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Synthesis, DNA binding properties and antibacterial activity of lanthanide complexes with 2-benzoylpyridine isonicotinoylhydrazone

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Lanthanide(III) complexes of general formula $[Ln(BPINH)_2(NO_3)](NO_3)_2$ (where, Ln = La, Ce, Pr, Nd, Sm, and BPINH = 2-benzoylpyridine isonicotinoylhydrazone) have been synthesized under mild reaction conditions with excellent yields. The structure of BPINH is determined using single crystal X-ray diffraction studies. The lanthanide complexes have been characterized by elemental analysis, molar conductance and various spectral techniques such as FT-IR, UV-vis, IR and ^{1}H-NMR spectroscopies. Electrolytic nature of complexes is investigated by conductivity studies. The spectral data suggest that the ligand acts as a neutral tridentate NNO-donor system. Electrochemical behaviour of metal complexes is investigated by using cyclic voltammetry. The complexes undergo quasi-reversible one-electron reduction. Absorption titration studies reveal that these complexes are avid binders ($K_b = 10^5$) to calf-thymus DNA. The antibacterial activities of the ligand and its lanthanide complexes have been screened *in vitro* against, *Bacillus subtilis* (MTCC-441) and *Staphylococcus aurous* (MTCC-3160) which are gram positive and *Salmonella typhi* (MTCC-735) and *Escherichia coli* (MTCC-1652) which are gram negative organisms. It has been observed the lanthanide complexes show more pronounced activity than the ligand (BPINH).

Keywords: Coordination chemistry, Lanthanum, Cerium, Praseodymium, Neodymium, Samarium, 2-Benzoylpyridine isonicotinoylhydrazone, Hydrazones, DNA binding, and Antibacterial activity

Hydrazones are a versatile class of ligands having a wide range of biological activities such as antimicrobial[1], antitubecular[2], anticonvulsant[3], anti-inflammatory[4], cytotoxic[5] and vasodilator[6] activities. Hydrazones derived from pyridine carbonyls are known to inhibit the proliferation of tumor cells to a greater extent compared to standard anticancer agents[7,8]. However, metal complexes of hydrazones show higher biological (antimicrobial[9-11], DNA-binding and cytotoxic[12]) activity than the ligand. It has also been shown that metal complexes of hydrazones are potent inhibitors of DNA syntheses[12] and cell growth in diseased organs.

Investigations of isonicotinoyl hydrazones is of interest, especially due to their pharmacological properties[13-15]. Isonicotinic acid hydrazide (INH) is the first line medication in the prevention and treatment of tuberculosis. It is one of the first anti-depressive drugs discovered. It is also used in the treatment of a wide range of bacterial diseases[16-20]. Hydrazones derived from condensation of isonicotinylhydrazine with pyridine carbonyls have been found to show better anti-tubercular activity[6] rather than INH. Metal complexes of isonicotinoyl hydrazones exhibit increased antitumour[21] and antibacterial activity[22].

The chemistry of lanthanide complexes is of interest owing to their variety of applications[23,24]. A survey of literature[23-28] indicates that the studies on lanthanide complexes of isonicotinoyl hydrazones are relatively less when compared with their transition metal complexes. Lanthanide(III) complexes of 2-benzoylpyridine isonicotinoyl hydrazone (BPINH) are not reported so far in the literature.

In the light of the above and in continuation of our ongoing research work[29,30], 2-benzoylpyridine isonicotinoyl hydrazones and its lanthanide complexes have been synthesized and characterized. The structure of BPINH is determined using single crystal X-ray diffraction studies. DNA binding properties of lanthanide complexes are uncovered using absorption spectrophotometry. Antibacterial activities of the ligand and its lanthanide complexes are determined using disc method.

Experimental

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

Elemental analyses were performed using a Perkin-Elmer 2400 CHNS elemental analyzer. Molar conductance of the complexes in DMF (10^{-3} *M*) solution was measured at 28 ^oC 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 660 C electrochemical analyzer and a conventional three electrode assembly, 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 hexaflourophosphate (TBAHP) as the supporting electrolyte. The melting points were determined using Buchi B450 melting point apparatus. The ESI (+) mass spectra were recorded on a waters ZQ-4000 liquid chromatography- mass spectrometer. The ^1H (300 MHZ) NMR spectra were recorded at room temperature on a Bruker Avance II 400 FT-NMR spectrometer at 27° C, using DMSO-d_6 as solvent and tetramethylsilane (TMS) as standard.

