

## Preparation and characterization of Trivalent lanthanide ion complexes with tridentate mono azo Ligand

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تحضير وتشخيص معقدات اللانثيدات مع ليكاند ثلاثي المخلب واحادي الأزو  
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### الخلاصة

يتناول البحث تحضير معقدات 4-(2-بيريديل أزو)- ريزورسينول مع عناصر اللانثانات في حالة صلبة، و بعد تحضير المعقدات الناتجة تم التعرف على تراكيب هذه المعقدات بواسطة التحليل الدقيق والقياسات التوصيلية المولارية والحساسية المغناطيسية و درست أيضا بوساطة (N.H.C) للعناصر تقنيات التحليل الطيفية ( كما الأشعة تحت الحمراء و الأشعة فوق البنفسجية- المرئية) كذلك فقد شملت الدراسة أيضاً إجراء التحليل الحرارية.

تم التعبير عن صيغ المعقدات بالصيغ الآتية

$[ \text{Ln}(\text{C}_{11}\text{H}_8\text{N}_3\text{O}_2)_3 ] \cdot \text{H}_2\text{O}$  Ln =  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Sm}^{3+}$ ;  $[ \text{Ln}(\text{C}_{11}\text{H}_8\text{N}_3\text{O}_2)_3 ]$  Ln =  $\text{Eu}^{3+}$ ,  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  يتصرف الليكاند كثلاثي السن متعادل و أحادي الشحنة بعد فقدانها لذرة من مجموعة الهيدروكسيل ، تظهر الأيونات الفلزية للثنائات تناسقا (deprotonated) الهيدروجين ninecoordination. مساويا الي تسعة في معقداتها.

### ABSTRACT

The lanthanide complexes of 4-(2-pyridylazo)-resorcinol are prepared in solid state. All compounds have been characterized by means of elemental analysis (C.H.N) molar conductance, magnetic susceptibility and analytical spectral studies IR and UV-Visible spectral techniques. While the complexes have additionally been characterized by differential thermal analysis data and are formulated as  $[ \text{Ln}(\text{C}_{11}\text{H}_8\text{N}_3\text{O}_2)_3 ] \cdot \text{H}_2\text{O}$  Ln =  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Sm}^{3+}$ ;  $[ \text{Ln}(\text{C}_{11}\text{H}_8\text{N}_3\text{O}_2)_3 ]$  Ln =  $\text{Eu}^{3+}$ ,  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$ . The results of these studies on the synthesis and structural characterization, suggest neutral lanthanide complexes in which the mono azo ligand being a uninegative (deprotonated form) and

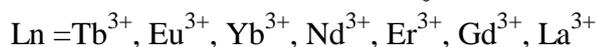
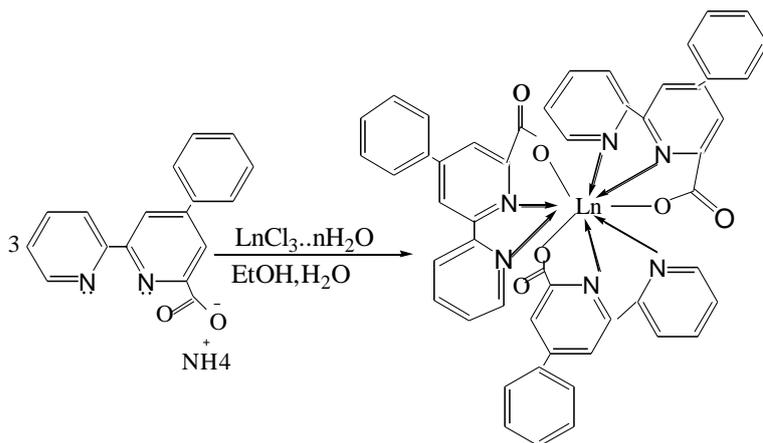
tridentate ligand. The absorption spectral profiles suggest a coordination number of nine around Ln(III) ions in the complexes.

Key words: Characterization, Lanthanide(III) complexes, Azo reagent, Spectral studies.

