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**Der Pharma Chemica, 2011, 3(2):292-304**
*(http://derpharmachemica.com/archive.html)*

**ISSN 0975-413X**
**CODEN (USA): PCHHAX**

# Synthesis, Characterization and Antimicrobial Study of Lanthanide(III) Complexes of 2-Anilino-N[1]-[pyridine-2-ylethylidene]acetohydrazide

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## ABSTRACT

*The heterocyclic ligand 2-anilino-N'-[(1E)-1-pyridin-2-ylethylidene]acetohydrazide (Apeah) was synthesized by coupling of 2-anilinoacetohydrazide with 2-acetylpyridine and characterized by IR, $^{1}H$ and $^{13}C$-NMR spectra, it was then reacted with Lanthanide(III) nitrates to form complexes of the type $[Ln(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$ where, Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Y(III). The metal complexes were characterized on the basis of elemental analysis, molar conductance, magnetic susceptibility measurements, TG/DTA and spectral (IR, $^{1}H$ and $^{13}C$-NMR, UV-Visible and EPR) studies. The spectral data revealed that the Apeah behaves in tridentate fashion coordinating through carbonyl oxygen, azomethine nitrogen and pyridine nitrogen. The molar conductance values adequately supported their 1:2 electrolytic natures. Both Apeah and complexes were screened for their antimicrobial study. An enhancement of antimicrobial activity of the Apeah was observed on complexation.*

**Keywords**: 2-acetylpyridine, 2-anilinoacetohydrazide, Lanthanide complexes, Hydrazone, Antimicrobial activity.

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## INTRODUCTION

Hydrazones possessing an azomethine (-NHN=CH-) group constitute an important class of compounds for new drug development. Therefore, many hydrazones have been synthesized as target structures and evaluated their biological activities. Acidhydrazides have frequently been investigated as potential tuberculostats [1-6] and hydrazones derived from 2-acetylpyridine are known to inhibit the proliferation of tumor cells to a greater extent compared to standard anticancer agents [7]. Hydrazides and their condensation products have displayed diverse range of biological properties such as bactericidal [8-9], anti-fungal [10], anti-tumor [11, 14], anti-malarial [15, 16].

Lanthanide complexes have found a role in cancer treatment as contrast imaging agents such as Gd(III) DTPA which is commonly used for MRI imaging of tumors. Radioisotopes of lanthanides have also been explored both for imaging and therapy [17, 18]. Several cerium(III) salts were reported to have antibacterial activity [19]. Systematic studies later confirmed that cerium nitrate had broad-spectrum antibacterial activity against a range of bacteria including *Pseudomonas aeruginosa* and *Staphylococcus aureus*.

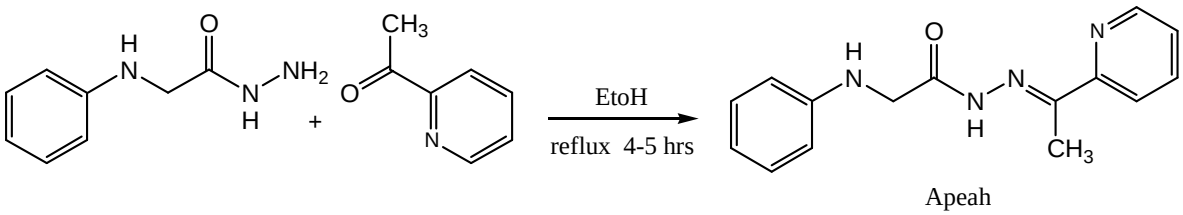
With the above points in mind and in continuation of our work on lanthanide(III) ions based antimicrobial agents [20,21], we have designed a new ligand (Apeah) by condensing 2-anilinoacetohydrazide with 2-acetylpyridine (Scheme 1). The lanthanide complexes of the same have been synthesized and characterized. The antimicrobial activity was screened for Apeah and its lanthanide(III) complexes.

## MATERIALS AND METHODS

All the chemicals used were of analytical grade, purchased from BDH, Rankem and Himedia. Commercial solvents were purified by standard methods and used [22]. The lanthanide nitrates were obtained by heating lanthanide oxides (99.9%) (Indian Rare Earths) with dilute nitric acid (50%) and evaporating the excess acid and dried in vacuum oven. 2-Anilinoacetohydrazide was prepared according to the procedure described in the literature [23].

### *2.1. Physical measurements*

Carbon, hydrogen, and nitrogen were determined on Carlo Erba CHN analyzer. IR spectra were obtained on a Nicolet 170 SX FT- IR spectrometer using KBr pellets, in the range 400-4000 $cm^{-1}$. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a JEOL-AMX-400 NMR spectrometer, using DMSO-$d_6$ as the solvent. Thermograms were recorded on a Perkin-Elmer (Pyris Diamond) analyzer in $N_2$ atmosphere at a heating rate of 10 $^{o}C$. Mass spectrum of the Apeah was recorded on a Thermofinnigan 1020 automated GCMS. UV-Visible spectra were obtained on a Hitachi 2001 spectrometer. EPR spectra of the Gd(III) complex was monitored on a Varian E-4X band spectrometer at both room temperature as well as LNT. Molar conductivities were measured on an Elico conductivity bridge having platinum electrodes. Magnetic moments were measured with a Faraday balance using $Hg[Co(NCS)_4]$ as the calibrant. Diamagnetic corrections were made by using Pascal's constants. The metal contents were determined by complexometric titrations with EDTA using xylenol orange as the indicator. Antibacterial and antifungal activities of the Apeah and its complexes along with the standard were carried out against the pathogenic bacteria *Pseudomonas aeruginosa* (PA), *Bacillus cirroflagellosus* (BC) and fungal *Penicillium notatum* (PN), *Aspergillus niger* (AN) by cup plate method.




