Polytechnic Journal

Polytechnic Journal

Volume 8 | Issue 2 Article 16

5-1-2018

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How to Cite This Article

Mohamad, Muharram Yaseen and Hussein, Kamaran Basheer (2018) "Synthesis of Some Lanthanide Complexes Derived From o-Vanphen," *Polytechnic Journal*: Vol. 8: Iss. 2, Article 16.
DOI: https://doi.org/10.25156/ptj.2018.8.2.180

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Polytechnic Journal: Vol.8 No. 2 (May 2018): Pp:264-276
http://epu.edu.krd/ojs/index.php/Journal

Synthesis of Some Lanthanide Complexes Derived From o-Vanphen

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Abstract

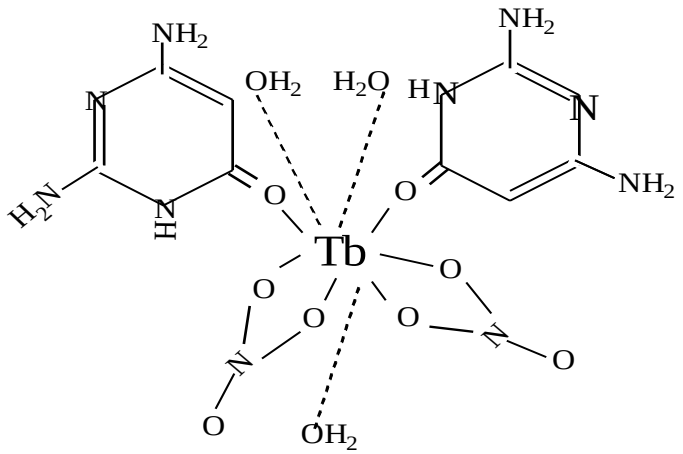
Formation of lanthanide (La, Ce & Nd) metal ion complexes of o-Vanillinphenylalanine (o-Vanphen) were prepared by the one-pot template, and having the general formula K[Ln(o-Vanphen)$_2$(H_2O)$_2$].H_2O where Ln stands for La(III), Ce(III) & Nd(III), o-Vanillin=$C_8H_8O_3$, phenylalanine=$C_9H_{11}NO_2$. The complexes were synthesized in the absolute ethanol the coordination of the complexes were determined by elemental analysis, UV-vis. , molar conductance and all the prepared compounds have been characterized by Infrared spectroscopy (FT-IR) and ^{1}H-NMR. The results suggest that the metal ions bonded to the ligand through the phenolic oxygen, carboxylic oxygen groups and the imino nitrogen, spectra of their complexes shows that the ligand acts as a tridentate manner through (ONO) donor atoms. Ln(III) metal ions are eight coordinate C.N=8 in those complexes. The analytical data of the complexes show the formation of 1:2 (M:L) metal to ligand ratio. The synthesized products were examined for antimicrobial activity against a variety of test organisms.

Keyword- Lanthanide(III), one-pot reaction, Amino acid, Complexes, Antimicrobial activity, Synthesis.

1- Introduction

Lanthanides are *f*-block elements, corresponding to the filling of the 4*f* electron shell. All lanthanide elements form trivalent cations, Ln^{3+}, that chemistry is mainly circumscribed by the ionic radius, which decreases regularly from La to Lu [1-3]. The number of studies with implies lanthanide complexes have rapidly increased on last ten years because of a wide capabilities of these metals as a photon receptors via antenna effects. High coordination numbers favor binding and catalyst functions

