



Synthesis of some lanthanide complexes with(o-V2Nph.H2)

Schiff-base ligand

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ABSTRACT

Naphthalene based schiff-base compounds were synthesized by a condensation reaction of one equivalent of 1,5-diamino naphthalene and two equivalents of 2-hydroxy-3-methoxy benzaldehyde as previously described[1]. The metals selected for the preparation of complexes were La(III) and Er(III) as nitrate salts. Hence, in total two metal complexes were synthesized, have been characterized by molar conductivity measurements, elemental analysis, infrared and Uv-vis. Spectral data were used to investigate the geometrical structure of the prepared complexes. La(III) complex was further identified using ¹H-NMR and ¹³C-NMR spectral. The results suggest that the Ligand acted as a neutral tridentate, coordinated through the oxygen atom (-OH) and azomethine nitrogen -CH=N-, and five water molecules out of the coordination sphere. The nitrate ions are bidentately coordinated to the metal ion. Which form very stable complexes with the Lanthanide metals (Ln³⁺). A Coordination number of nine may be assigned to the metal ion in the synthesized complexes the geometrical shape is tricapped trigonal prismatic. Biological activity studies on the representative have been done successfully.

Key words: *Lanthanide, trivalent ions, Schiff base, Synthesis, Antibacterial activity.*

INTRODUCTION

The chemistry of the azomethine group (-N=CH-) plays a vital role in the progress of chemistry science [2-13]. Schiff- base are the important class of Ligands due to their synthetic flexibility and sensitivity towards the central metal ion, are the class of interest compounds in the pharmaceutical field. They show biological activities, including antibacterial, antifungal and anticancer [14]. Certain Schiff-bases know to be liquid crystals[15,16] and are used in medicinal and polymer chemistry [17].

The chemistry of lanthanides has received much attention because of their power to coordinate with chelated Schiff-bases ligands, azodyes, etc. We are interested in synthesis to investigate novel lanthanide Schiff-base compounds [18]. Lanthanides refer the longest series in the periodic table. It is 4f- inner transition series. Ln (III) ions, because of their z+/r charge to radius ratio are the best ions to form stable complexes and a very wide rang of coordination numbers (6-12). The 4f- inner orbitals in the metal ions do not participate in bonding, well be screened by the 5s2 and 5p6 orbitals. Their spectroscopy and magnetic susceptibility are thus uninfluenced by ligand field.

EXPERIMENTAL

Materials and Methods – All the chemicals were supplied from BDH and Fluka are used without further purification. Metal salts and organic solvents were reagent grade. They include o-vanillin (ACROS organic UK), 1,5-Naphthalenediamine (Merck), Lanthanum nitrate pentahydrate $\text{La}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (BDH), Erbium nitrate pentahydrate $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Fluka), ethyl alcohol, benzene and DMSO are used. FT-IR spectra were recorded using KBr discs in 4000-400 cm^{-1} range on IR Affinity-1-Shimadzu spectrophotometer. UV-Visible spectra were recorded in ethanol and DMSO on Shimadzu-1800 UV-Visible spectrophotometer double beam. The conductivity of the groups was measured in DMSO using pH /Conductivity meter at room temp. The studies were conducted in the college of education Salahuddin University – Erbil, Iraq. The ^1H -NMR and ^{13}C -NMR were taken on a Bruker ultra shield 300 MHz with TMS as internal references, in Al-al-Bayt Central Labs (Jordan). Melting points determined by an Electrothermal melting point apparatus 9100 LTD (UK) and are uncorrected. For determining the stoichiometry of the Schiff-base metal complexes, the absorbance of a series of metal salt (in 50% EtOH+50% benzene) + ligand (in 50% EtOH+40% benzene) mixtures which were prepared from their 10^{-3} mol/L solution data were analyzed using Job's method [19]. Carbon, hydrogen and nitrogen (C.H.N) analysis were performed using Euro EA Elemental Analyzer 3000/Italy at the College of Education Ibn al-Haitham (The central service laboratory) University of Baghdad. Lanthanum and Erbium were determined by the oxalate-oxide method [20].