Apeah

**Scheme 1**

### *2.2. Synthesis of 2-anilino-N'-[(1E)-1-pyridin-2-ylethylidene]acetohydrazide (Apeah)*

The synthesis is outlined in scheme 1. 2-Acetylpyridine (1.21g, 10 mmol) was added to an ethanolic solution of 2-anilinoacetohydrazide (1.65g, 10 mmol). The reaction mixture was

refluxed for 4-5 hrs on water bath. The crystalline solid that separated on cooling was filtered and recrystalized from methanol (Yield: 90%, M.P:140 $^{o}$C).

### *2.3. Synthesis of complexes*

An ethanolic solution of $Ln(NO_3)_3$ (1 mmol ) was added to an ethanolic solution of the Apeah (0.536g, 2 mmol) and refluxed for 2-3 hrs at water bath temperature. The solution is concentrated to a small volume and macerated with petroleum ether leading to its solidification. The dark yellow solid obtained was filtered, washed with ethanol and air dried (Yield - 80%, M. P. > 250$^{o}$C).

## RESULTS AND DISCUSSION

The analytical data [Table 1] indicates that the complexes have 1:2 (Metal:Ligand) stoichiometry. The lanthanide complexes are stable, dark yellow in colour. They are sparingly soluble in ethanol, methanol and soluble in DMSO, DMF but insoluble in benzene, ether and chloroform. The molar conductance values [Table 1] of the complexes in DMSO at $10^{-3}$M are in the range 70.00 - 80.00 Ohm$^{-1}$ cm$^{2}$ mol$^{-1}$, indicating their 1:2 electrolytic nature [24].

**Table 1: Elemental analysis and physical parameters of Apeah and its Ln(III) complexes**

| Sl. No. | Compounds | Found (calculated %) | | | | Magnetic moments BM | Molar conductance Ohm$^{-1}$ cm$^{2}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | M | C | H | N | | |
| 1 | $C_{15}H_{16}N_4O$ | - | 67.00 (67.15) | 6.00 (6.01) | 20.81 (20.88) | - | - |
| 2 | $[La(Apeah)_2NO_3H_2O]\cdot 2NO_3$ | 15.75 (15.80) | 40.90 (40.96) | 3.80 (3.86) | 17.48 (17.52) | Dia | 70.43 |
| 3 | $[Pr(Apeah)_2NO_3H_2O]\cdot 2NO_3$ | 15.95 (15.99) | 40.80 (40.86) | 3.79 (3.85) | 17.45 (17.48) | 3.68 | 72.46 |
| 4 | $[Nd(Apeah)_2NO_3H_2O]\cdot 2NO_3$ | 16.35 (16.31) | 40.76 (40.71) | 3.81 (3.84) | 17.37 (17.41) | 3.40 | 75.46 |
| 5 | $[Sm(Apeah)_2NO_3H_2O]\cdot 2NO_3$ | 16.82 (16.88) | 40.38 (40.43) | 3.77 (3.81) | 17.33 (17.29) | 1.60 | 74.25 |
| 6 | $[Eu(Apeah)_2NO_3H_2O]\cdot 2NO_3$ | 17.00 (17.04) | 40.30 (40.36) | 3.84 (3.81) | 17.21 (17.26) | 3.70 | 80.05 |
| 7 | $[Gd(Apeah)_2NO_3H_2O]\cdot 2NO_3$ | 17.47 (17.52) | 40.08 (40.12) | 3.71 (3.78) | 17.10 (17.16) | 7.72 | 80.05 |
| 8 | $[Tb(Apeah)_2NO_3H_2O]\cdot 2NO_3$ | 17.60 (17.67) | 40.00 (40.04) | 3.75 (3.78) | 17.10 (17.13) | 9.80 | 78.92 |
| 9 | $[Dy(Apeah)_2NO_3H_2O]\cdot 2NO_3$ | 18.10 (18.00) | 39.82 (39.88) | 3.72 (3.76) | 17.00 (17.06) | 10.84 | 72.12 |
| 10 | $[Y(Apeah)_2NO_3H_2O]\cdot 2NO_3$ | 10.67 (10.72) | 43.40 (43.43) | 4.00 (4.10) | 18.51 (18.57) | Dia | 77.25 |

*The values in parenthesis are calculated ones. Dia : Diamagnetic.*

### *3.1. Infrared Spectra*

The important IR frequencies of Apeah and its complexes are given in Table 2. A strong band in the spectrum of free Apeah at 1676 cm$^{-1}$ is assigned to υ(C=O) (amide I) where as those at 1530 and 1247 cm$^{-1}$ are due to amide II and III respectively, arising from the υ(C-N) and υ(NH) modes [25]. Due to the presence of intermolecular hydrogen bonding between carbonyl oxygen and the hydrogen of NH group, the υ(C=O) is observed at a lower frequency (1676 cm$^{-1}$) compared to the literature report [11], where in the same was observed at 1700 cm$^{-1}$. A strong band at 1605

$cm^{-1}$ is assigned to the υ(C=N) group and υ(N-N) is observed at 1020 $cm^{-1}$. The pyridine ring stretching vibrations appear as a series of bands at 1578, 1554, 1458, 1432 $cm^{-1}$ [26].

