

**SPECTRAL CHARACTERIZATION AND DNA BINDING PROPERTIES OF
LANTHANIDE(III) COMPLEXES WITH 2-ACETYLPIRIDINE
ISONICOTINOYLHYDRAZONE (APINH)**

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ABSTRACT. The lanthanide(III) complexes of general formula of $[Ln(APINH)_2(NO_3)(NO_3)_2 \cdot nH_2O]$ (where, Ln = La, Ce, Pr, Nd, Sm; APINH = 2-acetylpyridine isonicotinoyl hydrazone, n = 0, 2 and 5 for La/Ce/Pr, Sm and Nd complexes, respectively) were synthesized under mild reaction conditions with excellent yields. The complexes were characterized based on elemental analysis, molar conductivity, and infrared spectroscopy. Molar conductivity data suggest that the complexes are 1:2 electrolytes. IR spectral data suggest that APINH acts as neutral tridentate ligand. Spectral data of complexes suggest that the ligand binds metal ion through pyridine-nitrogen, azomethine-nitrogen and amido-oxygen donor atoms. Electrochemical behaviour of metal complexes was investigated by using cyclic voltammetry. The complexes undergo quasi-reversible one electron reduction. The binding interaction of complexes with CT-DNA was investigated using absorption spectrophotometry. Based on spectral changes, *groove binding* of complexes to DNA is suggested.

KEY WORDS: Lanthanide(III) complexes, 2-Acetylpyridine isonicotinoylhydrazone, Spectral characterization, DNA binding

INTRODUCTION

Investigations of lanthanide complexes with polydentate ligands have received considerable attention because of their potential applications in various fields [1-11]. Hence, the synthesis of and characterization of newer lanthanide complexes is a potential field of research in inorganic chemistry. Though Sacconi has reported [12] lanthanide complexes of acetylacetone isonicotinoyl hydrazone in the year 1954, a literature review [13-15] indicated that the study of such complexes is relatively less when compared with transition metal complexes with this class of ligands.

The chemistry of lanthanide complexes is of interest owing to their applications in biology and medicine [16, 17]. Heterocyclic hydrazones as well as their metal complexes gained importance because of their pharmacological properties [18-20]. Metal complexes of isonicotinoylhydrazones exhibit antitumour [21] and antibacterial activity [22]. There is also much interest in the development of artificial nucleases. Artificial metallonucleases require ligands which effectively deliver metal ions to the vicinity of DNA. Investigation of metal-DNA interactions [23] has been an area of active research [24, 25]. Studies on chemical modification of nucleic acids with lanthanide complexes are of great interest in the design of chemotherapeutic drugs, regulation of gene expression and design of tools for molecular biology [26]. Synthesis and characterization of divalent transition metals with 2-acetyl-pyridyl-isonicotinoylhydrazone (APINH) are reported recently [27]. However, lanthanide complexes of APINH are not reported.

In the light of the above and in continuation of earlier work [28, 29] on DNA binding and cleavage activities of transition metal complex, herein we report synthesis, spectral characterization and DNA binding properties of lanthanide(III) complexes of 2-acetylpyridine isonicotinoylhydrazone for the first time.

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EXPERIMENTAL

Lanthanide nitrates, 2-acetylpyridine and isoniazid, purchased from Aldrich chemicals were used without further purification. Lanthanide salts were stored in desiccators to prevent hydration. CT DNA was purchased from Genie Biolabs, Bangalore, India.

Synthesis of 2-acetylpyridine isonicotinoylhydrazone (APINH)

A 5 mmol of 2-acetylpyridine (0.56 mL) dissolved in 20 mL of methanol was added to a methanolic solution of isonicotinic acid hydrazide (0.685 g, 5 mmol). The contents were taken in a round bottom flask stirred for 20 min. An yellow colored product was formed. It was collected by filtration, washed with a few drops of ethanol and dried in vacuum. Yield of the product was 85%, m.p.: 162-164 °C. Physicochemical and analytical data of APINH are given in Table 1

General procedure for the synthesis of lanthanide complexes

To the ligand (0.480 g, 2 mmol) dissolved in 20 mL of methanol, lanthanum(III) nitrate hexahydrate $[\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ (1 mmol) dissolved in 10 mL of methanol was added. The reaction mixture (taken in 100-mL round bottom flask) was heated under reflux on water bath for 2-4 h. Upon cooling solid substance was formed. It was collected by filtration, washed with 10 mL of hexane and dried in vacuum. Physicochemical and analytical data of lanthanide complexes are included 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 magnetic measurements were recorded at room temperature at various field strengths using Lakeshore VSM 7410 magnetometer. 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 $4000\text{-}400\text{ cm}^{-1}$ 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 measurements were made on the degassed (N_2 bubbling for 5 min) complex solution in DMF (10^{-3} M) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAHP) as the supporting electrolyte.