## INTRODUCTION

All lanthanides are f-block elements, with increased filling of the 4f electron shell. The most common oxidation state for the lanthanide ions is three. Because Ln(III) ions have intrinsically low extinction coefficients ( $\epsilon \sim 1-10 \text{ M}^{-1} \text{ cm}^{-1}$ ), the low absorption coefficients are due to f-f transitions. Which are parity forbidden. Therefore, it is common to indirectly excite lanthanide ions via an antenna chromophore, typically an organic molecule, that can readily transfer its energy to the lanthanide ion[1,2]. The advantages of lanthanide complexes luminescence are their narrow emission bands, large stoke's shifts and long life times ( $\mu\text{s}$ -ms). Because the 4f orbitals are shielded by the outer 5s and 5p orbitals, the chemical and physical properties of f-orbital ions are mostly insensitive to chemical environment. In addition, lanthanide ions have coordination numbers between 6 and 12, although for bulky ligands it is effectively 8-10, we sought neutral complexes that could be prepared easily. Because the coordination number for lanthanide ion with bulky ligands is generally nine[3,4]. Three such units bind to one lanthanide to form nine-coordinate neutral complexes, as shown in structure 1.

But the synthesis and characterization of its lanthanide metal complexes in the solid state not so far been reported . In this communication we report the preparation and characterization of some lanthanide complexes of 4-(2-pyridylazo)-resorcinol in the solid state. Their chemical formulae have been established using analytical, IR, UV-Visible spectra, magnetic moment and differential thermal analysis. Potentiometric studies of the complexes of lanthanides with 4-(2-pyridylazo)-resorcinol have been reported in the literature [5-8]. Moreover, 4-(2-pyridylazo)-resorcinol has also been used for chemical analysis (quantitative and qualitative) to determine a large number of metal ions [9-13]. The analytical applications of 4-(2-pyridylazo)-resorcinol take place very



Structure 1.  $\text{Ln}^{3+}$  complex with bipyridine carboxylic acid

Frequently in aqueous solutions where the reagent itself in its molecular form ( $\text{LH}_2$ ) and practically insoluble in water. For this reason the protolytic properties of ( $\text{LH}_2$ ), which can be characterized by the acidity constant of  $\text{LH}^+_3$  and the basicity constant of  $\text{L}^-$ , can be experimentally studied only in polar organic solvents (e.g; ethanol, dioxin and methanol) or in the corresponding aqueous-organic solutions [ 14 ] see figure 1.

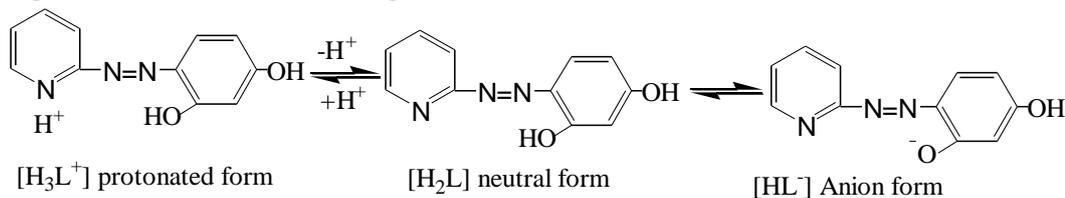


Fig.1. Protolytic reactions of 4-(2-pyridylazo)-resorcinol

## EXPERIMENTAL

### Chemicals

All chemicals used in this work were reagent grade (BDH / Merck), including 4-(2-pyridylazo)-resorcinol,  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Nd}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Sm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Er}(\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}$ ,  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , absolute ethanol, *N,N*-dimethyl formamide (DMF), NaOH, chloroform, diethylether,

buffer solution, methanol and calcium chloride. Distilled water was used through the experiment.