[4-6]. Schiff-bases are the class of essential compounds in the pharmaceutical field. They show biological activities, including antibacterial antifungal, and anticancer furthermore, Schiff-bases are utilized as a starting material in the industrial synthesis, Schiff-bases are a class of essential compounds in the pharmaceutical fields and have gained prominence for their anti-tuberculostatic activity [7-10]. Certain Schiff-bases are known to be liquid crystals [11], are used in medicinal [12], and polymer chemistry [13]. On the other hand, the lanthanide complexes, including the Schiff-bases formed by the condensation of amino acids and o-Vanillin are not so common. To date , a range of lanthanide complexes with Schiff-bases, prepared by the condensation of salicylaldehyde and naphthaldehyde derivatives (such as o-vanillin , or 5-Bromo-2-hydroxybenzaldehyde) with lysine [14] , 6-amino lysine [15] , phenylalanine [16] , tyrosine [17] , due to coordination variability of the Schiff-base ligands and the coordination features of the lanthanide central atoms (ability to employment the coordination numbers more than 12).The structures of these complexes are quite divergent. New eight and nine-coordinate luminescent europium(III) and terbium(III) complexes with carbonyl group coordination have been prepared using the monodentate ligand 2,4-diamino-6-hydroxy pyrimidine and characterized by x-ray and spectroscopic methods[18]. The molecular structure of the Ln^{3+}=Tb complex $[Tb(L)_2(NO_3)_2(H_2O)_3]$ shown in Fig.(1).



[$Tb(L)_2(NO_3)_2(H_2O)_3$] L=2,4-diamino-6-hydroxy pyrimidine

Fig.(1)- Molecular structure of the Tb(III) complex C.N=9.

2-Experimental Section

2.1-*Materials*

All the reagents, namely, hydrated lanthanide salts were of Analar grade (BDH). They were used in the form of nitrate without further purification.O – Vanillin, and phenylalanine (Aldrich), were used as received. Absolute ethanol, potassium hydroxide, (DMSO dimethyl sulfoxide $(CH_3)_2SO$ Alderich – 276855) and distilled water were used.

2.2-*Instruments*

UV-vis. Spectra were obtained in DMSO on (Shimadzu-1800 UV-Vis. Spectrophotometer double beam). The conductivity of the complexes was measured in DMSO using (pH/conductivity meter) at room temp. The studies were conducted in the college of education Salahaddin university,Erbil,Iraq. C.H.N analyses were carried out on solid compounds using (Euro EA Elemental analyzer 3000/Italy), and ^{1}H-NMR spectra were recorded at the college of Education (Ibn al-Haitham) the central service laboratory University of Baghdad.

Melting points were circumscribed by an Electrothermal melting point apparatus (9100, LTD, UK) and are uncorrected. For determining the Stoichiometry of the complexes mole ratio method were used [19]. Lanthanum, Cerium & Neodymium percentage were discovered by the oxalate-oxide method [20].

3- Results and Discussion

3.1-*Synthesis of complexes*

10mmol $Ln(NO_3)_3.xH_2O$, when Ln= La, Ce & Nd + 20mmol(3.30g) phenylalanine +20mmol(1.12g) KOH was dissolved in 20ml absolute ethanol and was mixed with 20mmol(3.04g) o-vanillin. The mixture was refluxed on a boiling water bath for 1.5 hours, the separated complex was washed with 50% ethanol and then with diethyl ether and kept over anhydrous $CaCl_2$ overnight in desiccator.

3.2-*Characterization of complexes*

The physicochemical data of the complexes are given in Table(1). All the newly synthesized complexes are colored solids and insoluble in common organic solvents . are soluble only in DMF and DMSO. The complexes thus formed were identical with those from the template synthesis. Yields ranged from Ca.80%. The molar conductance measures of the complexes in 10^{-3}M DMSO dimethyl sulphoxide is in the (83-91) $ohm^{-1}cm^{2}mol^{-1}$ which are relatively high, indicating their electrolytic nature. Complexes having the molar ratio of metal: ligand as 1:2 Table (1) shows the molar conductance values of the complexes, and the elemental analyses data confirm the composition of the prepared complexes with a general formula $K[Ln(o\text{-}Vanphen)_2(H_2O)_2].H_2O$ where Ln=La^{3+}, Ce^{3+} & Nd^{3+} .From the spectral data and the elemental analyses the structure of the prepared complexes may be formulated as shown in Fig.(2).