Identification of nitrate

The presence of nitrate in the complexes is confirmed by well known brown ring test [30].

DNA binding experiments

Interaction of complexes with calf thymus DNA was studied by electronic absorption spectroscopy. The interaction of the complexes with DNA was carried out in tris-buffer. Solution of calf thymus-DNA (CT-DNA) in (0.5 mM NaCl/5 mM Tris-HCl; pH = 7.0) buffer gave absorbance ratio at 260 nm and 280 nm of 1.89 indicating that the DNA was sufficiently free of proteins. The DNA concentration per nucleotide was determined by absorption coefficient ($6600\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) 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 20×10^{-6} M and varying the nucleic acid concentration ($0-17.4 \times 10^{-4}$ M). The ratio of $r = [\text{complex}]/[\text{DNA}]$ values vary from 8.84 to 1.10. Absorption titration experiments were performed by maintaining the metal complex concentration constant while gradually increasing the concentration of CT-DNA within 0-80 μM .

RESULTS AND DISCUSSION

The ligand, APINH was used for the preparation of transition metal complexes. Spectral data of APINH are as follows: IR spectra; Bands at 3189, 1668, 1623, 1581, 991 and 753 cm^{-1} are respectively assigned to $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$ (Amide I), $\nu(\text{C}=\text{N})$, $\nu(\text{Py ring})$, $\nu(\text{Py bending})$, and $\gamma(\text{Py ring oop bending})$ vibrations, respectively. $^1\text{H-NMR}$ spectra were recorded in *deuterated* DMSO. δ 7.36-7.62 (multiplet 4H), δ 8.60-8.94 (multiplet 4H), δ 8.13 (singlet 1H), δ 3.34 (singlet 3 H), are respectively assigned to pyridine, isonicotine, -NH and methyl proton. GC-MS (Figure 1) shows peak at (m/z) 240 corresponding to molecular ion peak of the ligand. The structure of the ligand is given in Figure 2.

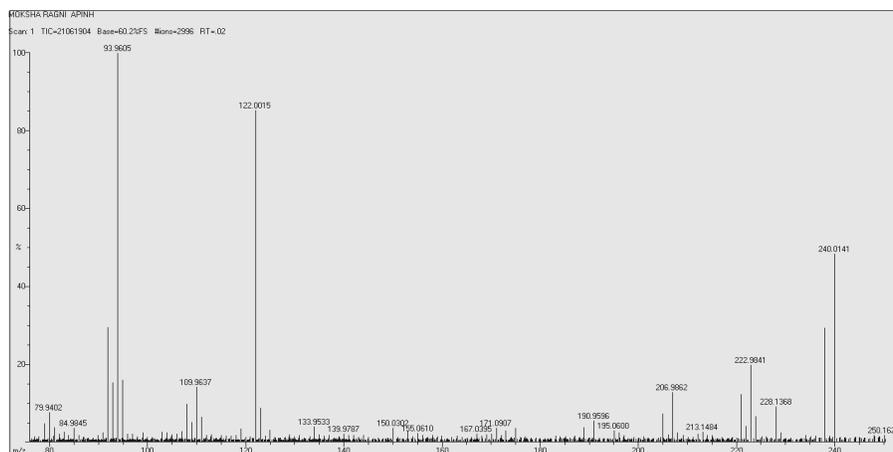


Figure 1. GC-MS spectrum of APINH ligand.