#### Preparation of the complexes

On slowly mixing a solution of 1mmol of lanthanide metal salt in absolute ethanol (10ml) was added to a solution of 1mmol 4-(2-pyridylazo)-resorcinol in ethanol (40ml). The pH of the mixture was adjusted between 8 and 10 by dropwise addition of NaOH solution (0.1M) and a dark red coloured precipitate was obtained. The slurry was then cooled to about 3-4 C<sup>0</sup> and kept at this temperature for 24h. The precipitate was extracted several times with ether by separation funnel until the ether layer acquired no colour. The combined ethereal extract was evaporated to dryness red coloured complex of the lanthanoid was obtained. It was then kept in vacuum desiccator for about 24h. and analysed. Yield 20-25%. In above preparation, the amount of ligand added to the metal ion solution was always less than the stoichiometric amount (1:1 in place of 3:1). If excess ligand was used, it gets extracted along with the complex in to the ether layer which was difficult to remove. By using excess lanthanoid salt, its hydroxide, which precipitates along with the metal complex, remained unextracted in the ethereal layer.

#### Analysis

The analyses of the metal ions were carried out gravimetrically by the standard oxalate method [ 15 ] in the college of science education chemistry department laboratory Salahaddin university. Carbon, hydrogen and nitrogen analyses were performed by the Micro Analytical section of the Stockholm university .

#### Measurements

Magnetic susceptibility measurements were made using Bruker Magnet BM6 at room temperature (25C<sup>0</sup>) in the college of science Mosul university chemistry department. The results are given in Table 1. The conductivity of the complexes were measured in *N,N*-dimethyl formamide and methanol using a Jenway conductivity meter 4200(0.93cell constant)(U.K). The results are given in Table 2. A digital philiphs pH-meter model pw9420 with a combined glass electrode was used to record the pH values. The pH meter was standardized with buffers of pH 4.00 and 9.00 supplied from BDH. The electronic spectra of the ligand and the complexes were obtained in chloroform solution using Cecil

UV-Visible spectrophotometer model Ce 3021 for absorbance measurements using 1 cm quartz cuvette, the study was conducted in the college of science education Salahaddin university-Erbil. Melting points were determined using Electro thermal 9100(U.K).

IR spectra were recorded with a Bio-Rad melin Excalibue-Series Spectrophotometer Class II Laser product 4000-400  $\text{cm}^{-1}$  range in the college of science education biology department. The samples were prepared as KBr pellets. Positions and assignments of the IR spectral bands of the ligand and the complexes are given in Table 3. The ratio M:L to be 1:3 ( of the metal ions and ligand) were determined by mole ratio method[16]. In addition, solutions of ligand  $1 \times 10^{-4}$  mol  $\text{L}^{-1}$  was prepared in ethanol and the solutions of metal salts prepared in the same way and adjusting its pH between 8-9 through mixing. The results were plotted in form of graph. Which shows the metal:ligand ratio M:L for complexes 1:3 using UV-Visible Spectrophotome. The differential thermal analytical curves were taken on (Stanton Red Croft TG 760) in the Stockholm university .

## RESULTS AND DISCUSSION

The analytical data of the complexes in Table 1. indicate the metal ligand ratio as 1:3 with general formula  $[\text{Ln}(\text{C}_{11}\text{H}_8\text{N}_3\text{O}_2)_3] \cdot \text{H}_2\text{O}$   $\text{Ln}=\text{Pr}^{3+}, \text{Nd}^{3+}$  and  $\text{Sm}^{3+}$  ,  $[\text{Ln}(\text{C}_{11}\text{H}_8\text{N}_3\text{O}_2)_3]$   $\text{Ln}=\text{Eu}^{3+}, \text{Er}^{3+}$  and  $\text{Yb}^{3+}$ . All the complexes were found to be stable at room temperature. All the complexes decomposed below  $300\text{C}^0$ , The molar conductance values of the complexes in DMF and methanol at  $25\text{C}^0$  when compared with these already reported [17 ], show non-electrolytes behaviour.

This is further supported by their insolubility in water , and high solubility in most of the non-aqueous solvents like chloroform, carbon tetrachloride, benzene, etc. The complexes when dissolved in organic solvents are not very stable and the deep red coloured solution gradually changes to orange-yellow. The ligand 4-(2-pyridylazo)-resorcinol has been reported to be a tridentate ligand where the bonding sites to the metal ion are oxygen of the hydroxyl group after deprotonation, and of the azo and the pyridine nitrogen atoms [ 18,19,20].

