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SYNTHESIS, SPECTRAL PROPERTIES DNA STUDIES OF LANTHANIDE (III) COMPLEXES OF 2-ACETYLPYRIDINE BENZOYLHYDRAZONE

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ABSTRACT

The lanthanide (III) complexes of general formula of [Ln(APBH)2(NO3)3] (where, Ln = La, Ce, Pr, Nd, Sm, and APBH = 2-acetylpyridine benzoylhydrazone) have been synthesized and characterized by elemental analysis, molar conductance, spectroscopic (UV, IR), electro chemical, thermal studies and single crystal x-ray diffraction studies. The binding properties of these complexes with calf-thymus DNA have been investigated by using absorption spectrophotometry. The complexes interact with calf thymus DNA strongly (with Kb values of~ 105 M-1) suggesting significant groove binding. The complexes show nuclease activity via oxidative path way.

KEY WORDS: Lanthanide (III) complexes, electro chemical, DNA binding and DNA cleavage.

INTRODUCTION

A great interest for 2-Acetoyl pyridine hydrazones and their metal complexes have been motivated wide variety of biological and pharmaceutical activities, such as anticancer, antitumor, antimicrobial and anti proliferative activities.[1-6]

The interaction of metal complexes with DNA is an area of passionate curiosity to both inorganic chemists and biochemists. Over the past decade, the DNA-binding metal complexes has been demonstrated that inorganic complexes can be used as foot-printing studies[7] as sequence specific DNA cleaving agents,[8] as diagnostic agents in medicinal applications[9] and for genomic research.[10, 11] The interaction of metal complexes with DNA suggests that the complexes may have potential biological and pharmaceutical activity depends on the mode of binding and affinity of binding with DNA.[12-14] The intercalative binding is strongest than the other models (grove and electrostatic), because in intercalative type of binding in which the intercalative molecule surface is sandwiched between the aromatic chromophore, heterocyclic base pairs of DNA.[15,16]

Coordination chemistry of lanthanides has developed into the wide variety of applications. Lanthanide(III) complexes are used in materials science and biology,[17] supramolecular Luminescent sensors and self-assemblies,[18] contrast enhancing agents in radiopharmaceuticals as MRI agents[19] and in medicine.[20] The DNA binding and cleavage properties of lanthanide complexes under physiological conditions[21,22] have attracted much attention and curiosity of bio-inorganic chemists. Applications of lanthanide complexes as chemical nucleases are the focus of current research. However, there have been only a few DNA-binding and DNA cleavage investigations of hydrazone lanthanide complexes have been reported.

Here in, we report synthesis, spectral characterization, DNA binding and cleavage activity of La(III), Ce(III), Pr(III), Nd(III) and Sm(III) complexes with 2-Acetylpyridine benzoylhydrazone (APBH).

Experimental

MATERIALS AND METHODS

All the reagents used in the synthesis of ligand (viz. 2-Acetylpyridine, and benzoyl hydrazine) and lanthanide nitrates were purchased from Sigma-Aldrich chemicals and were used without further purification. The solvents were obtained after being distilled by standard method. Lanthanide salts were stored in desiccators to prevent hydration. Agarose used in gel electrophoresis was purchased from Sigma-Aldrich. CT-DNA, pBR 322 were purchased from Genie Biolabs, Bangalore, India.

Synthesis of 2-acetylpyridine benzoyl hydrazone (APBH): A methanolic solution of Benzhydrazide (0.68gm, 5 mmol) was refluxed with 2-Acetylpyridiene (0.560 ml, 5 mmol) continuously for 4h. After adding a few drops of glacial acetic acid. There was no immediate formation of the product. Then the reaction mixture was kept aside for slow evaporation at room temperature. After 1day white crystalline product is obtained. The compound was collected by filtration washed with hot water and recrystallized from methanol and dried in vacuum. Analytical data of APBH are given in Table 1. The ^{1}H-NMR spectra ($CDCl_3$, ppm); δ 2.5 (singlet, 3H), δ 7.21 (singlet, 1H), δ 7.45-8.6 (multiplet, 9H), are respectively assigned to $-CH_3$ (carbonyl), NH- and pyridine + phenyl protons. LC-MS spectrum of APBH shows molecular ion peaks at (*m/z*) 239.