The experimental details of biological studies (antibacterial activity) are given in supplementary data.

For the synthesis of 2-benzoylpyridine isonicotinoylhydrazone (BPINH), 2- benzoylpyridine (0.475 g, 5 m mol) dissolved in 20 ml of ethanol was added to an ethanolic solution of isonicotinic acid hydrazide (0.685 g, 5 mmol). in a round bottom flask and stirred for 20 min. Glacial acetic acid (3-4 drops) was added to it and refluxed for 2-3 h on a water bath. The contents were cooled. On evaporation of the solvent a light yellow colored crystalline product was formed. It was collected by filtration. Yield; 76%, m.pt.: 186-188 °C, Anal, (%) C: 70.52(71.86); H: 4.63 (4.83); N: 19.54 (18.64); IR (Cm^{-1}); 3062, 1690, 1546 are assigned to ν(NH), ν(C=O) and ν(C=N) stretching vibrations respectively. ^1H-NMR spectra in DMSO solvent; δ (7.36-7.62) (multiplet 5H), δ (8.60-8.74) (multiplet 4H), 8.85-8.94 (multiplet 3H) δ (8.13) (singlet 1H), are respectively assigned to phenyl, pyridine, isonicotine, and -NH proton. GC-mass (*m/z*). A peak at 302 corresponds to molecular ion peak of the ligand. The other peaks are consistent with the structure of the BPINH ligand. (Fig. S1, Supplementary data).

For the synthesis of lanthanide complexes, to an ethanolic solution of BPINH (0.604 g; 2 mmol) taken in 100-mL round bottom flask, an aqueous solution of $Ln(NO_3)_3.6H_2O$ (0.433 g; 1 mmol) was added and the reaction mixture was heated on a water bath under reflux for 3 h. The reaction mixture was cooled to room temperature and the colourless product which separated out was collected by filtration, washed with ethanol followed by hexane and dried in vacuum. The analytical data of complexes are given in Table 1. Typical mass spectra of La and Ce complexes are given in Figs S2 and S3 (Supplementary data) respectively. Molecular ion peaks at 929 and 930 m/z values suggest molecular weights of $[La(BPINH)_2(NO_3)](NO_3)_2$ and $[Ce(BPINH)_2(NO_3)](NO_3)_2$ complexes respectively, in conformity with proposed molecular formula of complexes.

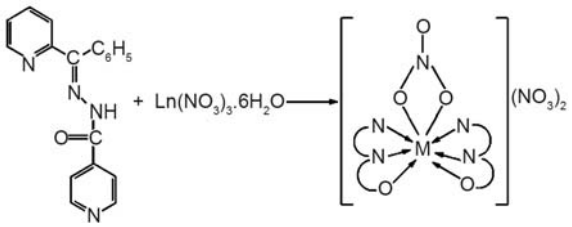
The ligand, 2-benzoylpyridine benzoylhydrazone was recrystalized from the slow evaporation of methanolic solution of compound.

Crystal data were collected on Enraf Nonius CAD4-MV31 single crystal X-ray diffractometer, at maximum X-ray power of 40 mA × 50 KV. The unit cell dimensions and orientation matrix were determined using 25 reflections and the intensity data of a given set of reflections were collected automatically by the computer. The data collected were reduced using SAINT program[31]. The trial structure obtained by direct method[32] using

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

Complex	Colour Yield (%)	M. wt.	M. pt[a] (°C)	Found (calc.) (%)			Λ_M[b]
				C	H	N	
$[La(BPINH)_2(NO_3)](NO_3)_2$	White (75)	929	202-204	46.55 (45.52)	3.01 (2.85)	16.59 (15.85)	110
$[Ce(BPINH)_2(NO_3)](NO_3)_2$	Yellow (78)	930	188-190	46.45 (45.52)	3.01 (2.85)	16.55 (15.65)	120
$[Nd(BPINH)_2(NO_3)](NO_3)_2$	Gray (58)	934	182-184	46.25 (45.45)	2.99 (3.10)	16.48 (15.10)	86
$[Pr(BPINH)_2(NO_3)](NO_3)_2$	Green (78)	930	182-184	46.45 (45.75)	3.01 (2.85)	16.55 (15.85)	138
$[Sm(BPINH)_2(NO_3)](NO_3)_2$	Yellow (79)	940	178-180	45.95 (44.85)	2.97 (3.04)	16.38 (15.10)	110

[a]Decomposition points; [d] Units, Ω^{-1} cm^2 mol^{-1}.