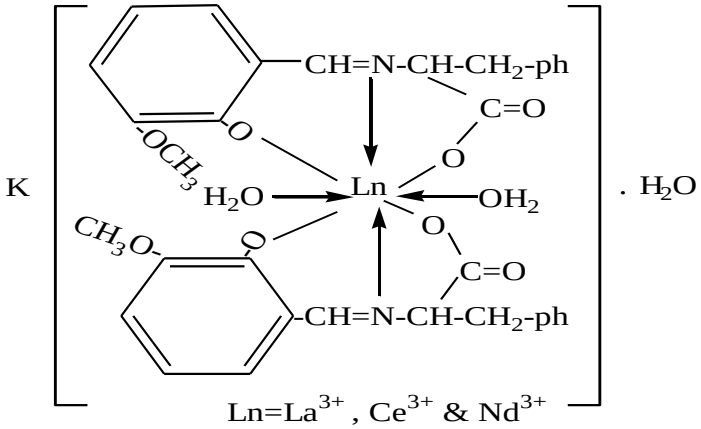
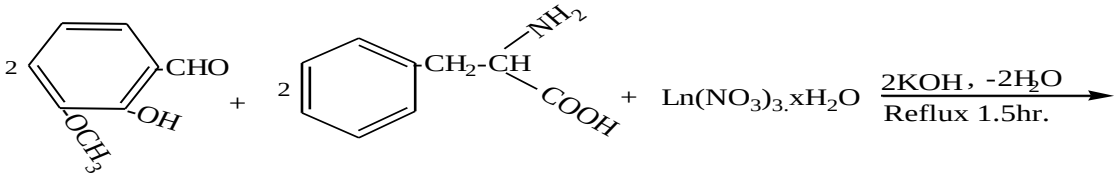


Fig.(2)- Suggested structure of Ln^{3+} complexes.

The IR spectra show that the Schiff-base ligand (H_2L) is coordinated to the metal ions in a tridentate method with ONO donor sites of the azomethine-N, it's found that the coordination number of metal ion atoms Ln^{3+} equal to eight.

The synthesized complexes were screened for their antibacterial activity against bacterial species. Lanthanide complexes were obtained from the reaction of 2:2:1 molar ratio of metal ions see scheme(1).

Scheme(1)-Synthesis of metal co



o-vanillin(2eq.) phenylalanine (2eq.) lanthanide salt (1eq.)

$K[Ln(0\text{-vanphen})_2(H_2O)_2].H_2O$

potassium[diaqua-bis(o-vanillinphenylalaninato)neodymiumate(III)].monohydrate wheneLn=Nd^{3+}

Scheme (1) – Synthesis of metal complexes by a one-pot template.

IR Spectra

IR data of the complexes are given in Table (2). The IR spectral data of the La and Ce complexes showed a band at 1624 cm^{-1}, which is assigned to υ(-CH=N-) stretching vibration.This group is also observable in the Nd(III) complex at 1622 cm^{-1} suggesting that the ligand has coordinated to the respective metal ions.

The bonding of the Ln^{3+} metal ions to the ligands through the nitrogen of azomethane and oxygen atoms of the hydroxyl group (–OH), is further supported by the presence of new bands is the 534-540 and 430-493 cm^{-1} range due to υ(Ln-O) and υ(Ln-N) vibrations respectively [21,22]. The peaks observed at 1496-1548 cm^{-1} can belong to the asymmetric vibrations of the carboxyl group, while the

symmetric vibrations of the carboxyl group were observed in the region of 1454-1467 cm^{-1}. A weak broad band in the region 3415-3442 cm^{-1} which assigned to the $(O-H)_{(H2O)}$ stretching vibration indicating the presence of water molecule within the structures of the complexes two water molecules inside coordination sphere per complex coordinated to the Ln(III) [23,24]. IR spectra indicate their similarity is most likely isostructural, the (IR) spectra of the prepared Ln(III) complexes were shown in Figures (2,3 & 4).