### Infrared spectra

The infrared data are shown in Table 3. Although the spectra of 4-(2-pyridylazo)-resorcinol and its chelates are complicated owing to the extensive overlap of a number of bands arising from  $\nu(\text{N}=\text{N})$ ,  $\nu(\text{C}=\text{N})$ ,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}-\text{H})$  and other bending modes in the region below  $1600 \text{ cm}^{-1}$  . The systematic shifts

in the positions of a few ligand bands in the spectra of the complexes suggest the probable bonding between the metal ion and the ligand. Some of these major shifts along with the conclusions drawn from them are given below. a) The IR bands observed at  $3080\text{ cm}^{-1}$  in the spectrum of the ligand are due to  $\nu(\text{C-H})$ . These bands are stable in position as well as in intensity when one goes from the ligand to the metal chelates indicating that these are purely due to  $\nu(\text{C-H})$ . It is interesting to note that instead of a well defined band, a very broad and weak band appeared in the spectrum of the ligand around  $3300\text{ cm}^{-1}$  due to  $\nu(\text{O-H})$ . This suggests intramolecular hydrogen bonding in the ligand which was confirmed earlier by NMR studies [21]. The ligand molecule can exist in equilibrium both in azo and hydrazone form as shown in Fig. 2. (I and II).

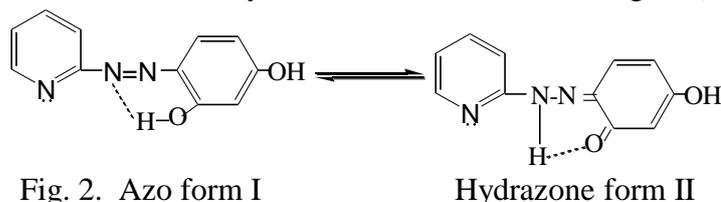


Fig. 2. Azo form I

Hydrazone form II

An intense band observed at  $1601\text{ cm}^{-1}$  in the spectrum of the ligand may be due to  $\nu(\text{C-O})$  of the hydrogen bond ring systems of the hydrazone form. Although the carbonyl band normally should appear around  $1600\text{ cm}^{-1}$ , such a bathochromic shift is observed in hydrogen bonded ring systems [22]. The band at  $1610\text{ cm}^{-1}$  in the ligand is shifted to lower frequencies ( $1596\text{-}1585\text{ cm}^{-1}$ ) in the metal chelate spectra as a result of the involvement of the  $\text{C=O} \cdots$  linkage in metal chelate bonding. In the spectra of  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Sm}^{3+}$  chelates, the weak and broad band around ( $3400\text{-}3480\text{ cm}^{-1}$ ) was evident for the presence of water molecule in these chelates.

b) The IR bands due to azo linkage are generally observed at  $1410$  and  $1384\text{ cm}^{-1}$  [23]. The main difficulty in the assignment of a frequency to azo linkage is that the band due to  $\nu(\text{N=N})$  would overlap with other IR bands from pyridine or resorcinol ring. However, the positions of the two bands at  $1490$  and  $1445\text{ cm}^{-1}$  present in the ligand spectra are shifted to  $1477$  and  $1384\text{ cm}^{-1}$ , respectively. These shifts suggest the linkage of the metal ion with the azo group of the ligand. IR spectra of the ligand also show a very weak band at ( $965\text{-}940\text{ cm}^{-1}$ ) due to  $\nu(\text{C-N})_{\text{py}}$ , which was replaced by a lower frequency ( $935\text{-}930\text{ cm}^{-1}$ ) in complexes spectra as a consequence of the coordination through nitrogen of pyridine ring. A band at  $1218\text{ cm}^{-1}$  present in the spectrum of the ligand was missing from the spectra of all the chelates [24], has assigned, according to a band at  $1272\text{ cm}^{-1}$  in the spectra of similar azo compounds [25], to the in-plane bending mode of C-O-H group. It is possible

that the band at  $1218\text{ cm}^{-1}$  may arise due to the in-plane bending mode of C-O-H and the fact that the corresponding band is missing in the spectra of metal chelates suggests the deprotonation of the C-O-H group for the band formation. This is essential in order to keep a charge balance between the metal ion and the ligand molecules.