Synthesis of lanthanide-BPINH complexes

Scheme 1

SHELXS-86, revealed the position of all non-hydrogen atoms and refined by full-matrix least squares on F^2 (SHELXS-97)[33] with the graphic tool DIAMOND for windows[34]. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were treated with a mixture of independent and constrained refinements.

DNA Binding property of lanthanide complexes with calf thymus DNA was studied by UV-vis spectroscopy. The intrinsic binding constants (K_b), were determined as described before[30].

Results and discussion

The ligand, 2-benzoylpyridine isonicotinoyl-hydrazone (BPINH) was characterized based on IR, NMR and mass spectral data. ^{1}H-NMR spectra (in deuterated DMSO solvent). δ (7.36-7.62) (multiplet 5H), δ (8.60-8.74) (multiplet 4H), 8.85-8.94 (multiplet 3H) δ (8.13) (singlet 1H), are respectively assigned to phenyl, pyridine, isonicotine, and -NH protons. As the ligand is obtained in the form of good quality crystals, it was further characterized by single crystal X-ray analysis.

The ligand crystallizes in triclinic, space group P-1. The structure refinement parameters are summarized in Table S1 (Supplementary data). Important bond distances and bond angles are given in Table S2 (Supplementary data). ORTEP diagram and Close packing diagram of BPINH are given Figs S4 and S5 (Supplementary data) respectively.

The complexes were prepared by reacting BPINH and lanthanide salts (Scheme 1). The complexes are stable at room temperature and non-hygroscopic and could be stored easily even at room temperature. The complexes are soluble in water, methanol, ethanol and readily soluble in acetonitrile (CH_3CN), DMF and DMSO. Our several attempts to obtain diffraction quality crystal for the complexes using different combination of solvents were not successful. The analytical data are consistent with the proposed molecular formulae of complexes. The molar conductivity values (97-120 Ω^{-1} cm^2 mol^{-1}) for the complexes suggest that these are 1:2 electrolytes[35].

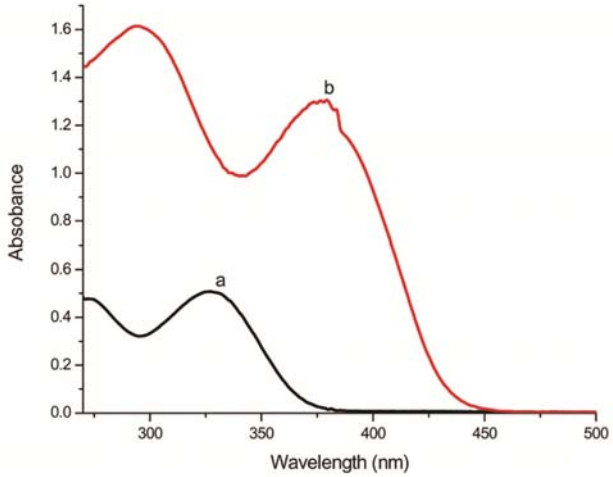


Fig. 1—Electronic spectra of (a) BPINH ligand and (b) $[Pr(BPINH)_2(NO_3)](NO_3)_2$ complex in DMF solvent.

^{1}H-NMR spectra (in deuterated DMSO solvent) of $[La(BPINH)_2(NO_3)](NO_3)_2$, δ (7.40-7.75) (multiplet 5H), δ (8.65- 8.86) (multiplet 4H), 8.87-8.98 (multiplet 3H) δ (8.13) (singlet 1H), are respectively assigned to phenyl, pyridine, isonicotine, and >NH proton. The peaks are slightly shifted to higher δ values, suggesting the complex formation between the ligand and metal. The presence of >NH proton indicates that and the ligand binds metal in amido form without deprotonation.

The electronic spectrum of ligand and its lanthanide(III) complexes were recorded in DMF. Typical electronic spectra of (a) BPINH ligand (b) $[La(BPINH)_2(NO_3)](NO_3)_2$ complex are shown in Fig. 1. In the electronic spectra of complexes a broad peak is observed in the high energy region at 29420 – 34370 cm^{-1} assigned to π - π* transition. A strong peak (Table S3, Supplementary data) is observed in the low energy region (26250–27030 cm^{-1}) of electronic spectra of complexes, which may be assigned to charge transfer transition[36].