In IR spectra of the complexes, bands due to υ(C=O) and υ(C=N) were shifted to lower wave number, compared to the free Apeah. This indicates coordination of the Apeah through carbonyl oxygen and azomethine nitrogen. Additional evidence for participation of υ(C=N) in coordination is given by the slight upward shift of υ(N-N) band in all the complexes [11]. The pyridine ring vibrations at 1578 and 1554 $cm^{-1}$ are merged to give a band in the region 1541-1547 $cm^{-1}$. The band at 1458 and 1432 $cm^{-1}$ undergo a shift to lower frequency by about 4-5 $cm^{-1}$ and 10-26 $cm^{-1}$ respectively. These changes in pyridine ring vibrations indicate the coordination of the pyridine nitrogen to the metal ion. The coordination of pyridine nitrogen suggests the rotation of Apeah across C-N bond, so as to facilitate the coordination through pyridine nitrogen. A band around 1384 $cm^{-1}$ indicates the presence of ionic nitrate. The presence of ionic nitrate was also confirmed by conductivity studies. The coordinated nitrate show six absorption bands at 1320, 1252, 819, 1036, 746 and 653 $cm^{-1}$ which are assigned to $\upsilon_4$, $\upsilon_1$, $\upsilon_6$, $\upsilon_2$, $\upsilon_3$ and $\upsilon_5$ vibrations respectively. The magnitude of $\upsilon_4$ - $\upsilon_1$ and $\upsilon_3$ - $\upsilon_5$ lies between 68-88 $cm^{-1}$ and 90-93 $cm^{-1}$ respectively, indicating the coordination of nitrate group in bidentate fashion [27, 28].

### *3.2. $^{1}H$ and $^{13}C$ NMR Spectral Studies*

$^{1}H$ NMR spectral studies of Apeah and its La(III) complex were recorded in DMSO-d6. The data are summarized in Table 3. Figure 1 gives the numbering system of Apeah followed for $^{1}H$ and $^{13}C$ NMR assignments. In $^{1}H$ NMR spectrum of Apeah [Figure 2a], two singlet's observed at 2.34 and 4.30 ppm are assigned to the protons of methyl ($C10H_3$) and methylene group ($C2H_2$) respectively. The peak due to NH proton attached to the phenyl ring is observed at 5.7 ppm and amide proton at 10.91 ppm. The aromatic protons are observed between 6.65 - 8.60 ppm. Four doublets at 8.60, 7.85, 7.42 and 6.62 ppm are assignable to H15, H12, H8 and H4 respectively. The triplets at 8.12 and 7.11 ppm are due to H13 and H6 respectively, where as multiplet at 7.40 ppm accounts for H14 of pyridine ring.

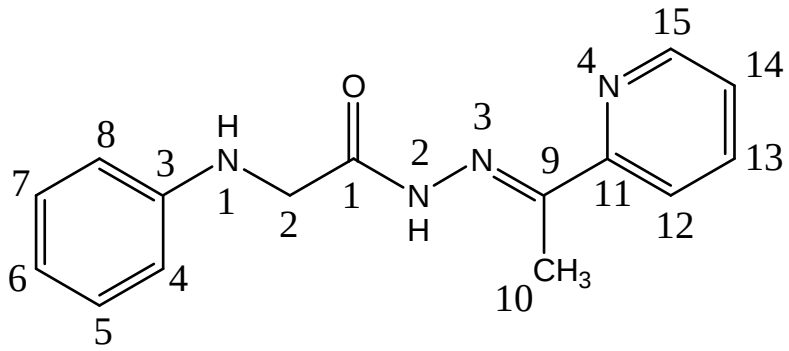



**Figure 1: Numbering system of Apeah**

On complexation, there is no noticeable change in the $^{1}H$ NMR spectrum of La(III) complex [Figure 2b] compared to the free Apeah.

$^{13}C$ NMR spectrum of Apeah [Figure 3] and its La(III) complex were taken in DMSO-d6 medium. The data is summarized in Table 3. In the free Apeah, the peak at 171.85 ppm is due to C1 of the >C=O group. The C9 of azomethine group was observed at 167.33 ppm. The signals observed at 155.20 and 148.00 ppm are ascribed to C11 and C15 adjacent to the pyridine nitrogen.