Electronic Absorption Spectrum

The 4*f*-electrons of lanthanides yield two types of transitions such as *f*-*f* and *f*-d transitions. The *f*-*f* transitions which give rise to sharp, narrow bands of comparatively weak intensities which are Laporte forbidden, whereas allowed *f*-d transitions are relatively broad and intense. The observed spectral transitions of the lanthanide ions are *f*-*f* transitions. Since the 4*f*-subshell of Ln(III) ions is well shielded by the filled 5s and 5p sub-shells, the energy levels of the 4*f*-electrons areonly little influenced by the environment of Ln(III) ion. The intensity of *f*-*f* transition is weak because of that these transitions are Laporte refused. Relaxation of this selection rule is decidedly less useful than that of d-d transitions. Because of the weak crystal field interaction[25].

The electronic spectra of their complexes were displayed in DMSO. The spectra of compounds are dominated by intense intra-ligand charge transfer (C.T) bands. The spectrum of all complexes shows an intense absorption band at 340 and 260 nm region assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, respectively of azomethine groups [26].Fig.(5) show electronic spectra of all complexes in DMSO as the solvent.

^{1}H-NMR Spectra of Nd(III) complex

The ^{1}H-NMR spectral data of Nd(III) complex was recorded in DMSO-d_6 solution. From the ^{1}H-NMR spectrum of Nd(III) complex disappearance (-OH) peak and shifting aromatic peak to higher value confirms the formation of the complex.

The peak at δ 2.49-3.49 would be due to DMSO protons. 1.1(doublet,2H,CH_2-ph), 1.23(Triplet,1H,HC-N), 4.58(Singlet,1H,HC=N), 4.71(Singlet,3H,OCH_3), 7.15-7.37(multiplet,6H,Ar-H) was due to aromatic protons. The spectra of Nd(III) complex were shown in Figure (6).

Antibacterial activity

The sensitivity of two kinds of bacterial which included Escherichia Coli, as gram-negative and Staphylococcus aureus as gram-positive. The effects of these compounds on two types of microorganisms are represented in Table(3). There are significant differences between the effects of the complexes used against various bacteria. The Nd(III) complex was highly effective against E.coli (Ec) and staphylococcus aureus (Sa) bacteria when compared with La(III) complex. The activity of the metal complexes can be explained by the overtone concept and chelation theory [27]. This approach involves the exposure of the zone of inhibition toward the diffusion of micro-organism on agar plate. The plates were incubated for 24hr. , at 37^0C, the zone of inhibition of bacterial growth around the disc was observed [28].

Conclusions

Three heavy lanthanide(III) complexes were prepared by one-pot template, potassium[diaqua- bis-(o-vanillin phenylalanine) Ln(III) monohydrate where Ln= La^{3+},Ce^{3+} & Nd^{3+} of the composition $K[Ln(o\text{-}vanphen)_2(H_2O)_2]$. H_2O .The complexes were colored, and the ratio of metal to the ligand is 1:2 in all complexes.Conductance value indicates the electrolytic nature of complexes.

IR and elemental analysis data indicated the presence of two coordinated water molecule; spectroscopic data suggested a plausible square antiprismatic geometrical structure around the Ln(III) metal ions as shown in Fig.2.

Acknowledgement

Authors are thankful to Mr.Dara technical man for providing necessary facilities and fruitful suggestions.

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Table(1)-Analytical and Physical data of the prepared complexes .

Molecular Formula	Colour	Yield%	m.p^{0}C	Elemental analysis Found(Calc.)% C	H	N	M	MolarConductivity Ohm^{-1} cm^2 mol^{-1}
K[La($C_{34}H_{36}O_{11}N_2$)] M.wt=827.10	Yellow	78	280	48.89 (49.32)	4.44 (4.35)	2.99 (3.38)	16.89 (16.68)	83
K[Ce($C_{34}H_{36}O_{11}N_2$)] M.wt=828.31	Pale Brown	80	240	49.00 (49.25)	4.01 4.34)	3.11 (3.38)	16.20 (16.91)	88
K[Nd($C_{34}H_{36}O_{11}N_2$)] M.wt=832.44	Olive Colour	76	225	48.83 (49.01)	4.11 (4.32)	3.12 (3.36)	17.11 (17.32)	91

Table (2)- Characteristic IR Spectra data of Ln(III) Complexes in Cm^{-1} .