Preparation of lanthanide [La(III), Ce(III), Pr(III), Nd(III) and Sm(III)] complexes (1-5): The Lanthanide complex was prepared by mixing hot ethanolic solution of APBH (2 mmol, 0.354 gm) and $Ln(NO_3)_3.6H_2O$ (1 mmol) dissolved in ethanol in 2:1 ratio in a clean 100-ml round bottom flask and the contents were refluxed at 60° C on water bath for 1-2days. There was no formation of the product. Then the reaction mixture was kept aside at room temperature. After few days, product is obtained. The complex was collected by filtration, washed with small quantity of ether. dark yellow coloured needle shape single crystals of cerium complex and white coloured single crystals of samarium complex were obtained on slow evaporation of the ethanol solution of mother compound at room temperature. These crystals are suitable for X-ray diffraction studies. Analytical data are shown in Table 1.

Physical measurements: The elemental analyses were performed using a Perkin-Elmer 2400 CHNS elemental analyzer. The molar conductance of the complexes in DMF (10^{-3}M) solution was measured at 28°C with a systronic model 303 direct-reading conductivity bridge. The electronic spectra were recorded in DMF with a Perkin Elmer UV Lamda -50 spectrophotometer. FT-IR spectra in KBR disc were recorded in the range 4000-400 cm^{-1} with a Perkin Elmer spectrum 100 spectrometer. The cyclic voltammetry was performed with a CH instruments 660C Electrochemical analyzer and a conventional three electrode, Ag/AgCl reference electrode, glassy carbon working electrode and platinum counter electrode. Nitrogen gas was purged and easurements were made on the degassed (N_2 bubbling for 5 min) complex solution in DMF (10^{-3}M) containing 0.1 M tetrabutylammonium hexaflourophosphate (TBAHEP) as the supporting electrolyte. TG-DTA performed with a Perkin Elmer STA 6000 simultaneous thermal analyzer operating at a heating rate of 10° C/min in the range of ambient temperature up to 800° C under nitrogen flow.

DNA binding experiments

Interaction of Lanthanide complexes with calf thymus DNA was studied by UV-vis spectroscopy. The interaction of the complexes with CT-DNA was carried out in tris-buffer. Solution of CT-DNA in (0.5mM NaCl/5mM Tris-HCl; pH = 7.0) buffer gave absorbance ratio at 260 nm and 280 nm of 1.89 indicating that the CT-DNA was sufficiently free of proteins. The DNA concentration per nucleotide was determined by absorption coefficient (6600 dm^3 mol^{-1} cm^{-1}) at 260 nm. Stock solutions stored at 4°C were used after no more than four days. The electronic spectra of metal complexes in aqueous solutions were monitored in the absence and presence of CT-DNA. Absorption titrations were performed by maintaining the metal complex concentration 20 $x10^{-6}$ M and varying the nucleic acid concentration (0 to 8.53 $\times10^{-6}$ M). Absorption titration experiments were performed by maintaining the metal complex concentration constant while gradually increasing the concentration of CT-DNA with each addition of 10 µl DNA. The ratio of r = [complex]/[DNA] values vary from 34.82 to 1.64.

DNA cleavage experiments: The Nuclease activity of lanthanide complexes was performed using agarose gel electrophoresis with pBR 322 DNA. After incubation for 30 min at 37°C, the samples were added to the loading buffer containing 0.25% bromophenol blue + 0.25% xylene cyanol + 30% glycerol, and solutions were loaded on 0.8% agarose gel containing 100 µg of ethidium bromide. Electrophoresis was performed at 75 V in TBE buffer until the bromophenol blue reached to 3/4 of the gel. Bands were visualized by UV Transilluminator and photographed. The efficiency of DNA cleavage was measured by determining the ability of the complex to form open circular (OC) or nicked circular (NC) DNA from its supercoiled (SC) form. The reactions were carried out under different conditions.