**Table 2: IR Spectral data of Apeah and its Ln(III) complexes**

| Sl. No. | Compound | υ(OH) water | υ(C=O) Amide I | υ(C=N) | υ(Py N) | Amide II | Amide III | Ionic $NO_3$ | -$NO_3$ bands | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | $\upsilon_4$ | $\upsilon_1$ | $\upsilon_6$ | $\upsilon_2$ | $\upsilon_3$ | $\upsilon_5$ |
| 1 | Apeah | | 1676s | 1605s | 1578s | 1530s | 1247sh | -- | -- | -- | -- | -- | -- | -- |
| 2 | $[Ln(Apeah)_2 NO_3 H_2O]\cdot 2NO_3$ | 3385 | 1646s | 1603sh | 1556m | 1523s | 1252sh | 1384m | 1319s | 1252m | 819w | 1036w | 746w | 669m |
| 3 | $[Pr(Apeah)_2 NO_3 H_2O]\cdot 2NO_3$ | 3384 | 1642s | 1602sh | 1547m | 1503s | 1254sh | 1383m | 1340s | 1250m | 822w | 1030w | 755w | 667m |
| 4 | $[Nd(Apeah)_2 NO_3 H_2O]\cdot 2NO_3$ | 3385 | 1644s | 1602sh | 1548m | 1530s | 1254sh | 1384m | 1338s | 1296m | 816w | 1020w | 753w | 658m |
| 5 | $[Sm(Apeah)_2 NO_3{}_2O]\cdot 2NO_3$ | 3387 | 1644s | 1602sh | 1550m | 1524s | 1250sh | 1383m | 1339s | 1250m | 820w | 1031w | 750w | 671m |
| 6 | $[Eu(Apeah)_2 NO_3 H_2O]\cdot 2NO_3$ | 3385 | 1642s | 1601sh | 1550m | 1522s | 1249sh | 1386m | 1339s | 1249m | 825w | 1031w | 755w | 669m |
| 7 | $[Gd(Apeah)_2 NO_3 H_2O]\cdot 2NO_3$ | 3381 | 1643s | 1603sh | 1547m | 1521s | 1249sh | 1383m | 1319s | 1249m | 821w | 1021w | 745w | 670m |
| 8 | $[Tb(Apeah)_2 NO_3 H_2O]\cdot 2NO_3$ | 3382 | 1644s | 1603sh | 1550m | 1524s | 1251sh | 1384m | 1335s | 1248m | 819w | 1042w | 742w | 668m |
| 9 | $[Dy(Apeah)_2 NO_3 H_2O]\cdot 2NO_3$ | 3387 | 1641s | 1603sh | 1546m | 1520s | 1248sh | 1385m | 1337s | 1248m | 822w | 1012w | 743w | 668m |
| 10 | $[Y(Apeah)_2 NO_3 H_2O]\cdot 2NO_3$ | 3375 | 1646s | 1603sh | 1543m | 1524s | 1252sh | 1384m | 1316s | 1223m | 818/w | 1015w | 751w | 680m |

*s = strong, sh = sharp, m = medium, b = broad, w = weak*

On complexation, the C1 of the >C=O group undergoes a downfield shift to 172.45 indicating the coordination of carbonyl oxygen to the metal. The C9 of the azomethine group also undergoes downfield shift from 167.33 to 168.07 ppm indicating its involvement in coordination. The C10 signal is shifted from 11.97 to 12.23 ppm due to the coordination of azomethine nitrogen. The signals of the pyridine ring [C11, C12, C13 and C15] showed a downfield shift indicating the coordination through pyridine nitrogen. Downfield shifts of C4, C5, C6, C7 and C8 indicate the coordination through carbonyl oxygen. These changes confirm the ligation through carbonyl oxygen, azomethine nitrogen and pyridine nitrogen.

**Table 3: $^{1}$H and $^{13}$C NMR Spectral Data of Apeah and Its La(III) complex**

| Proton | Apeah | La(III) complex | Carbon | Apeah | La(III) complex |
|---|---|---|---|---|---|
| -- | -- | -- | C1 | 171.85 | 172.45 |
| $C2H_2$ | 4.30(s) | 4.28(s) | C2 | 48.07 | 49.32 |
| -- | -- | -- | C3 | 147.97 | 148.07 |
| H4 | 6.62(d) | 6.62(d) | C4 | 112.29 | 116.19 |
| H5 | 6.51(t) | 6.50(t) | C5 | 129.40 | 129.59 |
| H6 | 7.11(t) | 7.10(t) | C6 | 120.84 | 121.46 |
| H7 | 7.38(t) | 7.38(t) | C7 | 124.62 | 124.68 |
| H8 | 7.42(d) | 7.42(d) | C8 | 117.91 | 117.95 |
| -- | -- | -- | C9 | 167.33 | 168.07 |
| $C10H_3$ | 2.34(s) | 2.34(s) | C10 | 11.97 | 12.23 |
| -- | -- | -- | C11 | 155.20 | 155.68 |
| H12 | 7.86(d) | 7.85(d) | C12 | 138.80 | 139.00 |
| H13 | 8.01(t) | 8.01(t) | C13 | 139.42 | 139.70 |
| H14 | 7.40(m) | 8.14(m) | C14 | 124.50 | 124.25 |
| H15 | 8.60(d) | 8.58(d) | C15 | 148.00 | 148.18 |
| N2H | 10.91(s) | 10.90(s) | -- | -- | -- |
| N1H | 5.71(s) | 5.70(s) | -- | -- | -- |