Compound	-CH=N-	$(OH)_{H2O}$	$(COO)_{sy}$	$(COO)_{asy}$	ν(C-O)	Ln-N	Ln-O
K[La$(L)_2(H_2O)_2$].H_2O	1624	3415	1082 1168	1467 1454 1382	1296	430	534 493
K[Ce$(L)_2(H_2O)_2$].H_2O	1624	3442	1082 1168	1467 1452 1381	1238	491	540
K[Nd$(L)_2(H_2O)_2$].H_2O	1622	3442	1082 1168	1467 1452 1386	1236	493	534

L=$C_{17}H_{15}O_4N$ or o-Vanphen

Table(3)- Antibacterial Activity Results.

Complexes	Ec.	Sa.
$K[La(L)_2(H_2O)_2].H_2O$	3mm	2mm
$K[Ce(L)_2(H_2O)_2].H_2O$	3mm	4mm
$K[Nd(L)_2(H_2O)_2].H_2O$	5mm	5mm

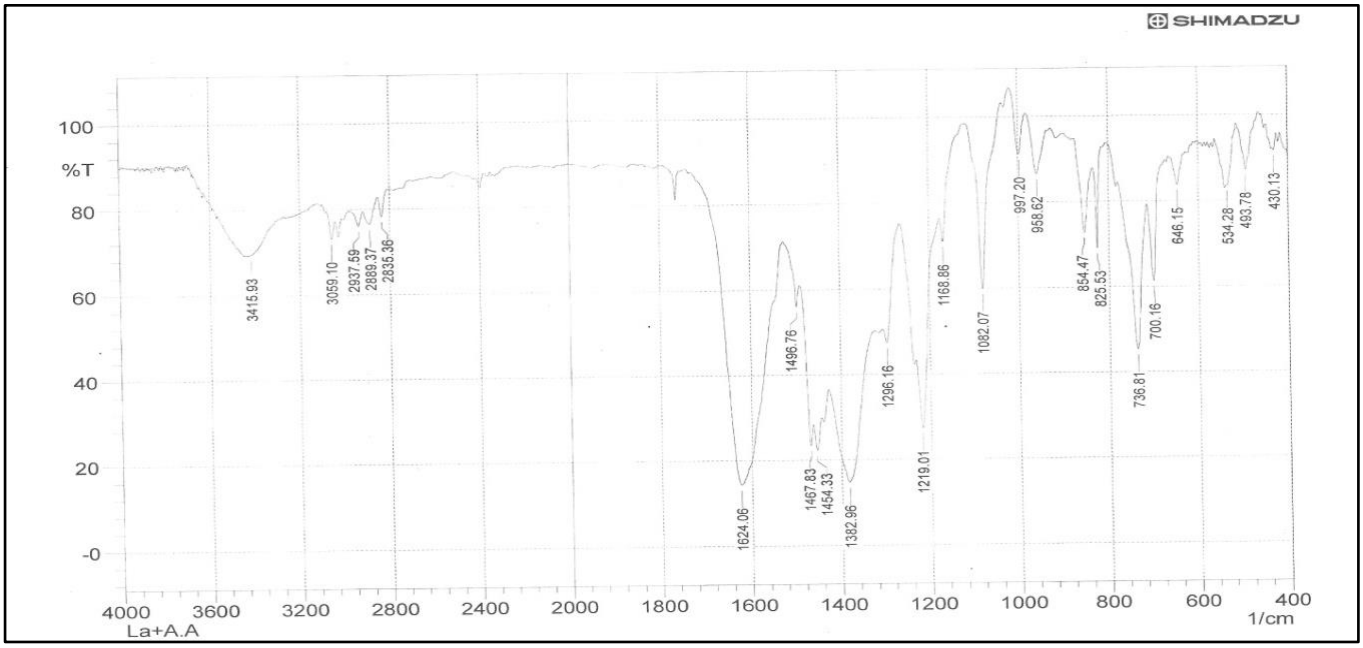

Fig.(2)- The IR spectra of $K[La(o\text{-}Vanphen)_2(H_2O)_2].H_2O$ complex.