SYNTHESIS OF Ln^{3+} COMPLEXES

The general method was adopted for the preparation of all the complexes. To (1 mmol. 0.426g) of synthesised Ligand dissolved in 30ml pure (ethanol/benzene) mixture (1:1) were poured into the beaker, and the compound was heated for 20min. during the mixing, to the boiling solution 1mmol. of the Lanthanide nitrate $\text{La}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ or $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution was added drop by drop the solution was heated for about 30min, it was concentrated to a small volume, and the produced complex was separated from it by filtration, washed with ethanol to remove excess Ligand and metal ions, respectively. The precipitate was then dried in the oven.

RESULT AND DISCUSSION

All result indicates that the La complexes have the chemical formula $[\text{La}(\text{L})(\text{NO}_3)_3] \cdot 5\text{H}_2\text{O}$ Where Er complex have the similar formula $[\text{Er}(\text{L})(\text{NO}_3)_3] \cdot 5\text{H}_2\text{O}$. The equivalent conductance values of the compounds in DMSO (10^{-3}M) at room temp. When compared with those already reported [21] by their indicate that they are non-electrolytes. This is further supported by their insolubility in water; they are insoluble in common organic solvents such as ethanol, methanol, benzene and carbon tetrachloride. The Schiff-base ligand (6,6'-(1E,1E')-(naphthalene-1,5-diylbis(azan-1-ylidene bis (methan-1-ylidene) bis (z-methoxy phenol) or (o-V₂Nph.H₂)) ($\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_4$) is yellow-orange colour, but the prepared complexes of this Ligand vary in the colour depending on metal ion type. The complexes are quite air-stable no hygroscopic some physical and chemical properties for chelate Complexes with La (III) and Er(III) metal ions are listed in Table (1)

The complexes decomposed above 250°C . Coordination numbers of the lanthanide ions normally are from 6 to 9, but are often higher with ligands of small bidentate ligands, such as nitrates. Monodentate ligands (F^- , H_2O , Cl^- , etc.) usually have a maximum coordination of 9 for lanthanides;

bidentate ligands normally form chelates that are 6, 7, or 8 coordinate, as LnK_3 , $\text{LnK}_3 \cdot \text{H}_2\text{O}$, LnK_4 , where K is a bidentate ligand. Monodentate ligands surrounding the Ln^{3+} form a coordination polyhedron based upon either a trigonal prism or the octahedron. Both polyhedral have 6-coordinate lanthanide ions, but the coordination may be expanded to 7, 8, or 9 by coordination of additional ligands through the square face of the trigonal prism [22]. The chelates were dissolved in DMSO and the conductivities of (10^{-3}M) of their solutions at 25°C , showed lower molar conductance values ($6.2\text{--}5.15$) $\text{Cm}^2\text{ohm}^{-1}\text{mole}^{-1}$ for the La and Er complexes respectively. Table (1) indicate the non-electrolytic nature of the complexes. Based on the analytical, physicochemical and spectral results, The structure of the chelate complexes shown in Fig. (1).