*s = singlet, d = doublet, m = multiplet, t = triplet*

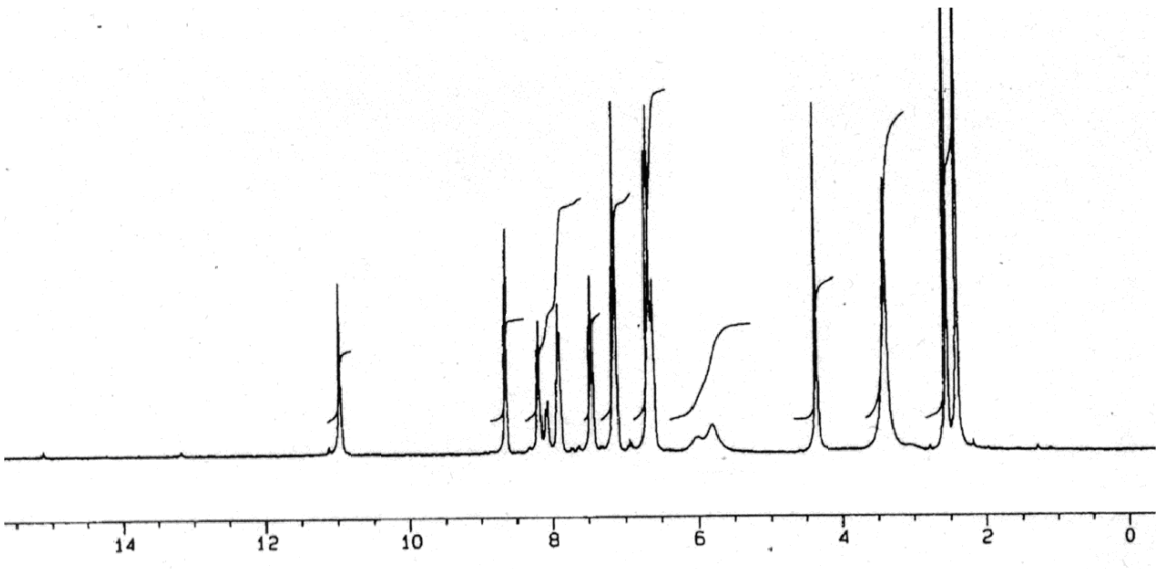



**Figure 2a: $^{1}$H NMR spectrum of Apeah**

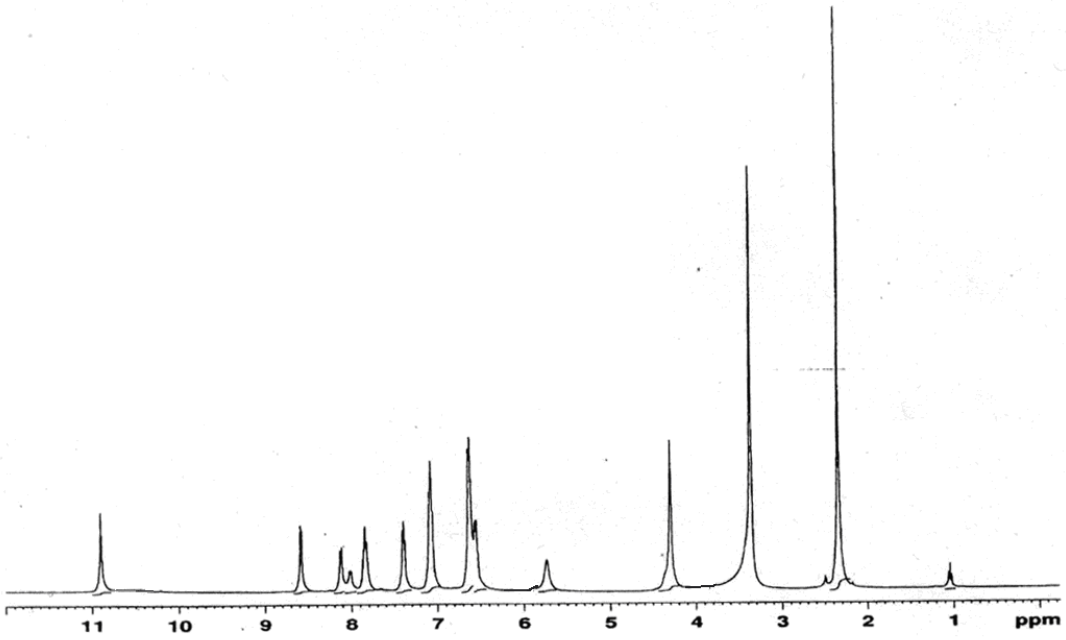



**Figure 2b: $^{1}$H NMR spectrum of La(III) complex**

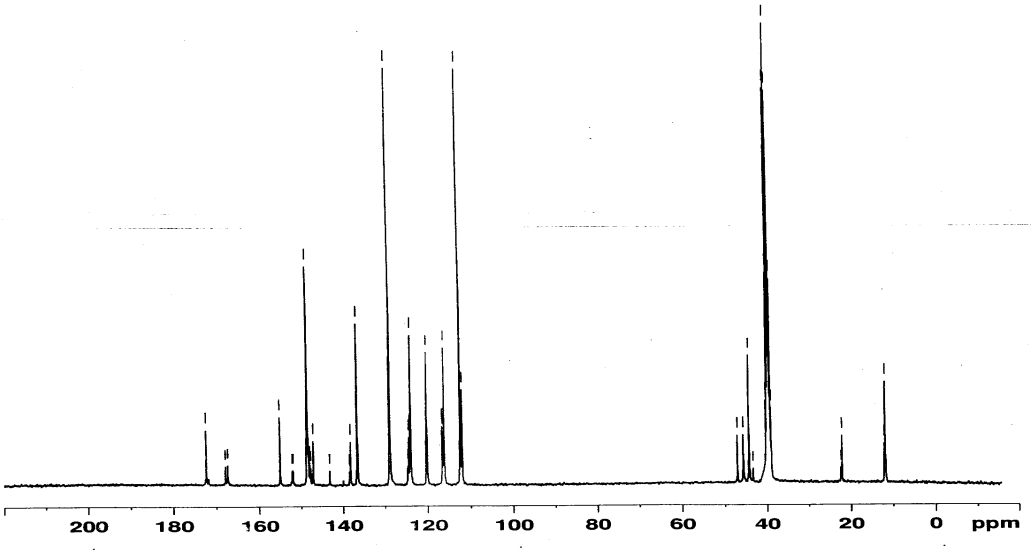



**Figure 3: $^{13}$C spectrum of Apeah**

### *3.3. Magnetic and EPR spectral studies*

The effective magnetic moments [Table 1] of all the complexes indicate that they are paramagnetic in nature except La(III) and Y(III) which are diamagnetic. The values obtained are similar to the Van Vleck and Frank [29], and Hund's [30] values except in case of Sm(III) and Eu(III) where slightly higher values were obtained. This is due to low J-J separation, which leads to thermal population of higher energy levels. The values obtained are similar to those of typical lanthanide ions [31] and indicate the non-involvement of 4f electrons in bonding due to their effective shielding by the $5s^2 5p^6$ octet.

The EPR spectra were recorded for $[Gd(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$ at room temperature (RT) and also at liquid nitrogen temperature (LNT). The 'g' values 2.00 (at RT) and 2.06 (at LNT) being almost the same and of similar line widths, indicate that the line widths are independent of

temperature [32]. Further, the complete absence of zero-field hyperfine splitting and the presence of broad bands indicate that the Gd(III) ion is located in a rather disordered environment caused by strain. These strains (caused by 'g' strain for the 'g' tensor distribution, D-strain for the zero field splitting distribution) arise due to random hydrogen bonds between water molecules and the complex leading to distortions, which lead to broad resonance EPR lines [33, 34].

