied and characterized physicochemical.

Experimental

Instrumentations

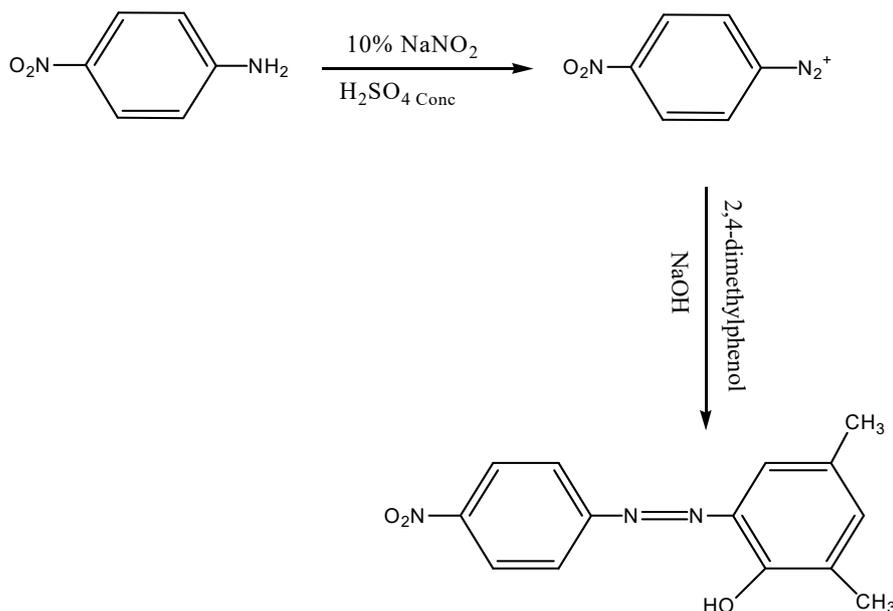
UV- Vis spectra were recorded on a Shimadzu UV- 160A Ultra Violet-Visible Spectrophotometer. IR- spectra were taken on a Shimadzu, FT-IR- 8400S Fourier Transform Infrared Spectrophotometer in the 4000- 400 cm^{-1} spectral regions with samples prepared as KBr discs. Atomic absorption was obtained using a Shimadzu A.A-160A Atomic Absorption/Flame Emission Spectrophotometer. The $^1\text{H-NMR}$ spectra were recorded on a Bruker-300 MHz Ultra Shield spectrometer at University of Al- al- Bayt using DMSO as the solvent and TMS as the reference. Micro elemental analysis (C.H.N) was performed at the Al- al- Bayt University, Jordan, using Euro vector EA 3000A Elemental Analyser. Conductivities were measured for 10^{-3} M solutions of complexes in ethanol at 25°C using Philips PW- Digital Conductmeter. In addition, melting points were obtained using Stuart Melting Point Apparatus.

Materials and Reagents

The following chemicals were used as received from suppliers: Yttrium nitrate pentahydrate (99.9%), Lanthanum chloride nonahydrate (98.8%) and Rhodium chloride monohydrate (98.8%) (Merck), 4-nitroaniline and 2,4-dimethylphenol (B.D.H).

Preparation of 2,4-Dimethyl-6-(4-nitro-phenylazo)-phenol Ligand (L)

A solution of 4-nitroaniline[11] (0.342g, 1mmole) (10ml) of EtOH solution contain (2ml) conc. H_2SO_4 was diluted with 10 ml H_2O , and diazotized at 5°C with NaNO_2 solution. The diazo solution was added drop wise with stirring to a cooled ethanolic solution of (0.305g, 1mmole) of 2,4-dimethylphenol. 25 ml of 1M sodium hydroxide solution was added to the dark colored mixture. The precipitate was filtered, 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 micro analysis.



Scheme (1)

Buffer Solution

Buffer solution, covering the pH range of 4-9, were prepared as 0.01 M solutions of ammonium acetate in distilled water. The required pH was obtained by the addition of either ammonia solution or glacial acetic acid.

Metal Salt Solutions

Solutions of (1×10^{-5} - 1×10^{-3} M) of the metal salt were prepared by dissolving appropriate weight of the metal salt in the buffer solutions.