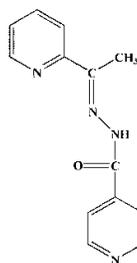
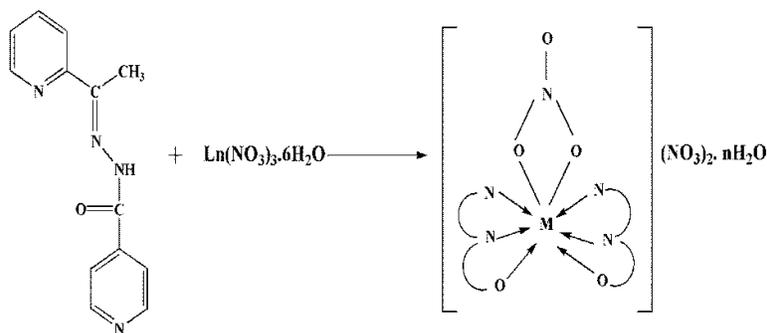


Figure 2. Structure of APINH ligand.

The complexes are obtained in good yields. The preparation of lanthanide complexes is given in Scheme 1. The complexes are stable at room temperature and non-hygroscopic and can be stored easily even at room temperature. The complexes are partially soluble in water, methanol, ethanol and readily soluble in acetonitrile (CH₃CN), DMF and DMSO.



Scheme 1. Synthesis of lanthanide complexes with APINH ligand.

The analytical data (Table 1) are consistent with the proposed molecular formulae {[Ln(APINH)₂(NO₃)](NO₃)₂·nH₂O (where, Ln = La, Ce, Pr, Nd, Sm; APINH = 2-acetylpyridine isonicotinoyl hydrazone, n = 0, 2 and 5 for La/Ce/Pr, Sm and Nd complexes, respectively)} of complexes. The molar conductivity values (97-120 Ω⁻¹ cm² mol⁻¹) for the complexes suggest that these are 1:2 electrolytes [31]. The presence of nitrate in the complexes was confirmed by brown ring test [30].

Table 1. Analytical and physico-chemical properties of APINH ligand and its lanthanide(III) complexes.

Complexes of APINH [*]	Colour (yield %)	Mol Wt.	M.P (°C)	Analysis found (calc %)			Molar conductivity (Ω ⁻¹ cm ² mol ⁻¹)
				C	H	N	
[La(C ₁₃ H ₁₂ N ₄ O) ₂ (NO ₃)](NO ₃) ₂	White (82)	805	220-224	39.75 (38.76)	2.78 (2.99)	18.13 (19.14)	113
[Ce(C ₁₃ H ₁₂ N ₄ O) ₂ (NO ₃)](NO ₃) ₂	Yellow (78)	806	218-220	37.70 (38.71)	2.97 (2.68)	20.10 (19.11)	129
[Nd(C ₁₃ H ₁₂ N ₄ O) ₂ (NO ₃)](NO ₃) ₂ ·5H ₂ O	Gray (75)	900	188-190	35.66 (34.65)	3.77 (3.58)	17.11 (16.10)	119
[Sm(C ₁₃ H ₁₂ N ₄ O) ₂ (NO ₃)](NO ₃) ₂ ·2H ₂ O	Yellow (80)	852	180-182	37.61 (36.60)	3.28 (3.19)	18.07 (17.06)	97
[Pr(C ₁₃ H ₁₂ N ₄ O) ₂ (NO ₃)](NO ₃) ₂	Green (76)	807	200-202	39.66 (38.67)	2.97 (2.46)	19.08 (20.09)	133

*APINH = (C₁₃H₁₂N₄O).

The room temperature magnetic hysteresis curves of Ce(III), Nd(III), Sm(III) and Pr(III) complexes exhibit characteristic patterns of paramagnetic component. The positive slope of the curve clearly indicates paramagnetic nature of the complexes [32]. The lanthanum(III) complex, [La(APINH)₂(NO₃)](NO₃)₂ is diamagnetic and other trivalent lanthanide complexes are paramagnetic. The observed magnetic moment values are less than theoretical values predicted for the trivalent lanthanide ions. This fact suggests that the 4f electrons/4f-orbitals do not participate in the bond formation of the metal to ligand [33].

Electronic spectra

The electronic spectra of ligand and their corresponding lanthanide(III) complexes are recorded in DMF. Typical electronic spectra (a) APINH ligand and (b) [La(APINH)₂(NO₃)](NO₃)₂ complex are shown in Figure 3.