RESULTS AND DISCUSSION

Physico-chemical properties: All the complexes are stable at room temperature, non-hygroscopic, soluble in DMF and DMSO. The analytical data are consistent with the proposed molecular formulae of complexes. Physical properties viz., colour of the complex, melting points and yields of the complexes are given in **Table 1.**

Table 1 Colors, analytical data, molar conductivities and melting points of the APBH ligand and its Lanthanide (III) complexes.

Compound	Colour	M.P °C	Yield %	Found (cal %)			Λm*
				C	H	N	
APBH	White	103-105	73	70.16 (70.28)	5.34 (5.48)	17.66 (17.56)	…
$[La(APBH)_2(NO_3)_3]$	White	230-232	68	41.92 (41.86)	3.11 (3.26)	16.73 (15.69)	12
$[Ce(APBH)_2(NO_3)_3]$	Yellow	210-212	69	41.65 (41.79)	3.06 (3.26)	15.51 (15.67)	13
$[Pr(APBH)_2(NO_3)_3]$	Light Green	222-224	71	41.81 (41.75)	3.15 (3.25)	15.46 (15.65)	16
$[Nd(APBH)_2(NO_3)_3]$	Light Pink	232-234	70	41.73 (41.58)	3.36 (3.24)	15.64 (15.59)	15
$[Sm(APBH)_2(NO_3)_3]$	Light white	217-219	63	42.51 (41.27)	3.14 (3.22)	15.62 (15.47)	19

* (Ω^{-1} cm^2 mol^{-1})

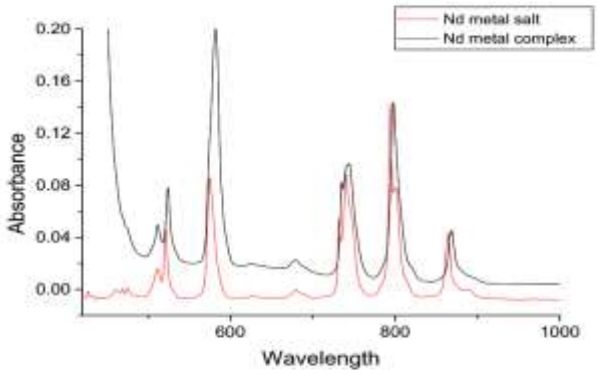
Conductivity measurements

All the complexes are freely soluble in dimethylformamide (DMF), hence the solutions of these metal complexes were prepared in DMF to perform conductivity measurements. Conductivity values of the solutions are measured at room temperature. The molar conductivity values (12-19 $\Omega^{-1}cm^2\ mol^{-1}$) for the complexes suggest that these are non-electrolytes.[23]

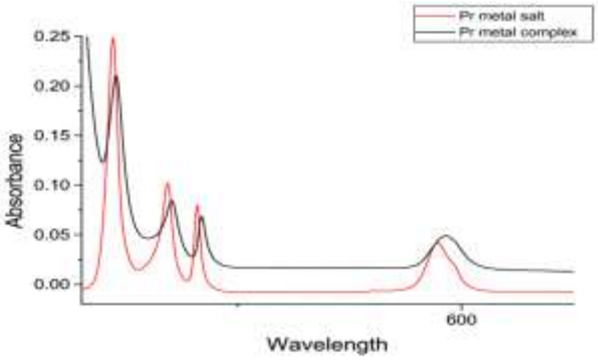
Electronic Spectra

Lanthanide complexes exhibit various colours due to the redistribution of electrons in the partially filled f-orbitals and referred to as f-f transitions. In absence of the ligands around the metal, the energy of all seven f-orbitals of a lanthanide metal ion are equal and are degenerate. The presence of ligands will result in splitting in the energy levels of these orbitals. In metal complexes some orbitals will interact more strongly than others. The exact form of interaction and energies of f-orbitals depend on the arrangements of ligands around the metal ions. In UV-visible, near IR region of electromagnetic radiation, the transition associated with electronic energy levels of the compound under investigation can be identified. The electronic spectral data of lanthanide complexes are recorded in dimethylformamide (DMF).