### *3.4. UV-Visible spectra*

The electronic spectral data of two representative complexes of $[Gd(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$ and $[Sm(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$ is given in Table 4. The free Apeah shows an intense band at 32154 $cm^{-1}$ assigned to the n → π* and two weaker bands at 37174 and 34843 $cm^{-1}$ assigned to π → π* transitions, respectively.

The electronic spectra of the complexes are dominated by Apeah bands, with a slight shift to higher or lower energy levels. This shift was attributed to the effect of crystal field upon inter electronic repulsion between 4f electrons [35]. The spectra of the complexes were similar with a slight shift of spectral bands to lower energy compared to the respective aqua ions [36]. The nepheleuxetic parameter (β) [37], bonding parameter ($b^{1/2}$) [38] and Sinha's covalency parameter (δ) [39] and angular covalency (η) for the Gd(III) and Sm(III) complexes are presented in Table 4. On comparison of the spectra with that of known compounds, it is concluded that the coordination number of the present complex is nine. As a representative, electronic spetrum of Gd(III) complex is given in Figure 4.

**Table 4: UV-Visible spectral data of Gd(III) and Sm(III) complexes of Apeah**

| Complex | Assignment | $\lambda_{max}$ of Ln(III) ion $cm^{-1}$ | $\lambda_{max}$ of Complexes $cm^{-1}$ | β | Related parameter |
|---|---|---|---|---|---|
| | | 32679 | 32520 | 0.99513 | δ = 0.35727% |
| $[Gd(Apeah)_2NO_3$ | n → π* | 34782 | 34904 | 1.00350 | $b^{1/2}$= 0.042190 |
| $H_2O]\cdot 2NO_3$ | π → π* | 37664 | 37313 | 0.99068 | η =0.05677 |
| | | | | β = 0.99644 | |
| | | 21477 | 21114 | 0.98309 | δ = 0.79121% |
| $[Sm(Apeah)_2NO_3$ | n → π* | 26624 | 26652 | 1.00105 | $b^{1/2}$ = 0.06264 |
| $H_2O]\cdot 2NO_3$ | π → π* | 27624 | 27412 | 0.99215 | η = 0.08895 |
| | | | | β = 0.99215 | |