Ligand Solution

Ligand solutions of (1×10^{-5} - 1×10^{-3} M) were prepared by dissolving a required weight of the ligand in ethanol.

Preparation of Metal Complex (general procedure)

An ethanolic solution of the ligand (L) (0.271g, 3mmole) was added gradually with stirring to the 0.120g, 0.134g and 0.075g of $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{LaCl}_3 \cdot 9\text{H}_2\text{O}$ and $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ dissolved in the buffer solution with the required pH. The mixture was cooled until dark color precipitate was formed, filtered, and washed several times with 1:1 water: ethanol mixture, then with acetone.

Results and Discussion

The ligand 2,4-Dimethyl-6-(4-nitro-phenylazo)-phenol (L) was prepared by coupling 2,4-dimethylphenol with the 4-NO₂.Phenol.diazonium in alkaline solution. The ligand (L) was sparingly soluble in water but soluble in organic solvents such as DMSO and DMF, stable toward air and moisture.

Synthesized ligand (L) was characterized by ¹HNMR, FT-IR, Elem.Anal. (C.H.N) and UV-Vis spectroscopic technique. The ¹HNMR spectrum of the ligand in DMSO (Figure 1) shows multiplet signal at $\delta=7.36-7.77$ ppm, which refers to aromatic protons[12]. A signal at $\delta = 4.32$ ppm appears due to hydrogen atom of the phenolic group[13]. The signal at $\delta= 3.33$ ppm is assigned to $\delta(\text{CH}_3)$ and the signal at $\delta=2.50$ ppm referred to DMSO-d₆ [14].

Interaction of the metal ions (Y^{III}, La^{III} and Rh^{III}) with the prepared ligand (L) has been studied in solution; an aqueous- ethanolic solution was always performed over wide molar concentration and acidity range. Colours of these mixed solutions were varied from brown to yellow. Different ranges of molar concentrations (10^{-5} - 10^{-3} M) of the mixed solutions, only concentrations in the range of 10^{-4} M obey the Lambert- Beer's law, and only these solutions showed intense colour. A calibration curve was fitted to data points in the range $1.10^{-4} - 3.10^{-4}$ M, which shows absorbance against molar concentration (Figure 2). Best fit straight lines were obtained with correlation factor of $R > 0.998$. The optimal concentration was chosen for complex solutions, and it was observed that the absorption maximum (λ_{max}) remained the same at different pH values. The influence of pH was also studied in the pH range of 4-8, and the absorbance- pH curves for each metal ion measured at λ_{max} are plotted in Figure(3). Figure (3) shows selective pH-absorbance curves. The plateaus of the curves represent the completion of the reaction and consequently represent the optimum pH value.

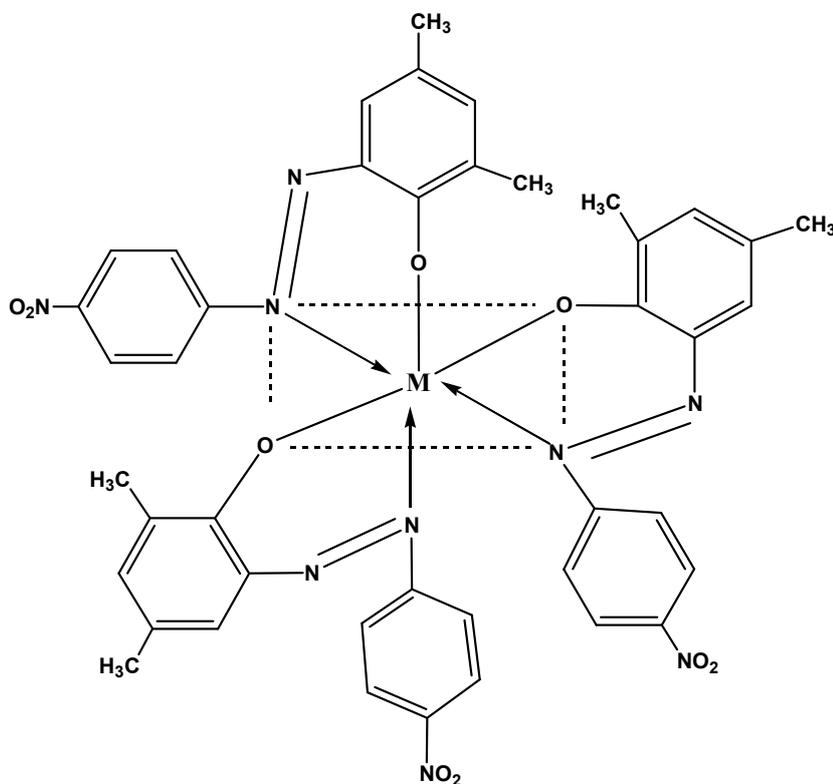
The composition of complexes formed in solutions has been established by mole ratio and job methods. In both cases the results reveal a 1:3 metal to ligand (L) ratio. A selected plot is presented in Figure (4). Table(2) summarizes the results obtained, as well as conditions for the preparation of the complexes.