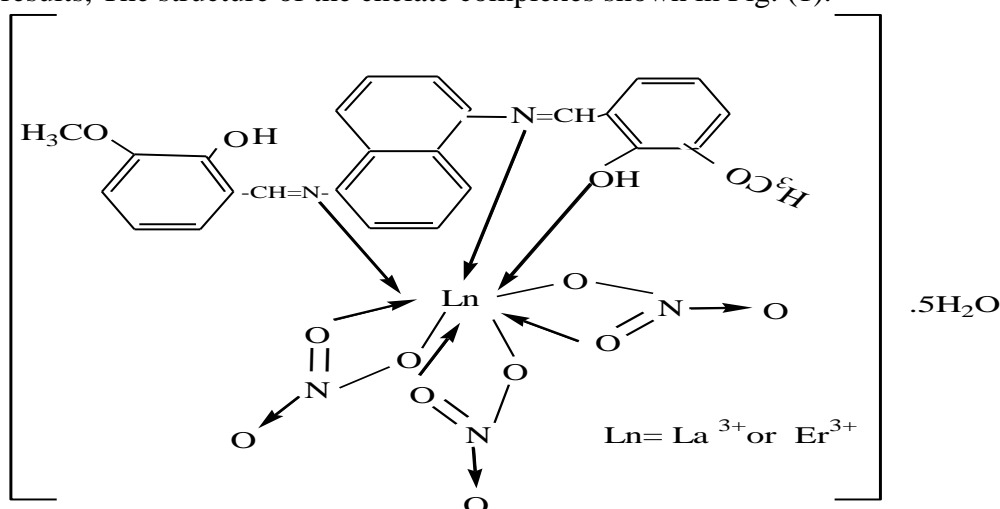


Fig.(1)Proposed structure of the lanthanide (III) complexes $[\text{Ln}(\text{L})(\text{NO}_3)_3] \cdot 5\text{H}_2\text{O}$

Electronic spectral of ligand and it's complexes

The $4f$ - orbitals in the Ln^{3+} ions do not participate directly in bonding, being well shielded by the $5s^2$ and $5p^6$ orbitals. Their spectroscopic and magnetic properties are thus largely Uninfluenced by the ligand. Small crystal field splitting and very sharp electronic spectra in comparison with the d-block metals [23], Fig.(2) show electronic spectra of Er(III) metal ion and $4f$ - $4f$ transition the observed wavelength in $(250\text{--}800)\text{cm}^{-1}$ rang. Ln (III) ions have intrinsically low extinction coefficients are ($\epsilon \sim 1\text{--}10 \text{ L mole}^{-1}\text{cm}^{-1}$), direct excitation is difficult without high-intensity sources. The low absorption coefficients are due to intra $4f$ transition, which are partially forbidden [24]. The absorption spectra of lanthanide (Ln^{3+}) cations result from $4f$ - $4f$ transitions in a manner analogous to the d-d transitions of the transition metals.

Absorption spectra of the lanthanide elements are thus typically sharp, line-like spectra as opposed to the broad absorptions of the transition metals. The $4f$ orbitals in the lanthanides are buried deep with the atom and the broadening effect of ligand vibrations is minimized [25], fig (2) shown spectra of Er^{3+} ion in ethanol (10^{-3}M), $\text{Er}^{3+}=[\text{Xe}]4f^{11}5s5p$ Electronic spectra of the complexes are similar for La and Er complexes showed no f - f bands in the measured region. Two maxima observed in the complexes spectrum ($270\text{--}340\text{nm}$) for each Er(III) and La(III) complexes assigned to be π - π^* and n - π^* transition indicates the presence of $-\text{CH}=\text{N}-$ band. The uv-vis. Spectra of the complexes are suffering blue shift.