IR spectral data of BPINH and its lanthanide complexes are given in Table S4 (Supplementary data). In the spectra of the lanthanide complexes, the band due to N-H stretching vibration in the free ligand form is not affected, precluding the involvement of >NH group in coordination. The appearance of this band in IR spectra of complexes suggests that the ligand remains in keto form in coordination. A considerable lowering of the $\nu_{(C=O)}$ frequency in complexes suggests involvement of amido oxygen in chelation. In the IR spectrum of the ligand, a peak due to ν(Py ring) is observed at 1580 cm^{-1}, which is

shifted to lower frequency indicating coordination of pyridine nitrogen to metal[37]. IR data suggest that the BPINH ligand acts as neutral tridentate ligand in lanthanide complexes.

The IR spectra of the complexes demonstrate the presence of coordinated nitrate. 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 NO_3^- (C_{2v}) group appear in the range of 1424- 1467 (ν_1) and 1252-1298 (ν_4) cm^{-1}. The frequency separation, $\Delta\nu = (\nu_1 - \nu_4)$ increases as the coordination of the 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 the range of 137-191 cm^{-1}, and is typical of bidentate bonding of nitrate[38, 39]. Another vibrational band is observed around 1380 cm^{-1} in the IR spectra of complexes, indicating the presence of ionic nitrate. (D_{3h} symmetry, free NO_3^-ion). IR data indicate that the complexes contain both free ionic nitrate and coordinated bidentate nitrate groups. The new bands in 412-418 and 530–543 cm^{-1} regions are assigned to ν (Ln–O) and ν (Ln–N) vibration respectively.

Based on molar conductivity, mass spectra, IR spectral data, a general structure (Fig. 2) is proposed for the complexes. The tridentate behavior BPINH ligand and the composition of complexes are in analogy with our previous observations[30].

The cyclic voltammetric profile of $[Nd(BPINH)_2(NO_3)](NO_3)_2$ complex is shown in Fig. S6 (Supplementary data). As the scan rate increases, separation between cathodic and anodic peaks increases, and the large separation(112- 253 mv) suggests quasi-reversible character. The electrochemical data are presented in Table S5 (Supplementary data). Repeated scans at various scan rates suggest the presence of stable redox species in solution. It may be inferred that Ln(III) complexes undergo reduction to their respective Ln(II) complexes[40,41]. Logarithmic values of stability constants (log *K*c) and standard free energy (change) values, the log K_C (0.132 – 0.898) and ΔG^o (510-1716) suggest that the complexes are stable in solution state.

Absorption spectra of $[Nd(BPINH)_2(NO_3)](NO_3)_2$ in the absence and in presence of CT-DNA are shown Fig. 3. The binding constants (Table 2) suggest that

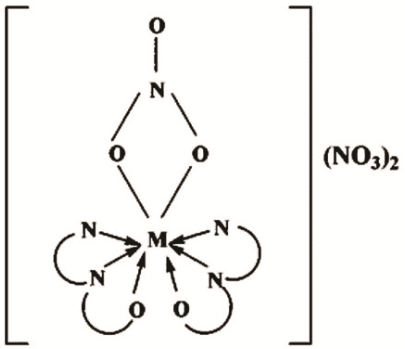


Fig. 2—A proposed general structure for the lanthanide(III) complexes

Where, N N O = an abbreviated structure of BPINH
M = La(III), Ce(III), Pr(III), Nd(III) and Sm(III)

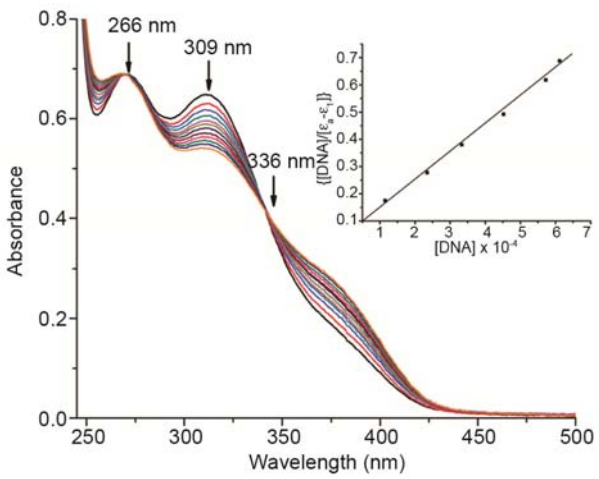


Fig. 3—Absorption spectra of $[Nd(BPINH)_2(NO_3)](NO_3)_2$ in the absence and in the presence of increasing concentration of CT-DNA; Insert is a plot of $[DNA]/(\varepsilon_a - \varepsilon_f)$ versus [DNA].