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

The molar conductance of 10^{-3} M in ethanolic solutions of these complexes indicated their non- electrolytic type[15], data are presented in Table 2. The UV- Vis spectrum of an ethanolic solution of the ligand 10^{-3} M displayed mainly two peaks, the first was observed at 350 nm due to the moderate energy $\pi-\pi^*$ transition of the aromatic rings and the second peak was observed at the 422 nm was referred to the $n-\pi^*$ transition of (-N=N) group[16]. The spectra of the prepared complexes dissolved in ethanol 10^{-3} M have been measured and the data obtained are included in Table (2). The large bathchromic shift of the absorption maximum (λ_{max}), assigned to ($n-\pi^*$) transition of the ligand (L), suggests the involvement of the ligand (L) in the bond formation with the metal ion. Figure 5 showed a comparison between the spectra of the ligand and Rh(III) complex.

In order to study the bonding mode of the ligand (L) with the metal ion, the FT-IR spectra of the free ligand (L) and the prepared complexes have been compared, and the data was tabulated in Table (3). The IR spectrum of the ligand (Figure 6) exhibited broad band at 3462 cm^{-1} , which was assigned to the stretching vibration of $\nu(\text{OH})$ group. This band was absent in the spectra of the prepared complexes (Figure 7), which indicated deprotonation and involvement of the enol oxygen in chelation[17,18]. Bands characteristic of the azo bridge vibration at 1489 cm^{-1} and 1429 cm^{-1} shifted to lower frequency with change in shape in spectra of the complexes, which is an indication of the engagement of this group in the coordination with the metal ion[19]. The appearance of new bands in the region (482-572) cm^{-1} are tentatively assigned to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ (Metal-Ligand) stretching bands[20,21].

According to the results obtained, an octahedral structure has been tentatively suggested to rhodium complex.



M = Y(III), La(III) and Rh(III)

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Table (1): Physical properties and elemental analysis of the ligand and its complexes.