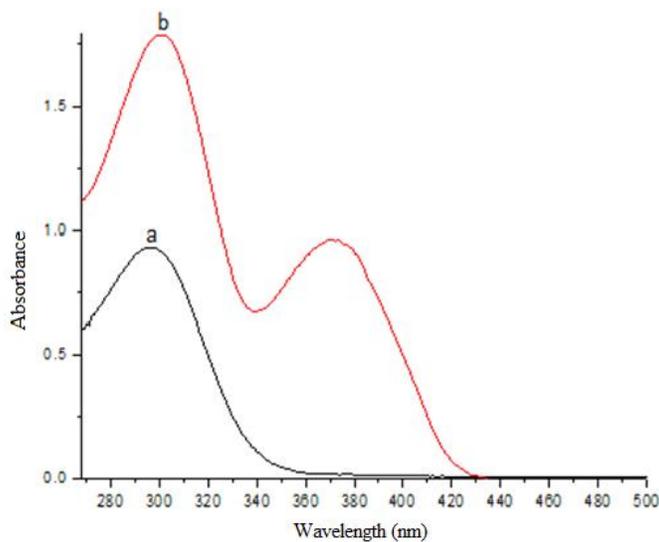


Figure 3. Electronic spectra of (a) APINH ligand and (b) [La(APINH)₂(NO₃)](NO₃)₂ complex.

In the electronic spectra of complexes a broad peak is observed in the high energy region at 33560-35720 cm⁻¹ assigned to π - π^* transition. A strong peak is observed in the low energy region (27030-27550 cm⁻¹) of electronic spectra of complexes. It is assigned to charge transfer transition. Electronic spectral data are given in Table 2.

Table 2. Electronic spectral data of the lanthanide(III) complexes.

Compound	λ_{\max} (nm)	ϵ	Band assignment
APINH Ligand	296 (33790)	938	π - π^*
[La(APINH) ₂ (NO ₃)](NO ₃) ₂	298 (33560) 363 (27550)	1600 1000	π - π^* CT
[Ce(APINH) ₂ (NO ₃)](NO ₃) ₂	298 (33560) 366 (27330)	1300 1000	π - π^* CT
[Nd(APINH) ₂ (NO ₃)](NO ₃) ₂ .5H ₂ O	298 (33560) 363 (27550)	760 1500	π - π^* CT
[Sm(APINH) ₂ (NO ₃)](NO ₃) ₂ .2H ₂ O	280 (35720) 370 (27030)	430 840	π - π^* CT
[Pr(APINH) ₂ (NO ₃)](NO ₃) ₂	294 (34015) 366 (27325)	1160 1060	π - π^* CT

ϵ = Molar absorptivity (L. mol⁻¹ cm⁻¹).

In the electronic spectra of complexes, absorption band due to f-f transition of lanthanide(III) ions is not observed. This is probably due to the fact that the f-f bands are weak and obscured by the intense M→L charge transfer band [33].

Infrared spectra

In the IR spectrum of APINH ligand a medium band is observed at 3178 cm^{-1} due to $\nu_{\text{N-H}}$ stretching vibration. IR spectral data of APINH and its lanthanide complexes are given in Table 3. In the spectra of lanthanide complexes, the band due to N-H stretching vibration of metal free ligand is not affected precluding the involvement of NH group in coordination. The appearance of NH band in the IR spectra of complexes suggests that the ligand remains in keto form in coordination [34]. Strong bands observed at 1668 and 1623 cm^{-1} are respectively assigned to $\nu_{\text{C=O}}$ and $\nu_{\text{C=N}}$ vibrations. In the spectra of complexes $\nu_{\text{C=O}}$ appears in 1631 - 1633 cm^{-1} region and $\nu_{\text{C=N}}$ appears in 1542 - 1556 cm^{-1} region. A considerable lowering of the $\nu_{\text{(C=O)}}$ and $\nu_{\text{(C=N)}}$ frequencies indicates participation of the amide oxygen and azomethine nitrogen in coordination to the metal [35]. In the IR spectrum of ligand, a peak due to ν (Py ring) is observed at 1581 cm^{-1} . It is shifted to lower frequency indicating coordination of pyridine nitrogen to metal [27].