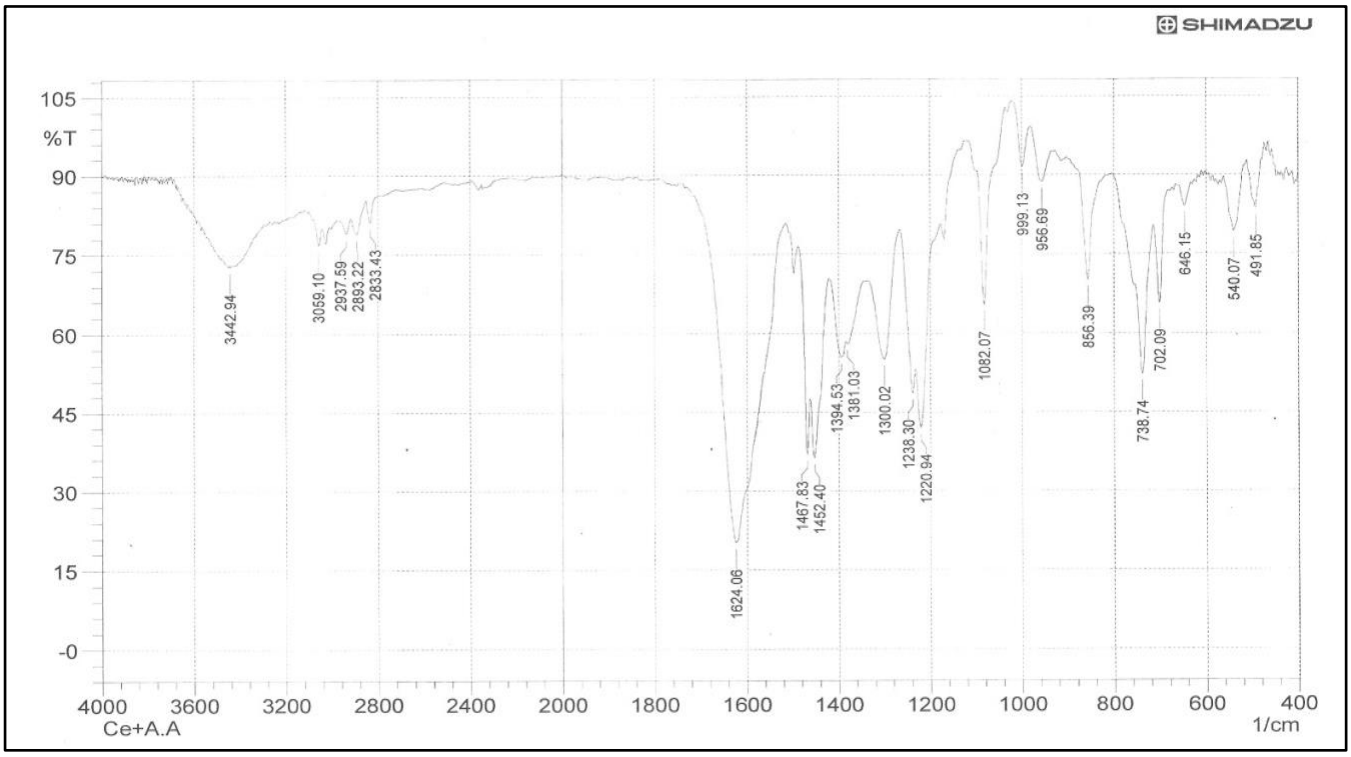

Fig.(3)- The IR spectra of K[Ce(o-Vanphen)$_2$(H$_2$O)$_2$].H$_2$O complex .