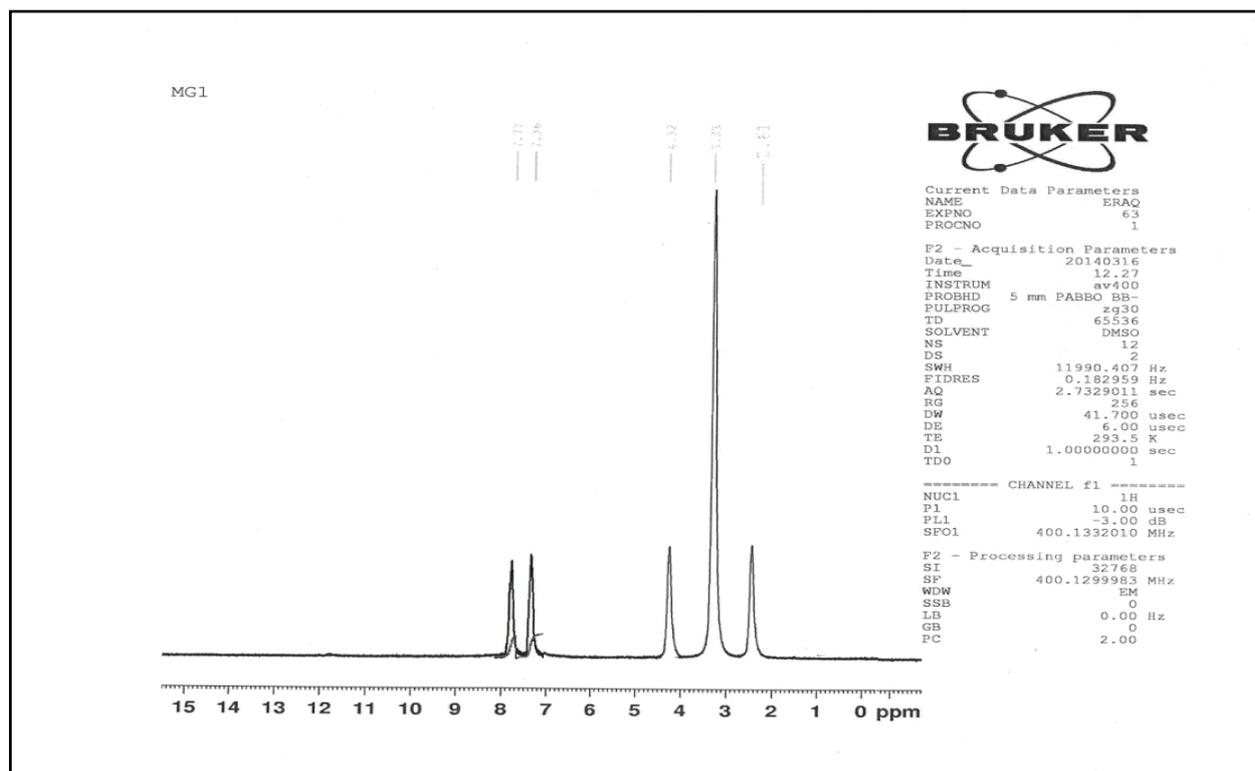
Compounds	Color	M.P ^o C	Yield %	Analysis Calc (Found)			
				M%	C%	H%	N%
Ligand(L)	Orange	246	82	-	61.99 (60.95)	4.79 (3.81)	15.49 (14.53)
[Y(L) ₃]	Brown	280	68	24.38 (23.74)	56.06 (55.73)	4.00 (3.95)	14.01 (13.75)
[La(L) ₃]	Deep brown	325	71	14.64 (13.96)	53.10 (52.58)	3.79 (2.93)	13.27 (12.88)
[Rh(L) ₃]	Deep yellow	>360	73	11.28 (10.93)	55.20 (54.88)	3.94 (3.15)	13.80 (12.63)

Table (2): Conditions for the preparation of the complexes and UV-Vis, 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
Ligand(L)	-	-	-	350 422	1.951 1.176	1951 1176	-
[Y(L) ₃]	8	2	1:3	394 547	0.836 0.381	836 381	18.37
[La(L) ₃]	7	2.5	1:3	348 490	0.926 0.627	926 627	12.85
[Rh(L) ₃]	7	2.5	1:3	284 395 530 969	1.472 0.483 1.371 1.126	1472 483 1371 1126	16.24

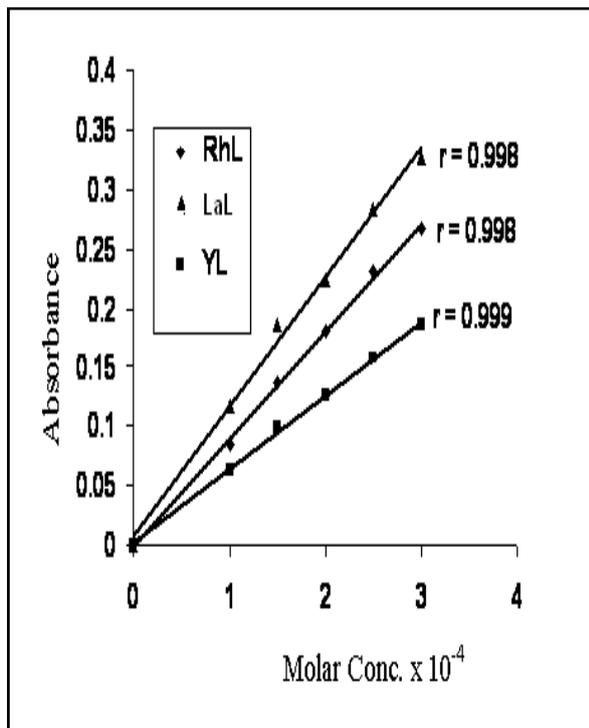
Table (3): The main frequencies of the ligand and its complexes (cm⁻¹).