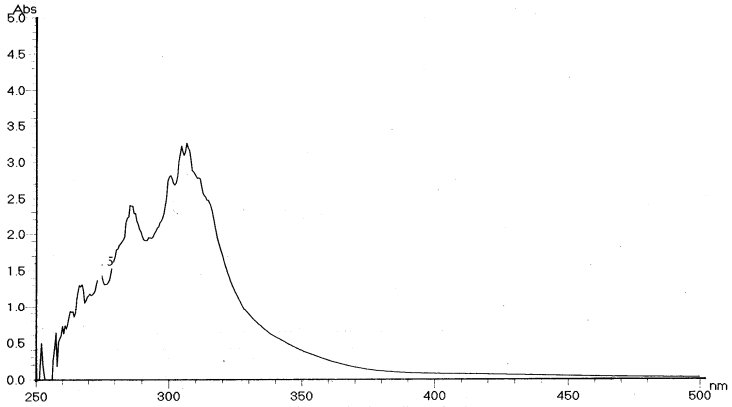



**Figure 4: UV-Visible spectrum of $[Gd(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$**

### *3.5. Thermal studies*

The TG/DTA of the representative Y(III) complex was carried out in nitrogen atmosphere at a heating rate of 10 $^{o}$C/min. The thermogram of $[Y(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$, [Figure 5] exhibits an initial weight loss of 2.00 % (Cal. 2.17 %) in the range of 200-240 $^{o}$C corresponding to the loss of one water molecule. Second weight loss of 14.5 % (Cal. 14.95 %) at 254 $^{o}$C corresponds to the loss of two ionic nitrates. Third weight loss of 7.00 % (Cal. 7.48 %) at 295 $^{o}$C corresponds to the loss of one coordinated nitrate. A further weight loss of 64 % (Cal. 64.66 %) in the range of 350-800 $^{o}$C corresponds to the loss of Apeah molecules. Finally the most stable oxide $Y_2O_3$ is formed on continued heating up to 1000 $^{o}$C. The percentage of metal obtained is in confirmation with the metal determinations.

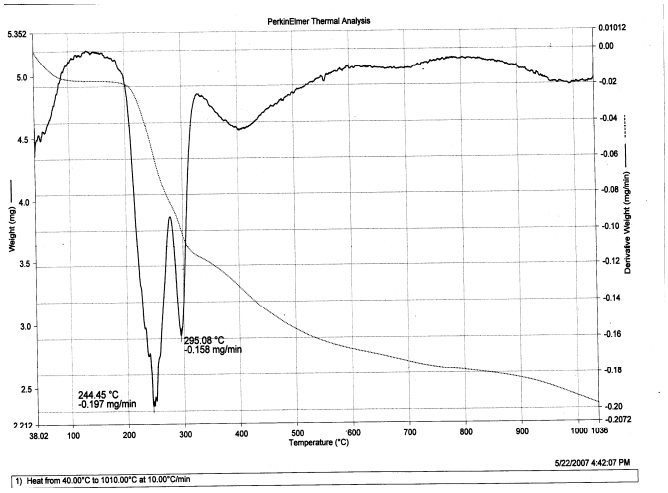



**Figure 5: Thermogram of $[Y(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$**

### *3.6. Mass spectral studies*

The molecular ion peak at m/z = 268 in the mass spectrum of Apeah [Figure 6] corresponds to its total molecular weight. The FAB mass spectrum [Figure 7] of $[La(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$ complex shows the molecular ion peaks at m/z = 879, supporting the proposed composition of the complexes.