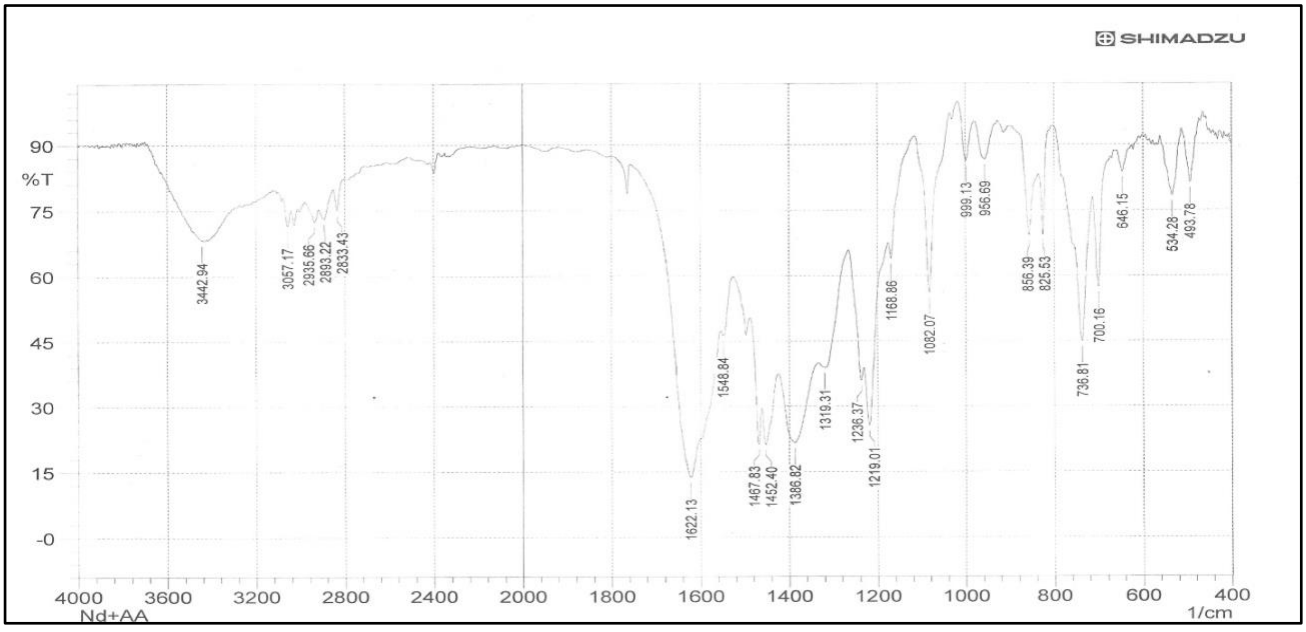

Fig.(4)- The IR spectra of K[Nd(o-Vanphen)$_2$(H$_2$O)$_2$].H$_2$O

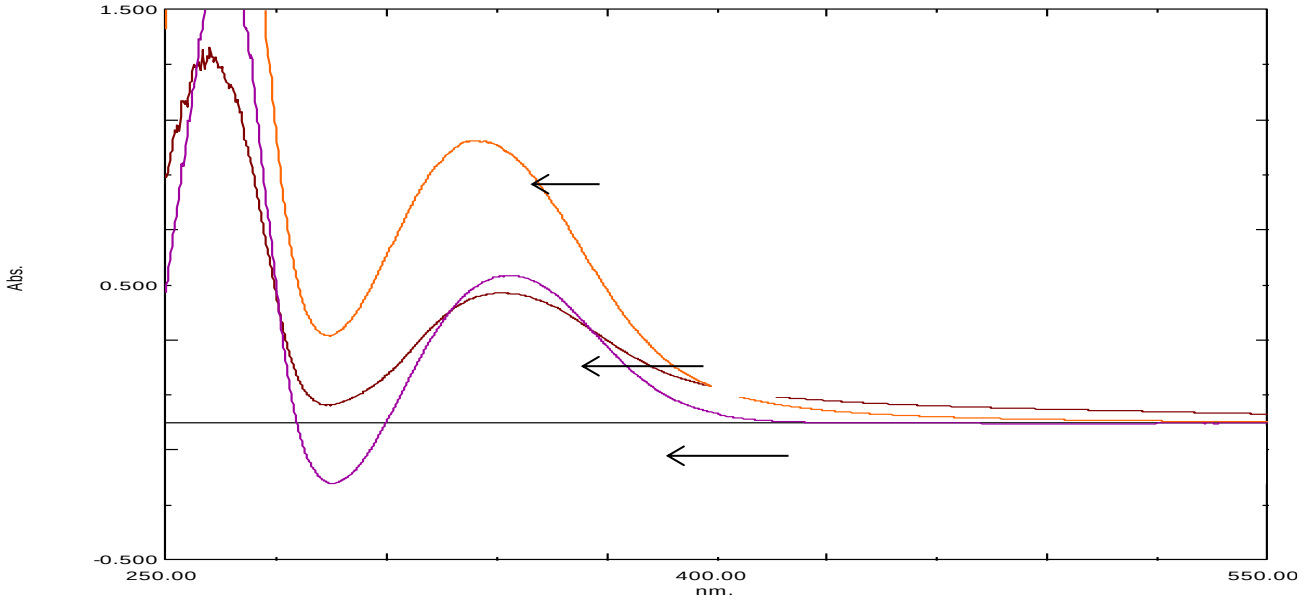