Compounds	ν (OH)	ν (-N=N-)	ν (M-N)	ν (M-O)
Ligand(L)	3462 br.	1489 sh. 1427 Sh.	-	-
[Y(L) ₃]	-	1462 sh. 1418 s.	572 w.	485 w.
[La(L) ₃]		1470 s. 1420 s.	567 w.	494 w.
[Rh(L) ₃]	-	1450 s. 1420 s.	553 w.	482 w.

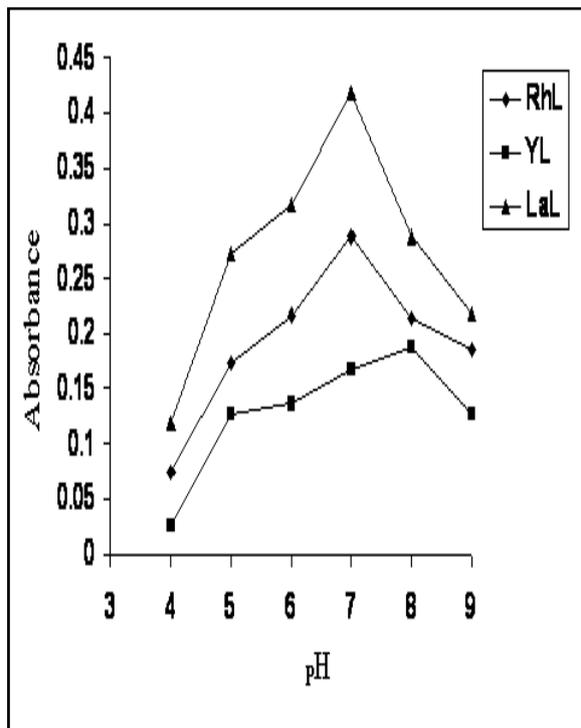


br = broad, s= strong, , sh = sharp, w = weak

Figure (1): ¹HNMR spectrum of the ligand.



Figure(2): Linear relation between molar concentration and absorbance.



Figure(3): Effect of pH on absorbance (λ_{max}) for complexes.