Electronic spectrum of the free ligand (APBH) in UV region shows an intense band at 295 nm and weaker band at 365 nm which are assigned to the π-π* and n-π*transition respectively. These are slight by shifted to higher or lower energy levels in absorption spectra of the lanthanide complexes. The electronic spectra of the lanthanide complexes in the visible region exhibit red shift of all the f-f spectral bands relative to the corresponding Ln(III) aquo ion, shown in Fig. 1. The shifts have been attributed by Jorgenson to the effect of crystal field upon interelectronic repulsion between the 4f electrons and are related to covalence in the metal-ligand bond. The values of the bonding parameters are given in Table 2. The positive and negative values of δ and $b^{1/2}$ for a complex correspond to covalent and ionic characters, respectively. The nephelauxetic ratio (β) is less than unity. The positive values of Sinha's parameter (δ) and the bonding parameter ($b^{1/2}$) suggest the occurrence of some covalent character in the metal–ligand bond.[24, 25] The small (δ %) values of the complexes indicate weak covalent bonding in the complexes. the small **b**^{½} values suggest a small participation of 4f orbitals in bonding.



(A)



(B)

Fig 1: Electronic absorption spectra of (A) $Nd(NO_3)_3.6H_2O$ (red) & $[Nd(APBH)_2(NO_3)_3]$ (black) and (B) $Pr(NO_3)_3.6H_2O$ (red) & $[Pr(APBH)_2(NO_3)_3]$ (black) in the visible region

Nephelauxetic ratio (β)

$$\beta = \frac{\nu_c}{\nu_f}$$

(where ν_c & ν_f = wave numbers of f-f transition in spectra of metal complex and free metal ion in solvent)

Bonding Parameter ($b^{1/2}$)

$$b^{1/2} = [\frac{1}{2}(1-\beta)]^{1/2}$$

Sinha's Covalency parameter (δ%)

$$\delta = \frac{1-\beta}{\beta}x100$$

Covalency angular overlap parameter (η)

$$\eta = \frac{1-\beta^{1/2}}{\beta^{1/2}}$$

Table 2: Electronic spectral data of the lanthanide complexes and related bonding parameter

complexes	Frequency (cm^{-1})		Red shift (cm^{-1})	Assignment	Covalent Parameter
	Lanthanide Aqua ion	Lanthanide complexes			
$[Pr(APBH)_2(NO_3)_3]$	16,977	16,863	116	$^3H_4 \rightarrow {}^1D_2$	β =0.9875
	20,746	20,661	86	$^3H_4 \rightarrow {}^3P_0$	δ% =1.26
	21,367	21,276	93	$^3H_4 \rightarrow {}^3P_1$	$b^{1/2}$ =0.079
	22,522	22,471	51	$^3H_4 \rightarrow {}^3P_2$	η =0.00633