c) Two new bands have appeared in the spectra of all the chelates, one between ( $520\text{-}470\text{ cm}^{-1}$ ) is due to  $\nu$  (M-N) coordination and the other one between ( $440\text{-}420\text{ cm}^{-1}$ ) is due to  $\nu$  (M-O) coordination. These vibrational bands support the involvement of nitrogen and oxygen atoms in complexation with metal ions [25,26]. The IR spectral study, thus, suggests the bonding of the metal ions with the pyridine nitrogen, the O-hydroxyl group, and the azo group of the ligand. Figure (4) and (5) shows IR spectra for the ligand and  $[\text{Nd}(\text{C}_{11}\text{H}_8\text{N}_3\text{O}_2)_3]\cdot\text{H}_2\text{O}$  complex.

#### Electronic spectra

The positions of absorption bands in the spectrum of the ligand in the aqueous and non-aqueous media corresponded with those given in the literature [27].

It presented broad maxima band in the visible region ( $403\text{nm}$ ). In the spectra of all the chelates the bands at  $523\text{-}535\text{ nm}$  and the are intensified to a very large extent. The positions of all the bands in the UV region remained practically constant. It therefore, appears that in the chelate formation, the nitrogen atom of the azo group and the oxygen atom of the C-O-H group after deprotonation are taking part [28,29]. The bands due to f-f transitions corresponding to the metal ions could not be located in the spectra of the chelates. This is what one should expect because the bands due to metal ions will be very weak ( $\epsilon \sim 1\text{-}10$ ) and they will be masked by the intense band of the ligand molecule. The absorption spectra of the lanthanid species are often characterized by line-like bands that result from "forbidden" intra f-f transitions. Again the factors that are responsible for energy absorption are so involved that no simple correlation between band positions and ground-state electronic configurations of the ions is possible [30], figures 6,7 and 8 shows UV-visible absorption spectra.

#### Magnetic moments

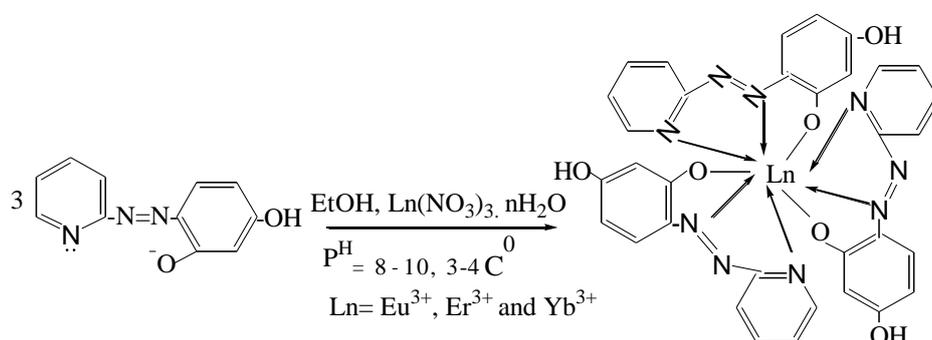
The values of the magnetic moments of the complexes are summarized in Table 1. These values compare very well with those measured for other simple compounds. Moments of the complexes, which were corrected for diamagnetism, showed very little deviation from the van Vleck values [30], indicating little participation of 4f-electrons in bond formation.

#### Differential thermal analysis

The differential thermal analysis curves indicate the decomposition of the complexes around 240-290C<sup>0</sup>. In case of Pr<sup>3+</sup>,Nd<sup>3+</sup> and Sm<sup>3+</sup> complexes a dehydration step beginning at about 110C<sup>0</sup> is observed indicating the presence of water molecule in these complexes as water of hydration. Azo compounds decompose thermally around 300C<sup>0</sup> forming nitrogen molecule and the free radical of the compound[31]. The following equations shows as the steps of Neodymium complex decomposition, thermal curves shown in fig.3 .