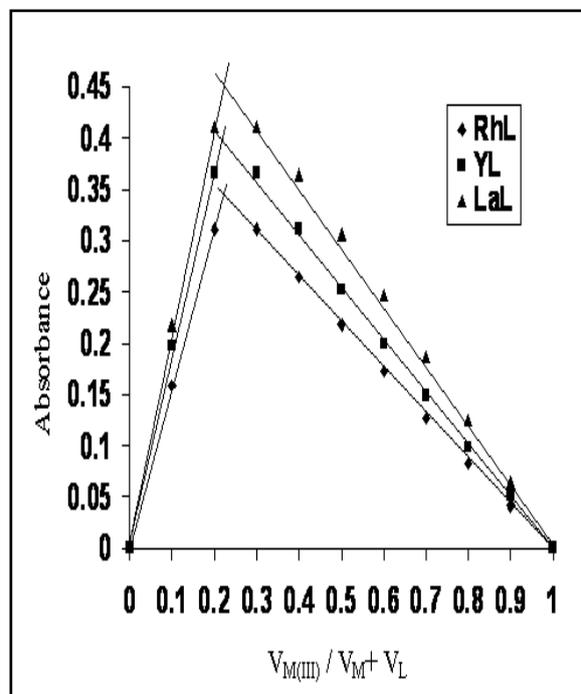
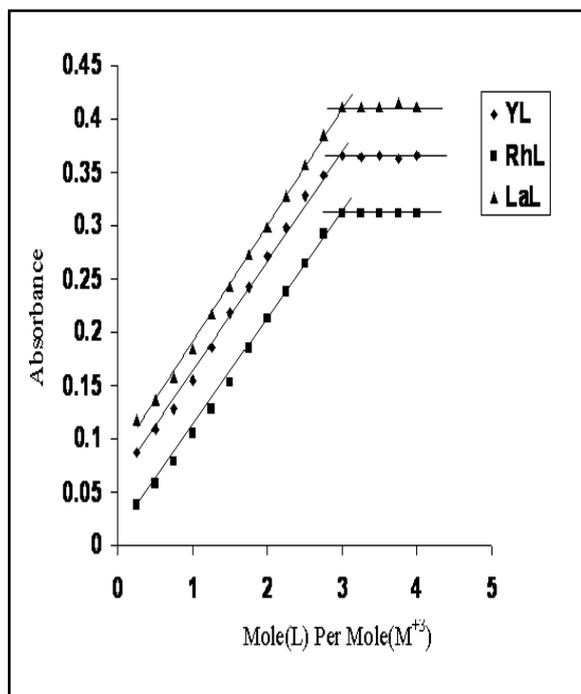


Figure (4): Mole ratio and Job methods for complex solution.