IR Spectra

The IR data of the ligand and their La(III) and Er(III) complexes as KBr pellets summarized in Table (2). The absorption bands of ligand (azomethine) linkage are observed at 1605 cm^{-1} a high to medium intensities band, was shifted to higher frequencies positive shift occur after complexation [26], $(1612-1608)\text{cm}^{-1}$ in La(III) and Er(III) complexes respectively. Indicating nitrogen coordination of the Schiff base may be due to the change in the bond order of the carbon to nitrogen. This is supported by the appearance of band at $543-646\text{ cm}^{-1}$ corresponding to the stretching vibration of M-N band. The infrared spectrum of the La(III) and Er(III) complexes under investigation displays a band at $(954-966)\text{cm}^{-1}$ respectively which is due to the presence of a coordinate OH group of 2-hydroxy-3-methoxy benzaldehyde to Ln(III) ions. Recommends that the ligand is coordinated to metal ion via OH group, in all complexes this change in shift is due to the lone pair density of oxygen atom towards metal atom. Bands at $422-514\text{ cm}^{-1}$ corresponds to M-O stretching vibrations. The observed new bands in the La (III) complex at $(1375-815)\text{cm}^{-1}$ medium bands are due to coordinated nitrate ion [27]. The symmetrical stretching frequency of the two (N-O) bonds nearest the metal atom, is in the range $(1006-1040)\text{cm}^{-1}$, suggesting that the nitrate group lie inside the coordination sphere. The bands corresponding to the $\nu(\text{OH})$ at $(3406-3371)\text{cm}^{-1}$ shows that the complexes contain water molecules out of coordination sphere which is agree with the results of elemental analyses. The IR spectra of the complexes are similar. The spectrum of La (III) complex shows two weak peaks $(2951-2843)\text{cm}^{-1}$ which assigned to $\nu(\text{C-H})$ aromatic and aliphatic respectively, these bands are instable in position in both ligand and chelated complexes.

NMR spectrum of Schiff-base ligand and it's metal complexes.

The ^1H -nmr spectrum of the lanthanum(III) complex recorded in DMSO- d_6 further substantiates the mode of coordination suggested by the electronic and(i.r) spectral studies. In complex of Schiff- base with La^{3+} Metal ion there is very small upfield shift in proton nmr and to ^{13}C -NMR when compared with free ligand because lanthanum is diamagnetic. The ^1H -NMR spectrum of the ligand presents the signal at $\delta 13.11\text{ ppm}$ due to the presence of (ph-OH) proton. The ^1H -NMR spectrum of the complex exhibited a signal for OH proton at 13.08 ppm , indicating that the OH group is coordinated to the metal ion without deprotonation, shifted by about 0.032 ppm in the spectra of the metal complex La^{3+} . The presence of a sharp singlet for the $-\text{CH}=\text{N}-$ proton in ligand spectra at 9.04 ppm , also proton of azomethine appeared at 9.05 ppm for La(III) complex. The multiplets of aromatic protons in (L) appeared within the range $\delta 8.14-6.95\text{ ppm}$ and they were not affected by chelation .

In ^{13}C -NMR spectrum of La(III) complex $-\text{CH}=\text{N}-$ and $-\text{C}-\text{OH}$ carbon atoms are observed at 164.64 and 148.21 ppm respectively[28]. The spectra of ^1H -NMR and ^{13}C -NMR for La^{3+} complex shown in Fig.(7,8).

Study of Biological Activity

Two choice species of bacteria were used in this study Escherichia coli (E.coli) as Gram-negative Bacteria and Staphylococcus Aureus (Staph.Aurous) as Gram-positive Bacteria [29], in nutrient agar medium, against two prepared Schiff-base complexes with La^{3+} and Er^{3+} metal ions. Using (DMSO) as a solvent and as a control were examined, the concentration of the compounds in this solvent was 25 mg per one milliliter using disc sensitivity test. This way involves the exposure of the zone of inhibition toward the diffusion of micro-organism on agar plate [30]. The plates were incubated for 24 h . at 37°C after incubation the average of inhibition zones was recorded. The results obtained are tabulated in Table(3).

The complex $[\text{Er}(\text{L})(\text{NO}_3)_3].5\text{H}_2\text{O}$ gave similar inhibition zone 5 mm for both staphylococcus and E.coli . The complex $[\text{La}(\text{L})(\text{NO}_3)_3].5\text{H}_2\text{O}$ showed more activity against staphylococcus than E.coli . Prepared complexes show good bacterial activities standard bacterial species in despite variety response expressed with inhibition zones according to the type of complex and bacteria.

Conclusion

The Schiff-base (o-V₂Nph-H₂) obtained by condensation of 1,5-diaminonaphthalene with 2-hydroxy-3-methoxybenzaldehyde reacts with lanthanide(III)nitrate salts to form mononuclear complexes of the type [Ln(L)(NO₃)₃].5H₂O where Ln=La³⁺ & Er³⁺.