Based on the elemental analyses and various physicochemical studies, proposed for the present complexes involving uninegative tridentate species in the 1:3 (metal:ligand) complexes see structure 2.

Reaction steps	TC <sup>0</sup>		
	Ti	Tf	Tmax.
1-[Nd(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].H <sub>2</sub> O $\xrightarrow{\Delta}$ [Nd(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ]+H <sub>2</sub> O	35	133	-----
2-[Nd(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ] $\xrightarrow[\text{fast}]{\Delta}$ 3C <sub>5</sub> H <sub>4</sub> N + [Nd(C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>3</sub> ]	250	300	279
3- [Nd(C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>3</sub> ] $\xrightarrow[\text{slow}]{\Delta}$ 3N <sub>2</sub> + 3C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> +Nd	300	484	331



Structure 2. The suggested Chemical formula of Lanthanides Complexes with 4-(2-pyridylazo)-resorcinol.

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**TABLE 1. Analytical Data and general behaviour of Ln(III) Complexes.**

Formula of the Copmlex	Analytis form Found (Calcd.)				Colour	m.pC <sup>0</sup>	μ <sub>eff.</sub> B.M
	M	C	H	N			
[Pr(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].H <sub>2</sub> O	17.50 (17.59)	49.49 (49.44)	2.96 (2.99)	15.70 (15.73)	Dark red	220 <sub>d.</sub>	3.85
[Nd(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].H <sub>2</sub> O	17.90 (17.93)	49.22 (49.24)	2.99 (2.98)	15.60 (15.66)	Dark red	295 <sub>d.</sub>	3.87
[Sm(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].H <sub>2</sub> O	18.59 (18.55)	48.83 (48.87)	2.93 (2.96)	15.50 (15.55)	Dark red	298 <sub>d.</sub>	1.60
[Eu(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].	19.16 (19.14)	49.80 (49.88)	3.00 (3.02)	15.80 (15.87)	Dark red	300 <sub>d.</sub>	3.30
[Er(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].	20.63 (20.67)	49.00 (48.93)	2.95 (2.97)	15.53 (15.57)	Dark red	245 <sub>d.</sub>	9.69
[Yb(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].	21.20 (21.23)	48.53 (48.59)	2.95 (2.94)	15.42 (15.46)	Dark red	230 <sub>d.</sub>	4.70
Ligand C <sub>11</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>	-----	61.40 (61.39)	3.70 (3.72)	19.50 (19.53)	Orang	-----	-----

d.= decomposition

TABLE 2. Molar conductance of complexes in DMF and methanol solutions, Conc.  $1 \cdot 10^{-4}$  mol L<sup>-1</sup>.

Metal Complex	$\Lambda_m$ ohm s <sup>-1</sup> cm <sup>2</sup>	
	In methanol	In DMF
[Pr(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].H <sub>2</sub> O	5.55	6.58
[Nd(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].H <sub>2</sub> O	2.91	3.95
[Sm(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].H <sub>2</sub> O	1.22	1.96
[Eu(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ]	1.35	1.77
[Er(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ]	0.99	1.13
[Yb(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ]	0.33	0.43

TABLE 3. IR frequencies in cm<sup>-1</sup> for the Ligand and complexes.

Complexes	$\nu(\text{N}=\text{N})$	$\nu(\text{C}-\text{H})$	$\nu(\text{C}=\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$	(OH) <sub>str</sub>
Ligand	1445	3080	1601	-----	-----	3300
[Pr(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].H <sub>2</sub> O	1389	2990	1590	515-465	442-425	3399
[Nd(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].H <sub>2</sub> O	1384	2995	1596	520-470	440-420	3483
[Sm(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ].H <sub>2</sub> O	1400	3000	1585	510-460	445-420	3400
[Eu(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ]	1405	3010	1595	500-460	438-418	3143
[Er(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ]	1400	2999	1580	498-463	440-424	3170
[Yb(C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ]	1398	3020	1588	505-455	435-420	3140