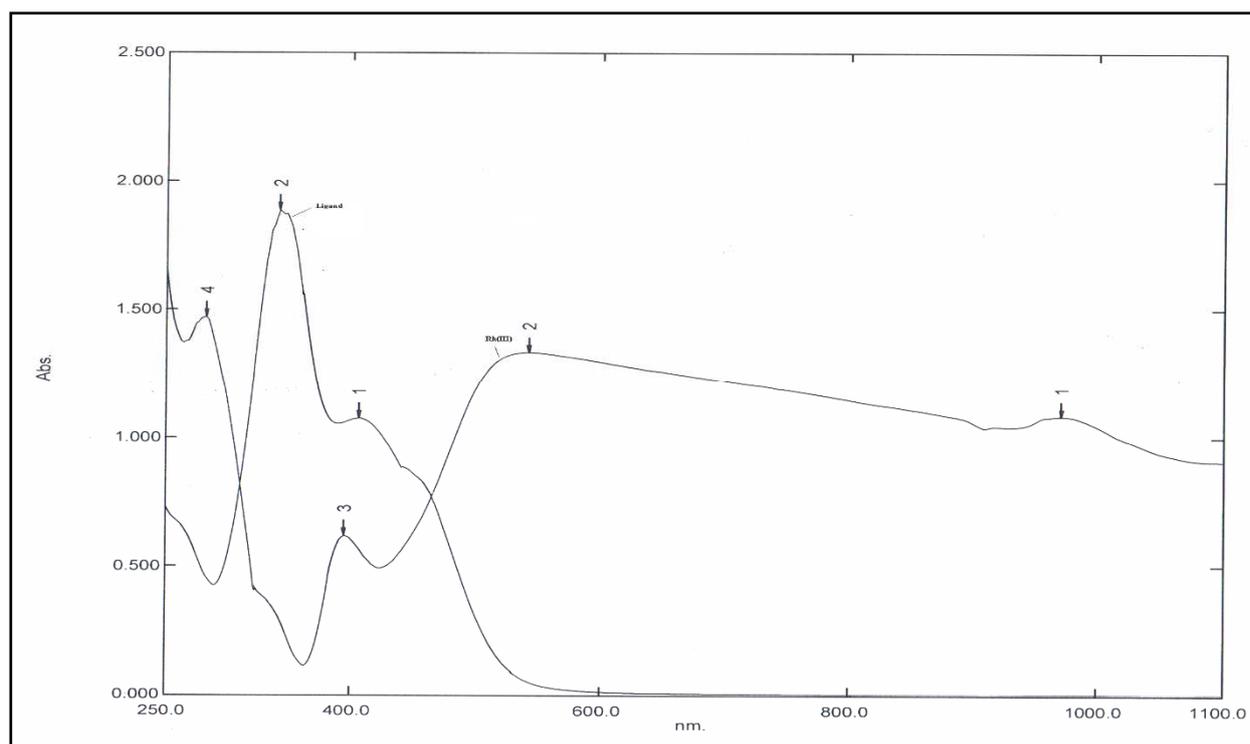


Figure (5): UV-Vis spectra of free ligand and Rh^{III} complex

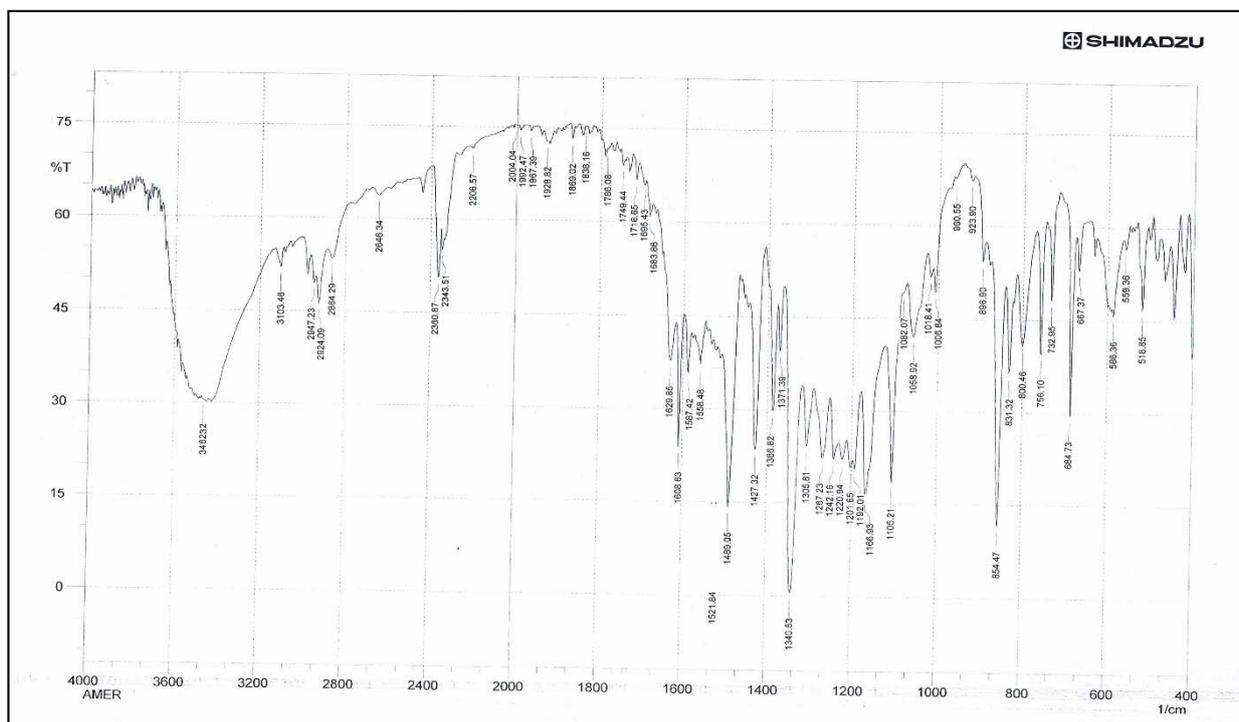


Figure (6): FT-IR spectrum of the ligand.