The total number of points of attachment to the central element is termed the coordination number (C.N). The C.N of a complex is influenced by the relative sizes of the metal ion and the ligands and by electronic factors, such as charge which is dependent on the electronic configuration of the metal ion. The La(III) and Er(III) complexes possess tricapped trigonal prismatic geometry around the central metal ion. The ligand and its metal complexes act as potent bactericidal agent. Further work with analogs is needed.

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Table(1)- Analytical and physical data of metal complexes and Schiff-base ligand.

Compounds	Color	Yield%	M.P °C	Molar conductivities in DMSO (cm ² ohm ⁻¹ mole ⁻¹)	Analysis % (Found/Caled.)			
					C	H	N	Metal
L=C ₂₀ H ₂₂ N ₂ O ₄ (o-V ₂ Nph.H ₂)	Orang	82	206*	-----	74.34 (73.23)	5.31 (5.16)	6.38 (6.57)	-----
[La(L)(NO ₃) ₃].5H ₂ O [La(C ₂₆ H ₃₂ N ₅ O ₁₈)]	Deep red	87.90	255*	6.2	36.45 (37.10)	3.08 (3.80)	8.76 (8.32)	16.00 (16.51)
[Er(L)(NO ₃) ₃].5H ₂ O [Er(C ₂₆ H ₃₂ N ₅ O ₁₈)]	Black	83.33	260*	5.15	34.89 (35.89)	3.75 (3.68)	6.13 (8.05)	20.33 (19.24)

*decompose

Table(2)- Selected IR Data of Schiff –base Ligand and their Metal complexes.

Compound	$\nu(\text{O-H})_{\text{H}_2\text{O}}$	$\nu(\text{C=N})$	$\nu(\text{NO}_3)$	$\nu(\text{NO}_3)$	$\nu(\text{NO}_3)$	Ln-O	Ln-N
Ligand	3434	1605	-----	-----	-----	-----	-----
[La(L)(NO ₃) ₃].5H ₂ O	3406	1612	1375	1489	1282	422	543
[Er(L)(NO ₃) ₃].5H ₂ O	3371	1608	1384	1463	1249	414	542

Table(3)- Antibacterial activity of the synthesized compounds.

No.	compound	E.coli(mm)	Stafilokocas(mm)
1.	[La(L)(NO ₃) ₃].5H ₂ O	4	5
2.	[Er(L)(NO ₃) ₃].5H ₂ O	5	5
3.	Schiff-base ligand	3	3

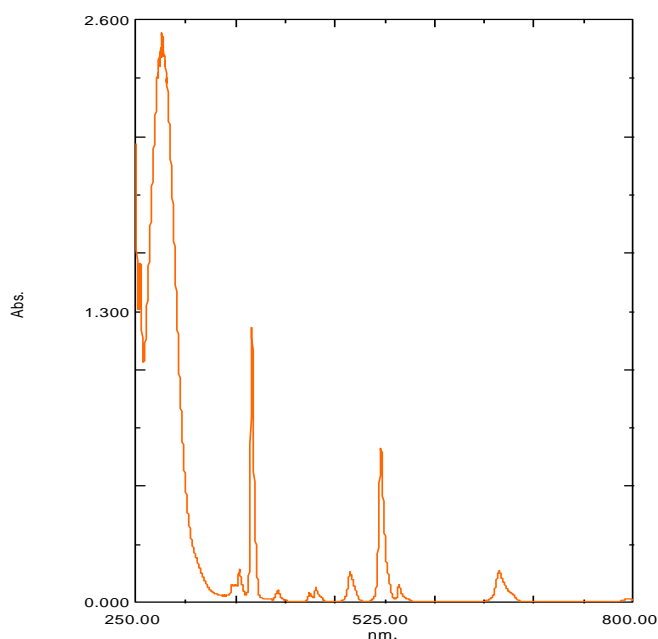


Fig.(2)- The Electronic spectraum of Er(III) metal ion Ligand and (conc. $1 \times 10^{-3} M$) in ethanol.