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

Compound	ν (O-H)	ν (N-H)	ν (C=O)	ν (C=N)	Frequencies of coordinated NO ₃ ligand				
					ν_1	ν_2	ν_3	ν_4	ν_1 - ν_4
APINH (ligand)	----	3189	1668	1623	1458	1119	787	1293	165
[La(APINH) ₂ (NO ₃)](NO ₃) ₂	----	3111	1633	1590	1444	1153	784	1218	186
[Ce(APINH) ₂ (NO ₃)](NO ₃) ₂	----	3107	1632	1542	1434	1038	784	1214	220
[Nd(APINH) ₂ (NO ₃)](NO ₃) ₂ .5H ₂ O	3480	3065	1632	1580	1466	1066	779	1281	185
[Sm(APINH) ₂ (NO ₃)](NO ₃) ₂ .2H ₂ O	3485	3065	1631	1585	1468	1101	779	1282	186
[Pr(APINH) ₂ (NO ₃)](NO ₃) ₂	----	3110	1633	1582	1441	1035	784	1217	224

IR data suggest that the ligand acts as neutral tridentate ligand in lanthanide complexes and it binds metal via pyridine-nitrogen, azomethine-nitrogen and amido-oxygen donor atoms. The broad and medium intensity bands in the range 3480 - 3485 are observed in IR spectra of Nd and Sm complexes. These bands are assigned to O-H stretching vibrations of lattice water [36].

The IR spectra of the complexes demonstrate the presence of both coordinated nitrate and ionic nitrate. The two strong bands are observed in complexes due to the presence of coordinated nitrates. The two strong bands associated with asymmetric and symmetric stretch of coordinated to NO₃⁻ (C_{2v}) group appear in the range 1434 - 1468 (ν_1) and 1214 - 1293 (ν_4) cm^{-1} . The frequency separation $\Delta\nu$ (ν_1 - ν_4) increases as the coordination of nitrate group increases from monodentate to bidentate and/or bridging. The magnitude of $\Delta\nu$ is used to establish the type of nitrate coordination. In the present complexes the $\Delta\nu$ is in between 165 - 224 cm^{-1} and is typical of bidentate bonding of nitrate [37]. The vibrational band is observed around 1380 cm^{-1} in IR spectra of complexes indicating the presence of ionic nitrate (D_{3h} symmetry, free NO₃⁻ ion). Thus IR data indicate the presence of both ionic nitrate and coordinated bidentate nitrate groups in complexes. The new bands in 412 - 418 and 530 - 543 cm^{-1} regions are assigned to ν (Ln-O) and ν (Ln-N) vibration, respectively.

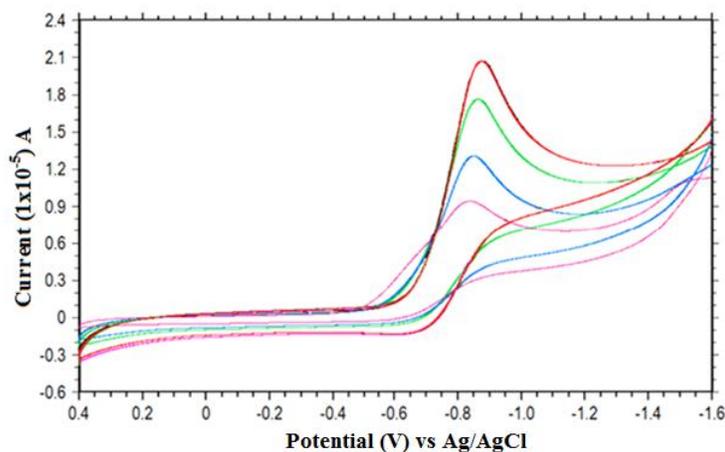
¹H-NMR spectral data of APINH ligand and [La(APINH)₂(NO₃)](NO₃)₂ complex are compared (Table 4). Peaks are slightly shifted to higher ppm in the spectra of complex indicating the complex formation between La(III) and APINH.

Electrochemical studies

Redox behavior of the lanthanide(III) complexes has been investigated by cyclic voltammetry in DMF using 0.1 M tetrabutylammonium hexafluorophosphate (TBAHP) as supporting electrolyte. The cyclic voltammetric profile of [Nd(APINH)₂(NO₃)](NO₃)₂.5H₂O complex is given in Figure 5.