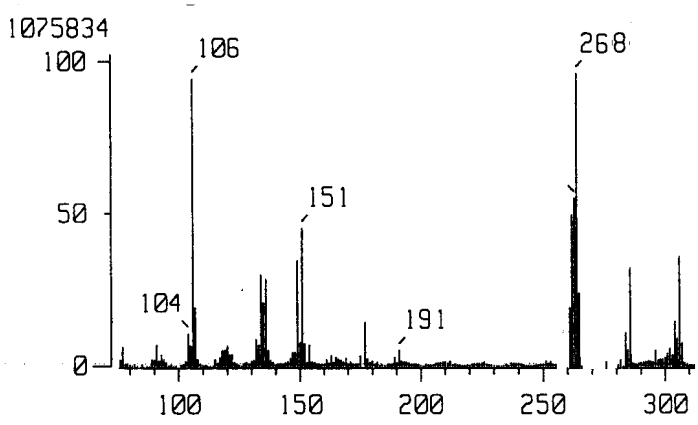



**Figure 6: Mass spectrum of Apeah**

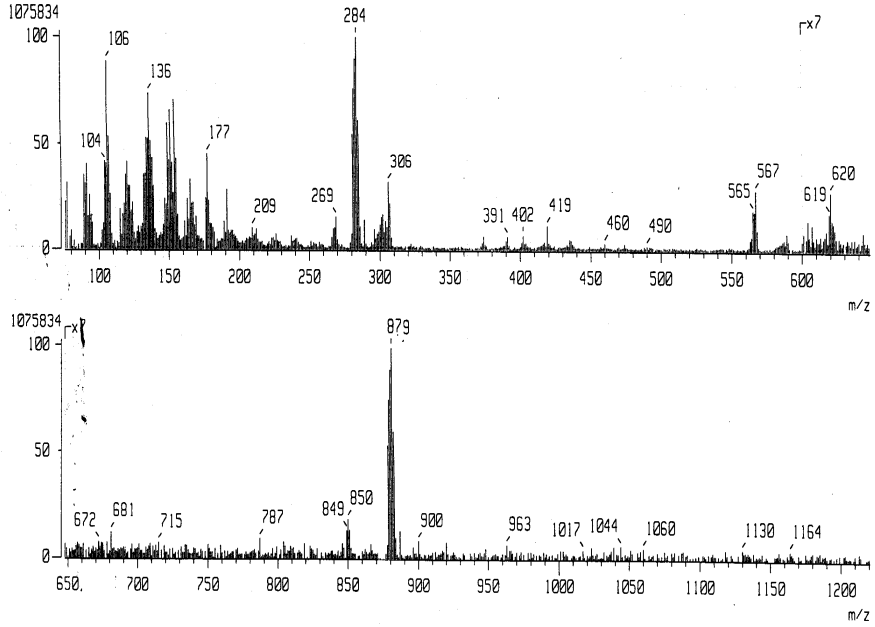



**Figure 7: Mass spectrum of $[La(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$**

**Table 5: Antibacterial and antifungal activity data of Apeah and its Ln(III) complexes**

| Sl. No. | Compound | Antifungal | | Antibacterial | |
|---|---|---|---|---|---|
| | | PN | AN | PA | BC |
| 1 | Apabz | + | + | + | + |
| 2 | $[La(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$ | ++ | ++ | ++ | ++ |
| 3 | $[Pr(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$ | ++ | ++ | ++ | ++ |
| 4 | $[Nd(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$ | ++ | ++ | ++ | ++ |
| 5 | $[Sm(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$ | ++ | ++ | ++ | ++ |
| 6 | $[Eu(Apabz)_2\ NO_3\ H_2O]\cdot 2NO_3$ | ++ | ++ | ++ | ++ |
| 7 | $[Gd(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$ | ++ | ++ | ++ | ++ |
| 8 | $[Tb(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$ | ++ | ++ | ++ | ++ |
| 9 | $[Dy(Apabz)_2\ NO_3\ H_2O]\cdot 2NO_3$ | ++ | ++ | ++ | ++ |
| 10 | $[Y(Apeah)_2\ NO_3\ H_2O]\cdot 2NO_3$ | ++ | ++ | ++ | ++ |
| 11 | Griseofulvin | +++ | +++ | - | - |
| 12 | Norfloxacin | - | - | +++ | +++ |

*Key to interpretation: (-) No inhibition zone= inactive; 1-5 mm (+) = Less active; 6-10mm (++) = moderately active; 11-15 mm (+++) = highly active; PN = Penicillium notatum, AN = Aspergillus niger; PA = Pseudomonas aeruginosa, BC = Bacillus cirroflagellosus.*

### *3.7. Biological studies*

The Apeah and the corresponding lanthanide(III) complexes along with the standards, Griseofulvin and Norfloxacin were screened *in-vitro* for their antimicrobial activity against two pathogenic bacteria [*Pseudomonas aeruginosa* (PA), *Bacillus cirroflagellosus* (BC)] and fungi [*Penicillium notatum* (PN), *Aspergillus niger* (AN)] using cup plate method [40] and the results are compiled in Table 5. The ligand (Apeah) was less active against PN, AN, PA and BC. On the other hand, the complexes were found to be moderately active against all the microorganisms used. The enhanced activity of the complexes is due to the synergistic effect that increases the lipophilicity of the complexes. Chelation decreases the polarity of the metal ion, which further leads to an enhancement of lipophilicity of the complex. Since the microorganism cell is surrounded by a lipid membrane which favours the passage of lipid soluble materials, increased lipophilicity allows the penetration of complex into, and through the membrane and deactivates

the active enzyme sites of the microorganisms [41]. However, the activity shown by the complexes is less than that of the standards used.

## CONCLUSION

The Apeah behaves in a tridentate fashion coordinating through pyridine nitrogen, azomethine nitrogen and carbonyl oxygen. A conformational change in the structure of the Apeah is observed due to its rotation about the C-N bond, which facilitates to coordinate in ONN fashion. Based on the analytical and spectral data, following structure [Figure 9] is tentatively proposed for the lanthanide(III) complexes having the general formula $[Ln(Apbz)_2\ NO_3\ H_2O]\cdot 2NO_3$, where Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), and Y(III). The antimicrobial activity of the Apeah was enhanced on complexation with lanthanide(III) ions.

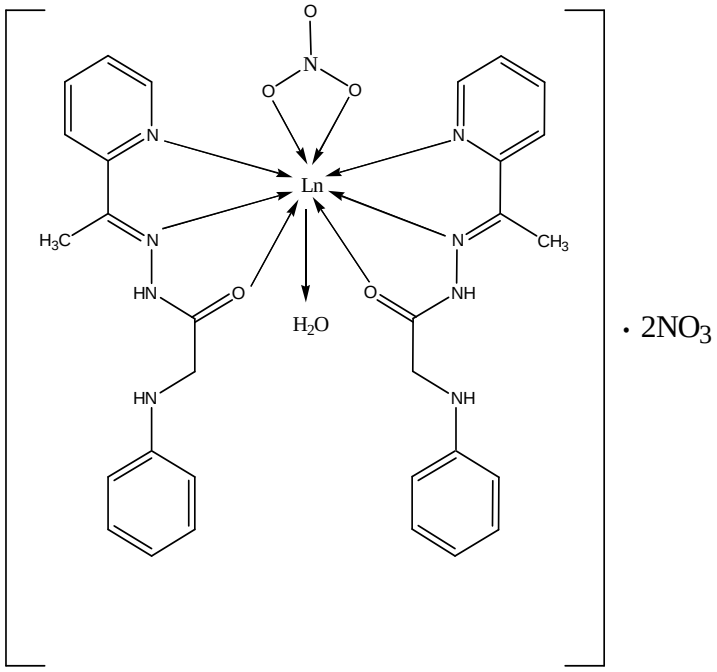



**Figure 9: Tentatively proposed structure of all complexes.**

**Acknowledgement**
The authors are thankful to I.I.Sc. Bangalore, I.I.T. Bombay, I.I.T. Roorkee and USIC, Dharwad for spectral studies. K.L.E. Pharmaceutical College, Hubli for antimicrobial studies, V. C. Havanur is thankful to B.V.B. College of Engineering and Technology, Hubli for the encouragement.

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