Fig.(5). Electronic absorption Spectrum of Ln(III) Complexes (conc.10^{-3}M in DMSO).

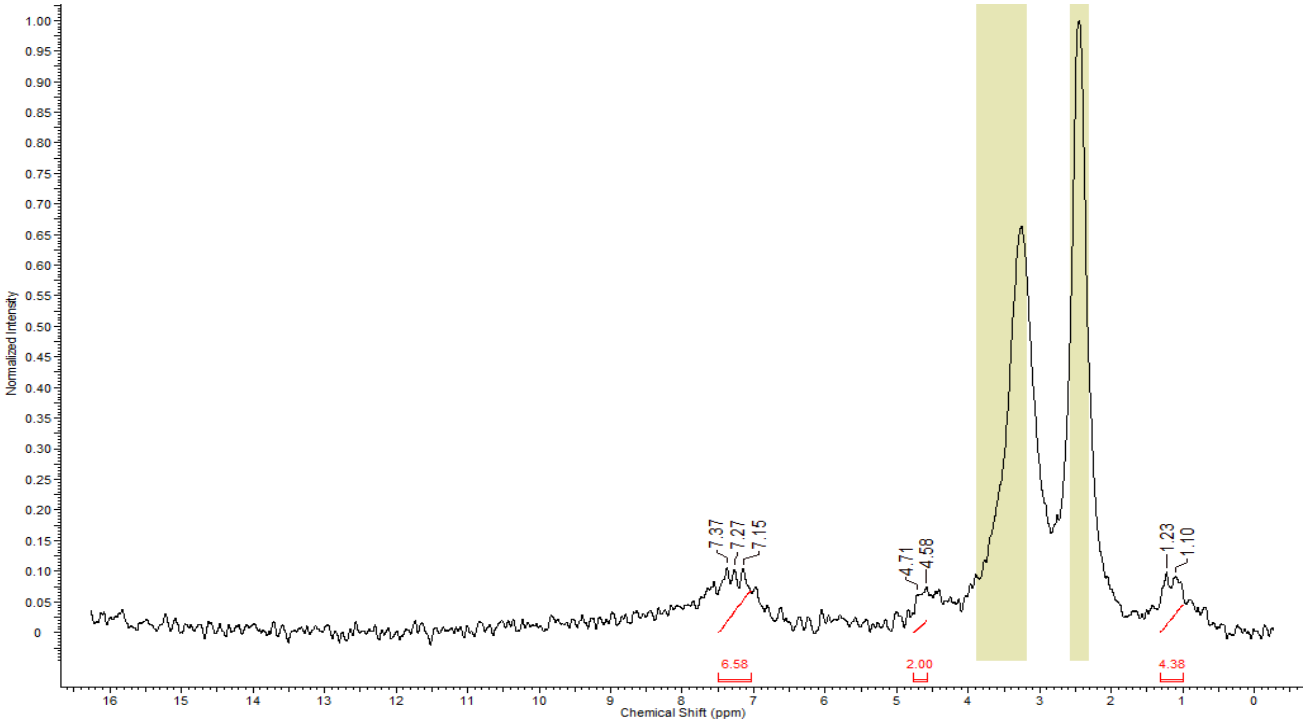

Fig.(6). ^{1}H-NMR spectrum of Nd(III) complex.