Table 2—Electronic absorption data upon addition of CT-DNA to the complexes

Complex	$\Delta\lambda_{max}$ (nm)		λ (nm)	H (%)	K_b (M^{-1})
	Free	Bound			
$[La(BPINH)_2(NO_3)](NO_3)_2$	310	311	1	+5.25	13.85×10^4
$[Ce(BPINH)_2(NO_3)](NO_3)_2$	312	313	2	+3.25	9.59×10^4
$[Nd(BPINH)_2(NO_3)](NO_3)_2$	309	311	2	+12.85	4.59×10^5
$[Pr(BPINH)_2(NO_3)](NO_3)_2$	275	277	2	+5.68	7.78×10^5
$[Sm(BPINH)_2(NO_3)](NO_3)_2$	311	312	2	+25.50	14.10×10^5

the complexes bind DNA very strongly. On addition of DNA, the absorbance of the complexes decreases (hypochromism) and absorption maximum of all complexes is shifted (1-2) nm wavelength (bathochromism). Two sharp isobestic points are observed (266 and 336 nm) in the spectrum of the Nd complex (Fig. 3) suggesting that there is only one mode of binding. When isobestic point is not a single point of intersection it indicates that there may be more than one form of binding mode[42]. Small bathochromic shift, low binding constant (K_b) values and large size of the complexes suggest propensity for groove binding of complexes to DNA.

The antibacterial activities of INH, BPINH and its lanthanide complexes were investigated. Typical photographs of agar plates showing antibacterial activity of BPINH and its lanthanide metal complexes are shown Fig. S7 (Supplementary data). The diameters (mm) of the zones of complete inhibition are given in Table S6 (Supplementary data). The antibacterial activities of our compounds are comparable to the activity of the standard drug, Streptomycin (*S. aurous*: 30 mm, *B. subtilis*: 28 mm, *E. coli:* 3 4 mm, *S. typhi*: 24 mm).

A comparison (Table S6) growth inhibition zones of INH, BPINH and its metal complexes indicates that metal complexes exhibit higher anti-bacterial activity than the free ligand, in analogy with previous observation[43-45]. Such increased activity of metal complexes is explained on the basis of chelation. The enhanced activity of the complexes can be explained on the basis of Overtone's concept[46] and Tweedy's Chelation theory[47] .

According to the overtone concept of cell permeability, the lipid membrane surrounding the cell favours the passage of only lipid-soluble materials, which means that liposolubolity is an important factor controlling antimicrobial activity. On chelation, the polarity of a metal ion is greatly reduced due to overlap with the ligand orbital and the partial sharing of its positive charge with the donor groups. In addition, it is also due to delocalization of the π-electrons over the whole chelating ring, thus enhancing the penetration of the complexes into the lipid membranes and the blocking of the metal binding sites of the enzymes of the micro-organisms[48].

In the present study a new ligand, (BPINH) was synthesized and characterized based on spectral data and X-ray data . La(III), Ce(III), Pr(III), Nd(III) and Sm(III) complexes of BPINH were synthesized and characterized. Physico-chemical and spectral studies reveal that the complexes have general formula $[M(BPINH)_2(NO_3)](NO_3)_2.nH_2O$ (where M = La, Ce, Pr, Nd, and Sm). BPINH acts as neutral tridentate ligand and NO_3^- acts as bidentate ligand. Two BPINH ligands occupy six coordination sites, and one NO_3^- ligand binds to another two coordination sites to form an octa-coordinate mononuclear complex. DNA binding properties of complexes were investigated using absorption spectrophotometry. Antibacterial activity of BPINH and its lanthanide complexes are reported.

Supplementary data

Supplementary data associated with this article, viz., Figs S1-S7 and Tables S1-S6 are available in the electronic form at http://www.niscair.res.in/info/ijcaIJCA55A(02)232-237_SupplData.pdf.

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