[Nd(APBH)$_2$(NO$_3$)$_3$]	11,560	11,520	41	$^4I_{9/2}\rightarrow{}^4F_{3/2}$	β =0.9957
	12,594	12,531	63	$^4I_{9/2}\rightarrow{}^4F_{5/2}$	δ %=0.43
	13,513	13,495	20	$^4I_{9/2}\rightarrow{}^4F_{7/2}$, $^3S_{3/2}$	$b^{1/2}$ =0.046
	17,391	17,182	209	$^4I_{9/2}\rightarrow{}^4G_{5/2}$, $^2G_{7/2}$	η =0.0022
	19,120	19,083	37	$^4I_{9/2}\rightarrow{}^4G_{7/2}$	
	19,569	19,531	38	$^4I_{9/2}\rightarrow{}^4G_{9/2}$	
[Sm(APBH)$_2$(NO$_3$)$_3$]	24,038	23,980	58	$^6H_{5/2}\rightarrow{}^6P_{5/2}$	β =0.9989
	22,675	22,650	25	$^6H_{5/2}\rightarrow{}^4G_{9/2}$	δ% =0.11
	21,598	21598	4	$^6H_{5/2}\rightarrow{}^4I_{13/2}$	$b^{1/2}$ = 0.023
	20,876	20,876	6	$^6H_{5/2}\rightarrow{}^4I_{11/2}$	η = 0.0006
	20,040	20,000	38	$^6H_{5/2}\rightarrow{}^6G_{7/2}$	

Infrared Spectra

The FT-IR spectra of complexes in the region 4000-400 cm^{-1} are analysed in comparison with that of the spectrum of metal free APBH. The characteristic IR peaks of APBH and its lanthanide complexes are given in Table 3. IR spectra of the five complexes are strikingly similar in relative positions and intensities of the peaks, which suggest a close structural relationship among the compounds. The IR spectrum of the free ligand shows strong band at 1675 cm^{-1}, which is attributable to stretching vibrations of the carbonyl group (ν(C=O)). The vibrational band at 1576 cm^{-1} can be assigned to the ν(C=N) of azomethine. In the IR spectra of their lanthanide(III) complexes, the ν(C=O) and ν(C =N) bands are shifted by 33–55, 06–16 cm^{-1}.The shifts of the ν(C=O) and ν (C=N) vibrations towards lower wave numbers on complexation indicate participation of the carbonyl oxygen and azomethine nitrogen in coordination to the metal ion.[26] The vibrational band at 3176 cm^{-1} can be assigned to the ν(N-H) for the free ligand. The ν(N-H) band is observed in the range 3188-3235 cm^{-1} in the spectra of complexes. The observance of ν(C=O) and ν(N-H) bands in the IR spectra of complexes indicate that the ligand acts as neutral tridentate ligand. The pyridine ring in-plane deformation mode observed at 629 cm^{-1} in the spectrum of APBH. The band is shifted to higher wave numbers (630-632 cm^{-1}) in the spectra of lanthanide complexes indicating coordination of the pyridine nitrogen [26] to form chelate ring structure.

The absorption bands assigned to the coordinated nitrate groups ($C2$v) are observed at about 1476-1474 cm^{-1} (ν_1), 1295-1297 cm^{-1} (ν_4), 1024-1026 cm^{-1} (ν_2) and 816-818 cm^{-1} (ν_3) for the nitrate complexes. The frequency separation [$\Delta\nu = \nu_1 - \nu_4$] between the asymmetric and symmetric stretching of this group can be used in the distinction between these binding states. The separation of the two bands (ν_1 and ν4) is in the range 169–179 cm^{-1}, which shows the presence of bidentate nitrates.[27, 28] The vibrational band is absent at 1384 cm^{-1} in IR spectra of complexes indicating the absence of ionic nitrate (D_{3h} symmetry), which is in agreement with the results of the conductivity experiments. The new bands in 416 -423 and 541 - 546 cm^{-1} regions are assigned to ν(Ln–O) and ν (Ln–N) vibration respectively.