Table 4. ¹H-NMR spectral data of APINH ligand and [La(APINH)₂(NO₃)₂](NO₃)₂ complex.

Ligand (APINH)	Complex	No. of protons	Assignment
3.340	3.439	3H(s)	Methyl
7.360-7.623	7.469-7.657	4H(m)	Pyridine
8.136	8.139	1H(s)	-NH
8.637-8.943	8.649-8.962	4H(m)	Isonicotinoylhydrazone

Figure 5. Cyclic voltammograms of [Nd(APINH)₂(NO₃)₂](NO₃)₂.5H₂O complex at different scan rates.

As the scan rate increases separation between cathodic and anodic peaks increases suggesting quasi-reversible character of cyclic voltammogram. The electrochemical data of the complexes are presented in Table 5.

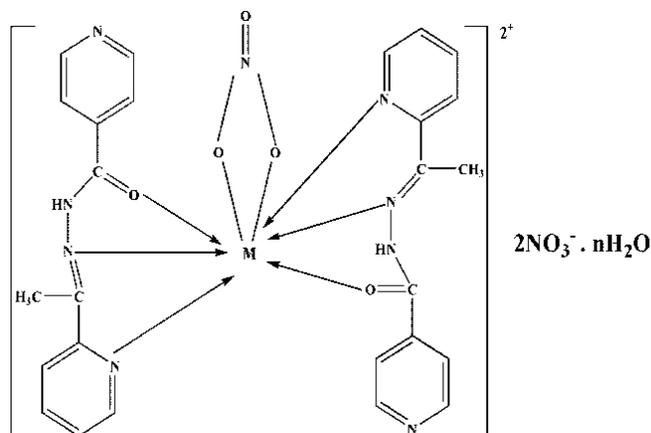
Table 5. Cyclic voltammetric data of lanthanide(III) complexes.

Complex	Redox couple	E _{pc} V	E _{pa} V	ΔE (mV)	E _{1/2}	log K _c ^a	-ΔG ^{°b}
APINH (ligand)	...	-0.95	-0.75	250	0.85
[La(APINH) ₂ (NO ₃) ₂](NO ₃) ₂	III/II	-0.550	-0.799	249	0.675	0.390	2243
[Ce(APINH) ₂ (NO ₃) ₂](NO ₃) ₂	III/II	-0.552	-0.705	153	0.628	0.15	864
[Nd(APINH) ₂ (NO ₃) ₂](NO ₃) ₂ .5H ₂ O	III/II	-0.849	-0.602	247	0.725	0.119	688
[Pr(APINH) ₂ (NO ₃) ₂](NO ₃) ₂	III/II	-0.852	-0.599	253	0.725	0.109	628

^alog K_c = 0.434ZF/RT ΔE_p, ^bΔG[°] = -2.303RT log K_c.

Repeated scans at various scan rates suggest the presence of stable redox species in solution. E_{1/2} values are incorporated in Table 5. It may be inferred that Ln(III) complexes undergo reduction to their respective Ln(II) complexes. The complexes have large separation (154-205 mV) between anodic and cathodic peaks indicating quasi-reversible character [38].

Based on molar conductivity and IR spectral data, a general structure (Figure 6) is proposed for the complexes.



M = La(III), Ce(III), Pr(III), Nd(III) and Sm(III); n = 0, 2 and 5 for La/Ce/Pr, Sm and Nd complexes.

Figure 6. A general structure for lanthanide complexes.