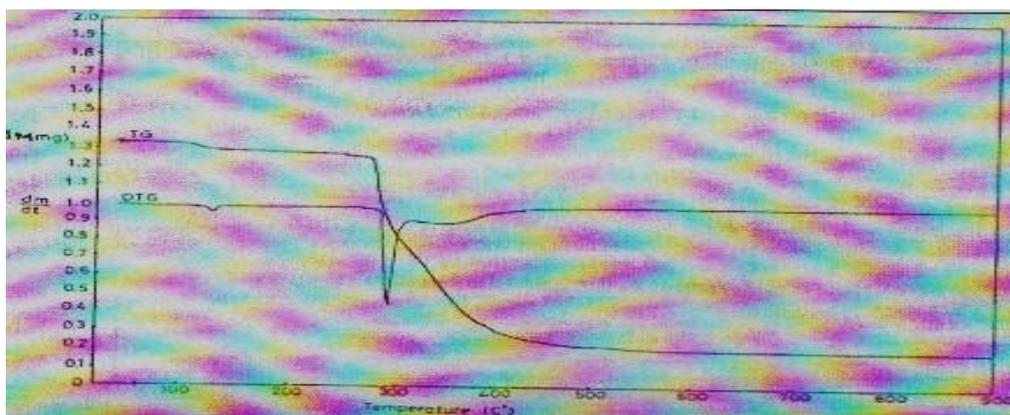


Fig. (3). Thermal curves of Nd(C<sub>11</sub>H<sub>8</sub>N<sub>3</sub>O<sub>2</sub>)<sub>3</sub>·H<sub>2</sub>O Complex.

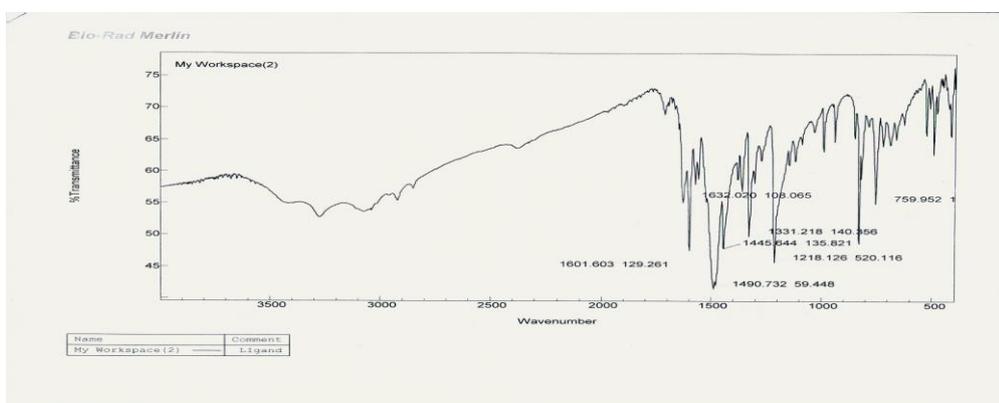


Fig.(4) Infrared spectra of mono azo ligand.

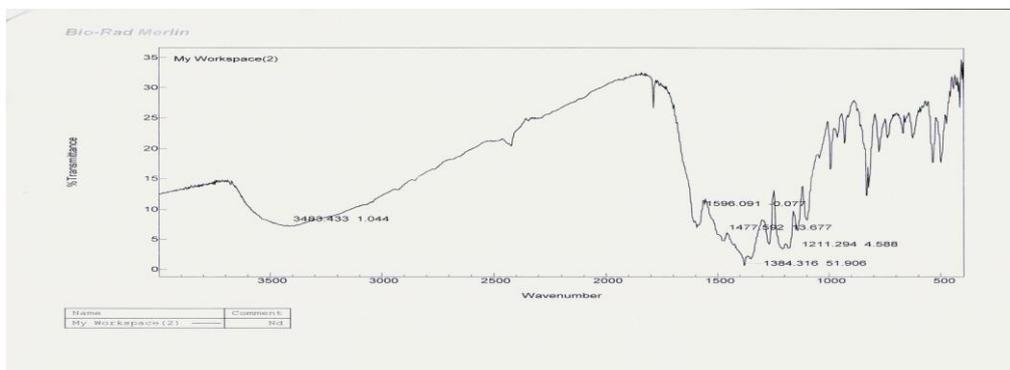


Fig. (5). Infrared spectra of [Nd(C<sub>11</sub>H<sub>8</sub>N<sub>3</sub>O<sub>2</sub>)<sub>3</sub>]·H<sub>2</sub>O complex.