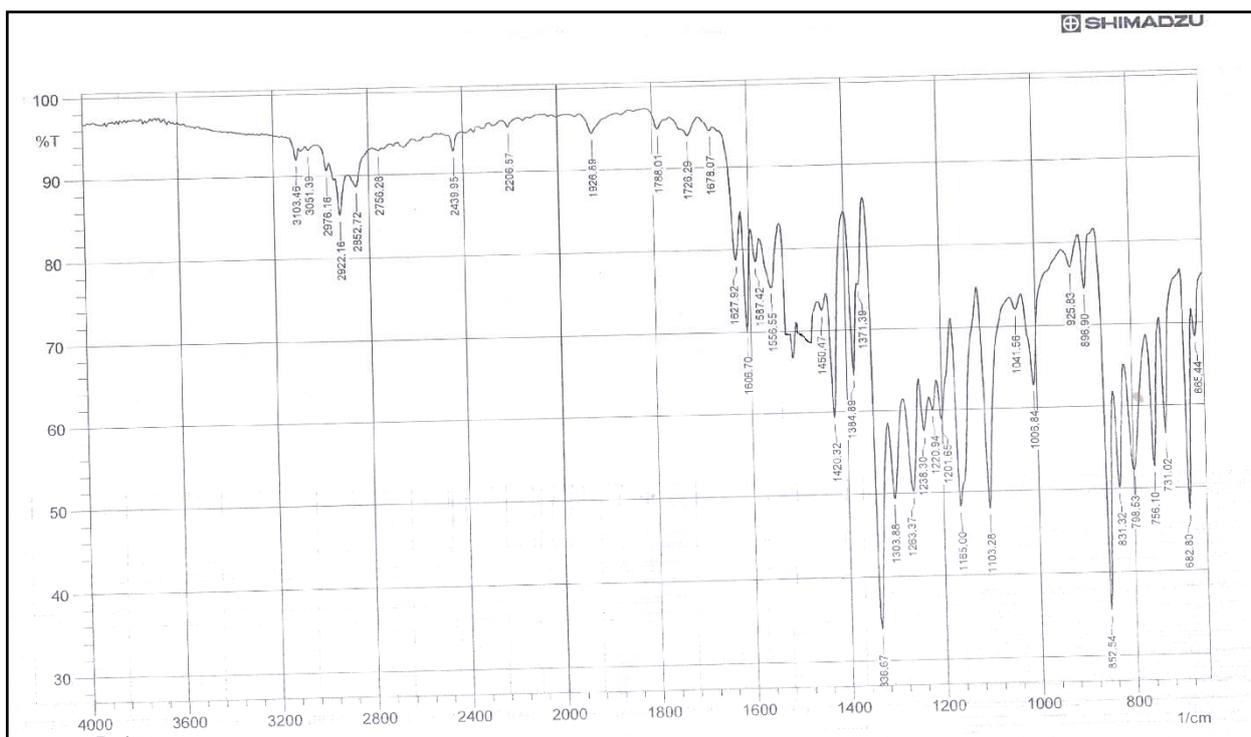


Figure (7): FT-IR spectrum of the $[\text{Rh}(\text{L})_3]$ complex.

تحضير وتشخيص ودراسة طيفية لمعقدات الليتيريوم (III)، اللانثانيوم(III) والروديوم (III) مع 2،4- ثنائي مثيل -6- (4- نيترو- فينيل آزو)- فينول

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الخلاصة

حضرت معقدات الليتيريوم، اللانثانيوم والروديوم الثلاثية الشحنة مع الليكاند 2،4- ثنائي مثيل -6- (4- نيترو - فينيل آزو)- فينول المشتقة من تفاعل ازدواج 4-نايتروانيلين مع 2،4- ثنائي مثيل فينول. شخّصت المركبات المحضرة بوساطة أطياف الرنين النووي المغناطيسي، الأشعة تحت الحمراء وفوق البنفسجية- المرئية والتحليل الدقيق للعناصر (C.H.N)، فضلا عن قياسات التوصيلية الكهربائية. درست تراكيب المعقدات باستعمال طريقتي النسب المولية والمتغيرات المستمرة، وخضعت محاليل هذه المعقدات لقانون لامبرت - بير ضمن مدى التراكيز (3×10^{-4} - 1×10^{-4} M) ومن النتائج الطيفية والتحليلية وجد ان نسبة التفاعل هي (3:1) فلز: ليكاند. ومن النتائج المحصول عليها تم اقتراح الشكل ثماني السطوح للمعقدات المحضرة.

الكلمات مفتاحية:- المعقدات، العناصر الإنتقالية، الدراسات الطيفية، اصباغ الأزو.