Table 3 Infrared spectral data(cm^{-1}) for the APBH ligand and its lanthanide(III) complexes

Compound	**ν(N-H)**	**ν(C=O)**	**ν(C=N)**	**ν(NO$_3^-$)**				
				ν_1(NO$_3^-$)	**ν_4(NO$_3^-$)**	**ν_2(NO$_3^-$)**	**ν_3(NO$_3^-$)**	**ν_1-ν_4**
APBH	3176	1675	1576	…	…	…	…	…
[La(APBH)$_2$(NO$_3$)$_3$]	3235	1642	1570	1476	1297	1026	817	179
[Ce(APBH)$_2$(NO$_3$)$_3$]	3199	1633	1560	1474	1295	1024	816	179
[Pr(APBH)$_2$(NO$_3$)$_3$]	3202	1624	1565	1476	1307	1024	818	169
[Nd(APBH)$_2$(NO$_3$)$_3$]	3188	1620	1564	1474	1296	1024	817	178
[Sm(APBH)$_2$(NO$_3$)$_3$]	3201	1624	1563	1474	1296	1025	817	178

Cyclic voltammetry

Redox behavior of the lanthanide(III) complexes has been investigated by cyclic voltammetry using 0.1M tetrabutylammonium hexaflourophosphate (TBAHEP) as supporting electrolyte. The cyclic voltammetric profiles of [Ce(APBH)$_2$(NO$_3$)$_3$] complex are given in Fig 2. A plot of i_p vs $\upsilon^{1/2}$(scan rate) is linear (Fig. 3) pointing towards diffusion controlled nature of reduction wave. In the reverse scan there is no anodic peak confirming the irreversible nature of electrode process. All these facts suggest the diffusion-controlled nature of the electrode process. The cyclic voltammograms of La(III), Ce(III). Pr(III), Nd(III) and Sm(III) gave irreversible waves. Their cathodic peak potentials are -1.15 [La(III)], -0.92 [Ce(III)], -0.83[Pr(III)], -0.94[Nd(III)] and -0.81[(Sm(III)]. The cathodic peak is due to the reduction of Ln(III) to Ln(II).[29]

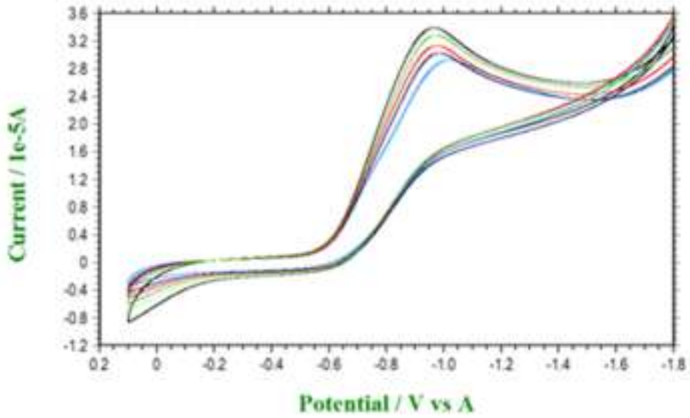


Fig 2: Cyclicvoltammetric profiles of the cerium complex at different scan rates 25-125 mV/s.

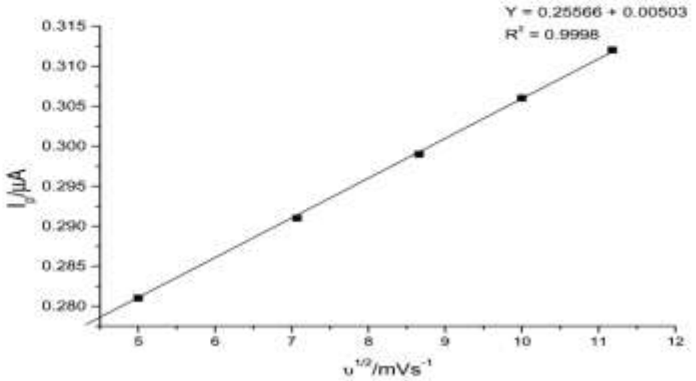


Fig 3: Plot of peak current vs scan rate for cerium complexes.