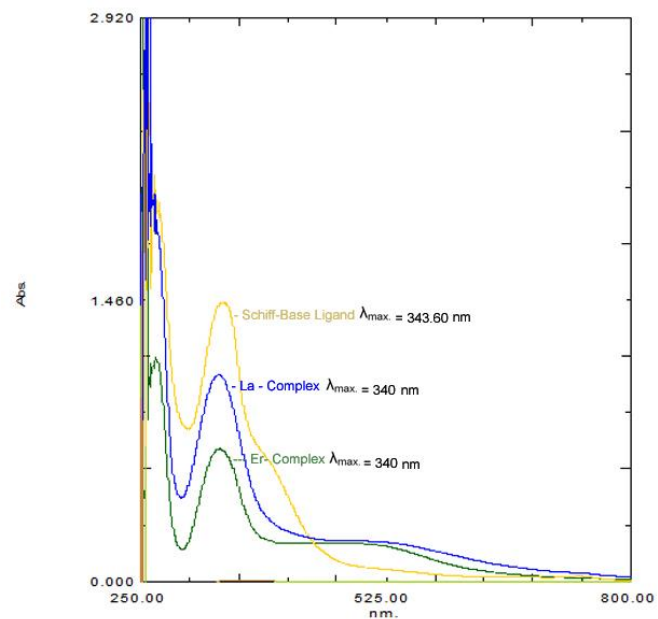


Fig.(3)- The Electronic spectraum of Complexes (Conc. 1×10^{-3} in DMSO)