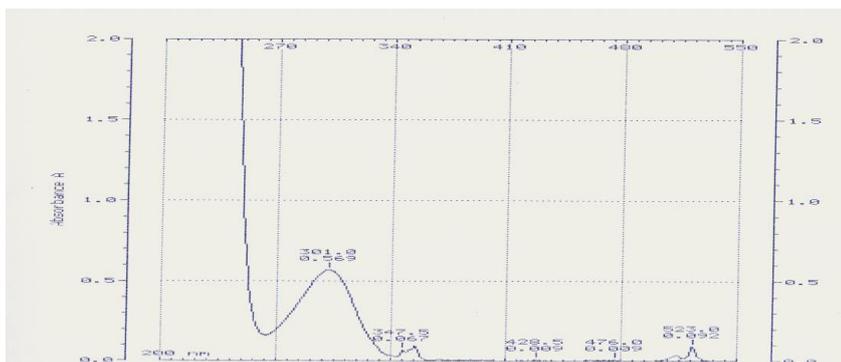


Fig. (6) Absorption spectra of the  $f^3$  species  $Nd^{3+}$  in distilled water  $1 \times 10^{-4}$  M.

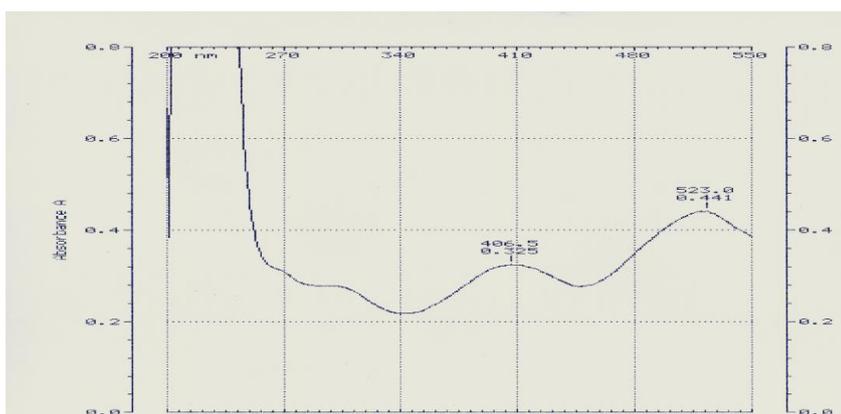


Fig. (7) Absorption spectra of  $[Nd(C_{11}H_8N_3O_2)_3] \cdot H_2O$  complex in ethanol  $1 \times 10^{-4}$  M.

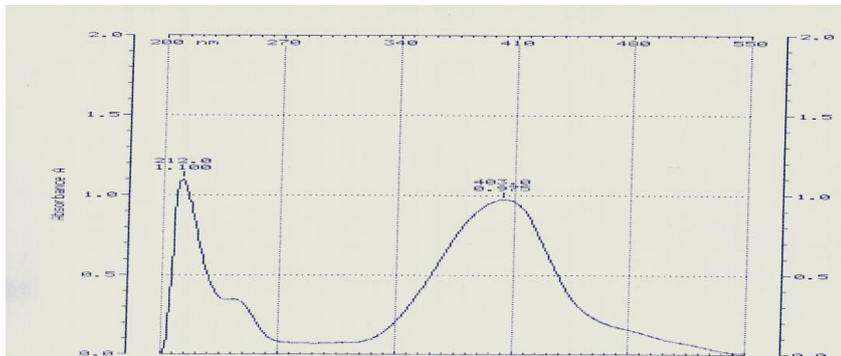


Fig. (8) Absorption spectra of the ligand in ethanol  $1 \times 10^{-4}$  M.