DNA binding studies

Electronic absorption spectroscopy is an effective method for examining the interaction of DNA with metal complexes. Hyperchromic and hypochromic effects are the spectral changes when a complex interacts with DNA and forms a new complex. In general, a complex binding with DNA through intercalation usually results in hypochromism and bathochromism of the absorption band due to the intercalative mode involving a strong π-stacking interaction between the aromatic chromophore and base pairs of DNA.[30] The binding interaction of complexes with CT-DNA was monitored by comparing their absorption spectra with and without CT-DNA. All the complexes exhibit an intense absorption band in 298-300.5 nm region attributed to π→π* transition. Absorption spectra of $[La(APBH)_2(NO_3)_3]$ in the absence and in presence of CT-DNA are shown Fig 4. The intrinsic binding constants (K_b), was determined by using the equation,

$[DNA] / (\varepsilon_a-\varepsilon_f) = [DNA] / (\varepsilon_b-\varepsilon_f) + 1/ K_b(\varepsilon_b-\varepsilon_f)$ ----------------(1)

Where [DNA] is the concentration of DNA in base pairs, ε_a, ε_b and ε_f are apparent extinction coefficient ($A_{obs/}[M]$), the extinction coefficient for the metal (M) complex in the fully bound form and the extinction coefficient for free metal (M) respectively. A plot of $[DNA] / (\varepsilon_a-\varepsilon_f)$ versus [DNA] gave a slope of $1/(\varepsilon_b-\varepsilon_f)$, and vertical intercept equal to $1/ K_b(\varepsilon_b–\varepsilon_f)$; K_b was calculated from these values. The binding constants (Table 4) for lanthanide complexes are almost similar and independent of metal ion. This observation suggests that the complexes do not bind DNA via coordination (No direct Metal- DNA bond formation). On addition of DNA, the absorbance of the complexes decreases (hypochromism). Negligible red shift (0.5 – 1.5 nm) in band position is observed for lanthanide complexes.[31] These observations suggest groove binding of complexes to DNA.

Table 4 Electronic absorption data upon addition of CT-DNA to the complexes

Compound	**λ_{max} (nm)**		**Δλ**	**H(%)**	**K_b (M^{-1})**
	Free	**bound**			
$[La(APBH)_2(NO_3)_3]$	298	299.5	1.5	29.71	$1.32x10^5$
$[Ce(APBH)_2(NO_3)_3]$	298	299	1	32.50	$1.40x10^5$
$[Pr(APBH)_2(NO_3)_3]$	299	300	1	34.46	$1.43x10^5$
$[Nd(APBH)_2(NO_3)_3]$	299	299.5	0.5	31.42	$1.39x10^5$
$[Sm(APBH)_2(NO_3)_3]$	299	300.5	1.5	30.42	$1.38x10^5$

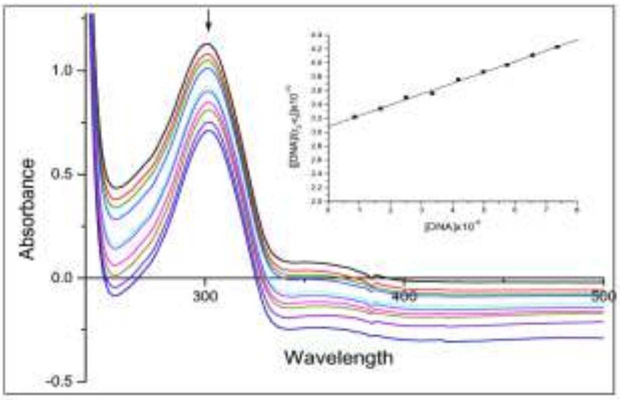


Fig 4: Absorption spectra of $[La(APBH)_2(NO_3)_3]$ in the absence and in the presence of increasing concentration of CT-DNA; top most spectrum is recorded in the absence of DNA and below spectra on addition of 10 µl DNA each time.