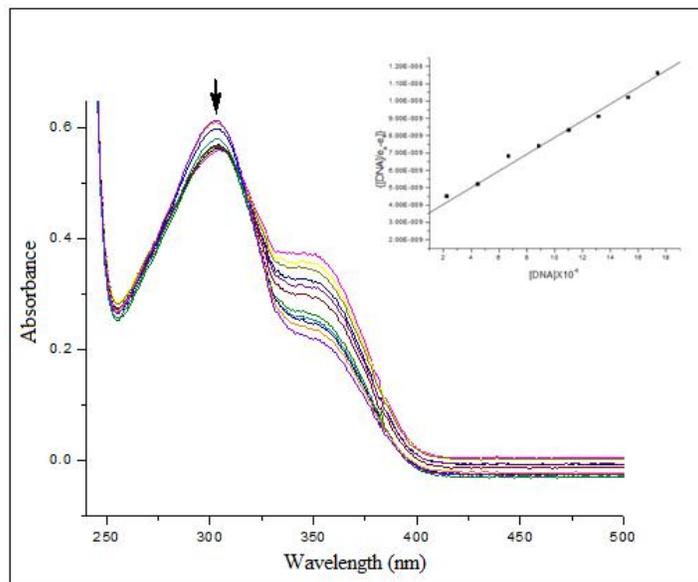


Figure 7. (A) Absorption spectra of $[\text{Nd}(\text{APINH})_2(\text{NO}_3)](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ in the absence and in the presence of increasing concentration of CT-DNA; top most spectrum is recorded in the absence of DNA; and (B) a plot of $[\text{DNA}]/(\epsilon_a - \epsilon_f)$ versus $[\text{DNA}]$.

DNA binding studies

Electronic absorption spectroscopy is an effective method for examining the interaction of DNA with metal complexes. 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 due to $\pi \rightarrow \pi^*$ transition. Absorption spectra of $[\text{Nd}(\text{APINH})_2(\text{NO}_3)](\text{NO}_3)_2$ in the absence and in presence of CT-DNA are shown Figure 7.

The intrinsic binding constants (K_b), were determined by using the equation,

$$[\text{DNA}]/(\epsilon_a - \epsilon_f) = [\text{DNA}] / (\epsilon_b - \epsilon_f) + 1/K_b(\epsilon_b - \epsilon_f) \quad (1)$$

where $[\text{DNA}]$ is the concentration of DNA in base pairs, ϵ_a , ϵ_b and ϵ_f are apparent extinction coefficient ($A_{\text{obs}}/[\text{M}]$), 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 $[\text{DNA}]/(\epsilon_a - \epsilon_f)$ versus $[\text{DNA}]$ gave a slope of $1/(\epsilon_b - \epsilon_f)$, and vertical intercept equal to $1/K_b(\epsilon_b - \epsilon_f)$; K_b was calculated from these values. The binding constants (Table 6) for suggest that the complexes bind DNA very strongly.

Table 6. Electronic absorption data upon addition of CT-DNA to the complexes.

Compound	λ_{max} (nm)		$\Delta\lambda/\text{nm}$	H (%)	K_b (M^{-1})
	free	bound			
$[\text{La}(\text{APINH})_2(\text{NO}_3)](\text{NO}_3)_2$	288	290	2	18.28	4.71×10^4
$[\text{Ce}(\text{APINH})_2(\text{NO}_3)](\text{NO}_3)_2$	338	340	2	7.51	4.36×10^4
$[\text{Nd}(\text{APINH})_2(\text{NO}_3)](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$	305	306	1	6.65	3.67×10^4
$[\text{Sm}(\text{APINH})_2(\text{NO}_3)](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	343	345	2	10.61	3.82×10^4
$[\text{Pr}(\text{APINH})_2(\text{NO}_3)](\text{NO}_3)_2$	339	341	2	19.51	4.12×10^4

On addition of DNA, the absorbance of the complexes decreases (hypochromism) and absorption maximum of all complexes is shifted (2 nm) to higher wavelength (bathochromism). The bathochromic shift (1-2 nm) is not much for assigning intercalation mode of binding of the complexes with DNA. Binding constants are of the order of 10^4 . The complexes are large. These observations suggest groove binding of complexes to DNA [39]. In addition, strong electrostatic attraction may be present between cationic complexes and poly anionic DNA.

CONCLUSIONS

A new ligand APINH is synthesized and characterized based on spectral data. La(III), Ce(III), Pr(III), Nd(III) and Sm(III) complexes of 2-acetylpyridine isonicotinoylhydrazone (APINH) have been synthesized and characterized. Physico-chemical and spectral studies reveal that the complexes have general formula $[\text{M}(\text{APINH})_2(\text{NO}_3)](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ (where, M = La, Ce, Pr, Nd, and Sm). APINH acts as neutral tridentate ligand. IR data suggest that the complexes contain both ionic and coordinated bidentate NO_3^- ligand. Two APINH ligands occupy six coordination sites, and one NO_3^- ligands another two coordination sites to form octa-coordinate mononuclear complexes. Absorption titrations suggest groove binding of complexes to DNA.

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