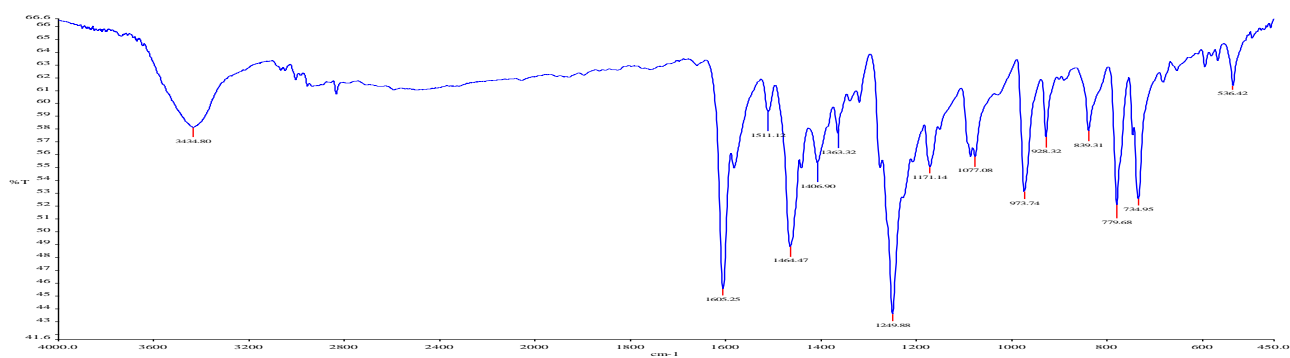
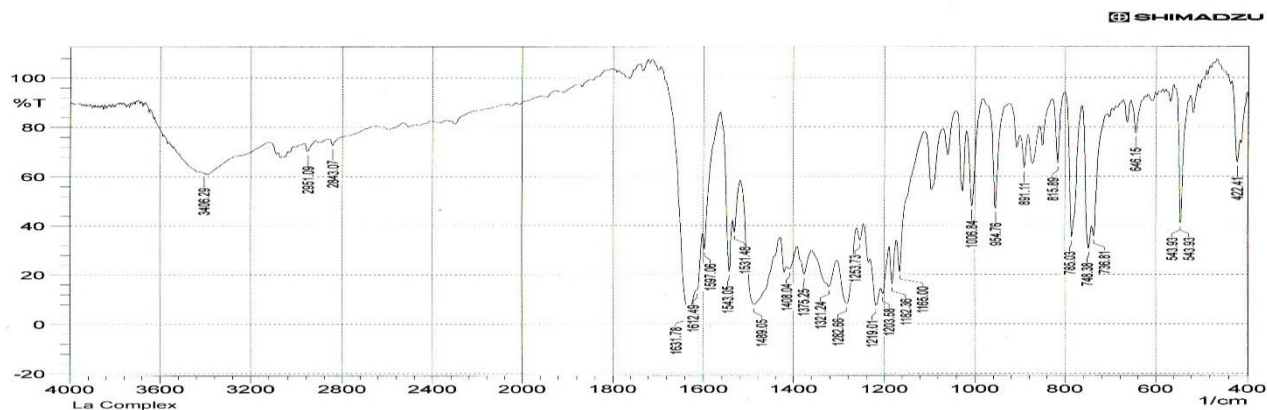
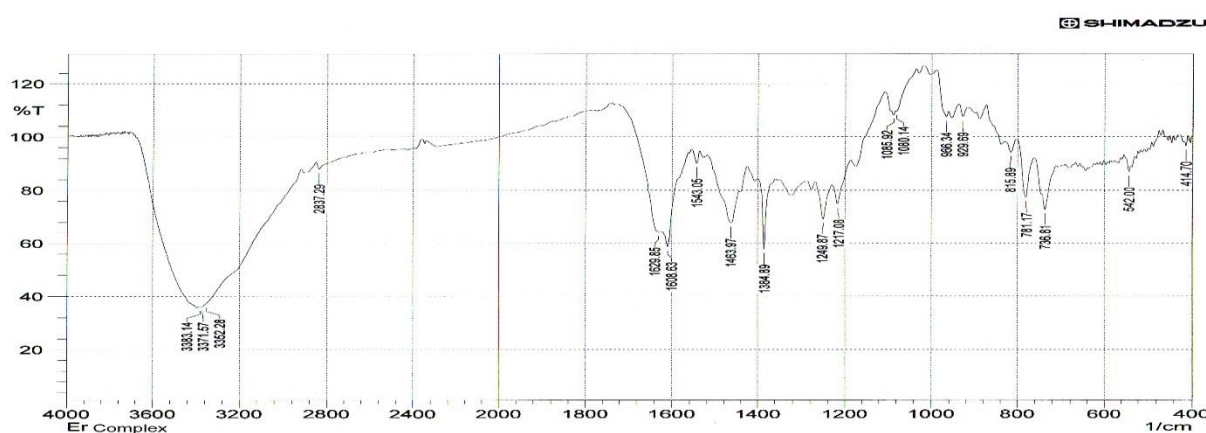
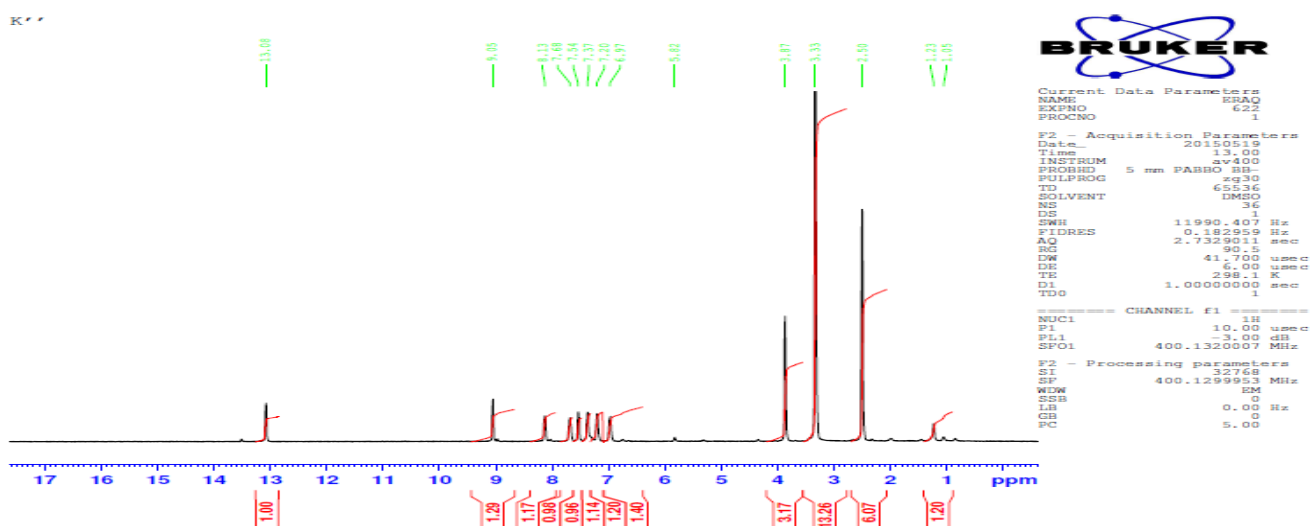