DNA Cleavage studies

Nuclease activity of lanthanide complexes derived from 2-acetylpyridine benzoylhydrazone (APBH) has been studied by agarose gel electrophoresis using pBR 322 plasmid DNA in Tris-HCl/NaCl (50mM/5mM) buffer(pH-7) in the presence and in absence of H_2O_2 as an oxidant at micro molar concentration for 30 min incubation period at 37° C. In the presence of H_2O_2 the super coiled DNA (form I) is changed into nicked form (form II). Fig. 5 and 6. show the cleavage activity of lanthanide complexes. In the presence of H_2O_2 the complexes cleave DNA more effectively [lanes 4, 6 and 8 in Fig 5; lanes 4, 6 in Fig 6], which may be due to the reaction of hydroxyl radical with DNA like Fenton mechanism.[32] These hydroxyl free radicals participate in the oxidation of the deoxyribose moiety.[33] The order of nuclaese activity is as follow in the presence of hydrogen peroxide.

Ce complex > Pr complex > Nd complex > Sm complex > La complex

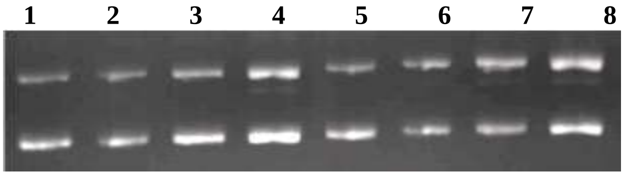


Fig 5: Agarose gel (0.8%) showing results of electrophoresis of 1 µl of pBR322 Plasmid DNA; 4 µl of Tris–HCl/NaCl (50 mM/5 mM) buffer (pH-7); 2 µl of complex in DMF($1x10^{-3}$ M); 11 µl of sterilized water; 2 µl of H_2O_2 (total volume 20 µl) were added, respectively, incubated at 37°C (30 min); Lane 1: DNAcontrol; Lane 2: DNA control + H_2O_2; Lane 3: Lanthanum complex+ DNA; Lane 4: Lanthanum complex + DNA + H_2O_2; Lane 5: Cerium complex+ DNA; Lane 6: Cerium complex+ DNA + H_2O_2; Lane 7:Samarium complex+ DNA; Lane 8: Samarium complex + DNA+H_2O_2.

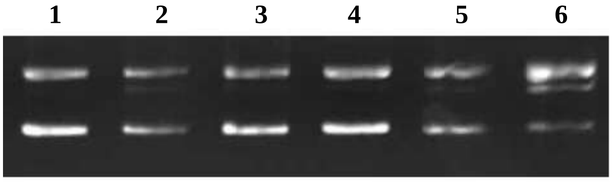


Fig 6: Agarose gel (0.8%) showing results of electrophoresis of 1 µl of pBR322 Plasmid DNA; 4 µl of Tris–HCl/NaCl (50 mM/5 mM) buffer (pH-7); 2 µl of complex in DMF($1x10^{-3}$ M); 11 µl of sterilized water; 2 µl of H_2O_2 (total volume 20 µl) were added, respectively, incubated at 37°C (30 min); Lane 1: DNA control; Lane 2: DNA control + H_2O_2; Lane 3: Praseodymium complex+ DNA; Lane 4: Praseodymium complex+ DNA + H_2O_2; Lane 5: Neodymium complex+ DNA; Lane 6: Neodymium complex+ DNA+H_2O_2;

CONCLUSIONS

La(III), Ce(III), Pr(III), Nd(III) and Sm(III) complexes of 2-acetylpyridine benzoylhydrazone(APBH) have been synthesized and characterized. Physico-chemical and spectral studies reveal that the complexes have general formula $[Ln (APBH)_2 (NO_3)_3]$ (where Ln = La, Ce, Pr, Nd, and Sm). APBH acts as neutral tridentate ligand and NO_3^- acts as bidentate ligand. Two APBH ligands occupy six coordination sites and three NO_3^-ligands another six coordination sites to form 12- coordinate complexes mono nuclear complexes.

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