Fig.(4)- The IR spectra of Schiff- base Ligand (o-V2Nph.H2).


 Fig.(5)- The IR spectra of La³⁺ Complex.

 Fig.(6)- The IR spectra of Er³⁺ Complex.

 Fig.(7)- The ¹H-NMR spectra of the [La(L)(NO₃)₃].5H₂O complex.

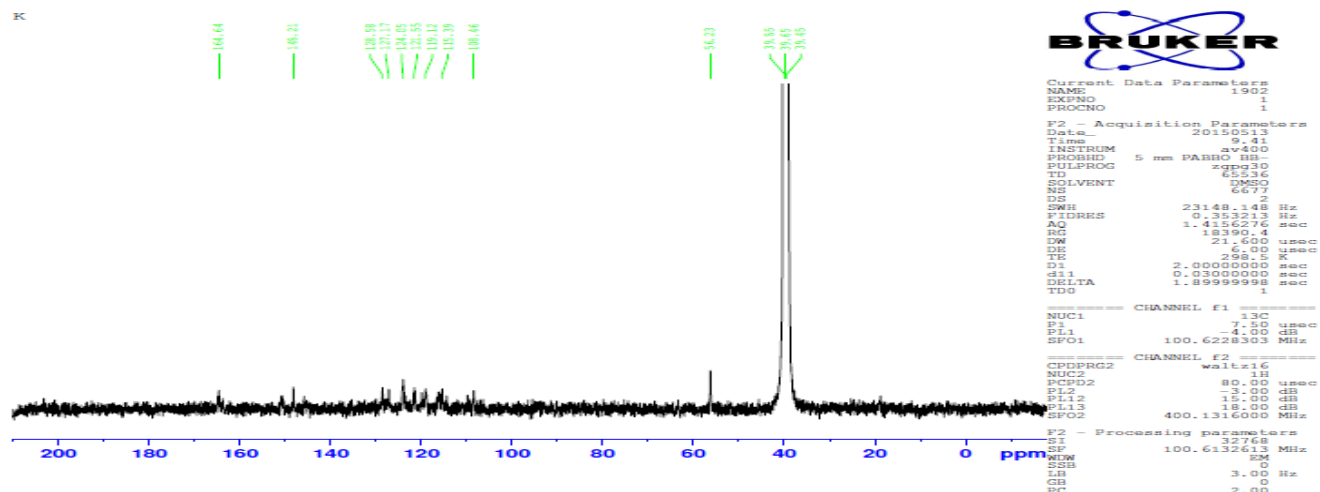


Fig.(8)-The¹³C-NMR Spectra of the[La(L)(NO₃)₃].5H₂O complex.