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Synthesis and characterization of some Lanthanide (III) Complexes based on 2, 6-Diphenylisonicotinic acid

Zewdu Gebeyehu*, Jennifer Klein and Charles E. Milliron III

Department of Chemistry, Columbus State University, Columbus, GA 31907, USA.

E-mail: Gebeyehu_zewdu@columbusstate.edu

ABSTRACT: This paper presents the synthesis of four mononuclear lanthanide (III) complexes, possessing 2, 6-Diphenylisonicotinate as a ligand. The complexes were synthesized in aqueous solution at room temperature in a one to three molar ratios of the Ln (III) salt and the ligand, respectively. The white or grayish powdered complexes that formed were characterized by elemental analysis, FTIR, UV, and Fluorescence spectroscopy. The FTIR absorption spectra indicated that 2, 6-Diphenylisonicotinate acts as a bidentate ligand and coordinates to Ln (III) through the carboxylate oxygen and the adjacent carbonyl oxygen (-C=O). The UV absorption spectra of the complexes are similar in band profile and shape to the spectrum of the ligand except a slight blue shift of the absorption maxima. The excitation and emission spectra of the complexes are very much similar to that of the ligand with minor differences in excitation and emission wavelengths. The elemental analysis results show a good agreement between the calculated and found percentages of CHN. Based on the elemental analysis and spectroscopic results of the four complexes, we suggest that the compounds formed are nine coordinate around the metal center and have the general formula $\text{Ln}(\text{C}_{18}\text{H}_{12}\text{NO}_2)_3 \cdot 3\text{H}_2\text{O}$.

Keywords: CHN analysis, 2, 6-Diphenylisonicotinic acid, FTIR, Lanthanide complexes, Photoluminescence

INTRODUCTION

Lanthanide (III) complexes have been subjects of extensive research in the past two decades because of their having important properties that make them very promising in various types of applications. Some of these properties include: the lanthanide ions have long lived luminescent emission that arises from transition between the 4f energy levels, they have narrow and sharp emission band at characteristic wavelengths ranging from green to near IR regions (Sabbatini and Guardigli, 1993; Takalo, et al., 1996; Mathis, 1993; Werts, 2000), and have interesting optical and chemical characteristics (Pagnot, et al., 2000; Bünzli, et al., 2007). These properties make lanthanide (III) complexes attractive for applications in fluoroimmunoassays (Werts, et al., 2000), optical devices (Slooff, et al., 1998), signal amplification (de Sa et al., 2000), optical fiber (Bünzli and Eliseeva, 2010), and solar cells and other light sources (Santa-Cruz, et al., 1995). However, Ln (III) ions have a very low molar extinction coefficient due to forbidden 4f-4f transitions, thereby making the direct lanthanide

excitation very inefficient. To overcome this inefficiency, a strongly absorbing organic chromophore is coordinated to Ln (III) as light absorber. The coordinated organic chromophore harvests the light and transfers it to Ln(III), by what is known as antenna effect and this results in more intense lanthanide ion emissions (Cui, et al., 2012; Chen, et al., 2010; Armelao et al. 2010). Multi-dentate ligands with S-, N- and O-donor atoms are excellent reagents in the fabrication of lanthanide complexes. In the past two decades, different types of organic reagents possessing S-, N- and O- donor ligands have been coordinated to the lanthanide ions to serve as sensitizers (Borisov and Klimant 2008; Fu, et al., 2010; Jiang, et al., 2010; Kadjane, et al., 2008; Ramya, et al., 2010; de Bettencourt Dias and Viswanathan, 2006; Chen, et al., 2013; Huang, et al., 2009; Fang, et al., 2011). The ability of sensitization is enhanced when these donor atoms are part of aromatic organic groups. Mono- and dicarboxylate aromatic ligands derived from orotic acid (Li, et al., 2004); nalidixic acid (El-Shenawy, et al., 2014) and pyridine-2,6-dicarboxylic acid (Tanase, et al., 2007) were used to synthesize lanthanide complexes that showed strong

*Author to whom correspondence should be addressed.

luminescence.

In our research work, we used 2, 6-Diphenylisonicotinic acid that consists three aromatic rings that can absorb strongly in the UV region due to the presence of delocalized π -electrons. Also, based on hard-soft acid-base theory, the carboxylate end of the acid can bond to the lanthanide (III) ions. Therefore, we expect 2, 6-Diphenylisonicotinate to coordinate strongly to the metal center, and also absorb radiant energy and then transfer this energy efficiently to the lanthanide ions. So far, we have not come across reports that showed the use of 2, 6 -Diphenylisonicotinate as a ligand in preparing metal complexes. The only report available is its use in the synthesis of alkynylgold(III) complexes possessing bis-cyclometalating ligand derived from 2,6-Diphenylisonicotinate (Au, V. K. *et al.*, 2015). In this paper we present the synthesis and characterization of four lanthanide (III) complexes possessing 2,6 -Diphenylisonicotinate as a ligand.

Experimental

Reagents and materials.

2, 6-Diphenylisonicotinic acid was purchase from Acros Organics and used after reacting it with an equivalent amount of sodium hydroxide solution to make its sodium salt. The lanthanide metal salts, $MCl_3 \cdot 6H_2O$ ($M = Eu, Gd, Nd$) and $Er(NO_3)_3 \cdot 5H_2O$ were obtained from Sigma Aldrich and used as received. Infrared spectra were collected from 4000-650 cm^{-1} using PerkinElmer FTIR equipped with ATR crystal. Elemental analysis of carbon, hydrogen and nitrogen were performed on PerkinElmer 2400 series II CHNSO analyzer. UV-Vis measurements were conducted on Cary 300 Bio spectrophotometer and the excitation and emissionspectrum were taken on Cary fluorimeter.

Synthesis of the complexes

Synthesis of $Eu(C_{18}H_{12}NO_2)_3 \cdot 3H_2O$

0.1731 g (4.72×10^{-4} mole) of $EuCl_3 \cdot 6H_2O$ was dissolved in 10.0 mL of distilled water. 0.4014 g, (1.46×10^{-3} mole) of 2, 6-Diphenylisonicotinic acid was suspended in 10.0 mL distilled water and then treated with an equivalent amount of NaOH (1.46 mL, 1.0 M) till the pH was between 6 and 7. This sodium salt solution was added drop by drop to the Eu(III) solution while stirring at room temperature. A white precipitate formed

immediately. The mixture was stirred for one hour, filtered, washed three times with distilled water, three times with methanol and dried overnight under vacuum. The mass of the product obtained was 0.3773 g (77.8%).

Synthesis of $M(C_{18}H_{12}NO_2)_3 \cdot 3H_2O$ ($M = Gd$ and Nd).

Aqueous solutions of 0.1113 g of $GdCl_3 \cdot 6H_2O$ (3.00×10^{-4} mole) and 0.1196 g (3.33×10^{-4} mole) of $NdCl_3 \cdot 6H_2O$ were placed in two separate beakers and each treated with three equivalents of 2,6 -Diphenylisonicotinate salt aqueous solution. These resulted in an immediate formation of grayish and white precipitates respectively. The mixtures were stirred for one hour, filtered, washed three times with distilled water, three times with methanol and dried under vacuum. 0.2623 g (84.6%) and 0.2871 g (84.7%) of the respective powdered substances obtained.

Synthesis of $Er(C_{18}H_{12}NO_2)_3 \cdot 3H_2O$

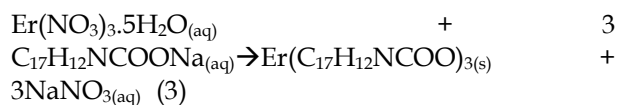
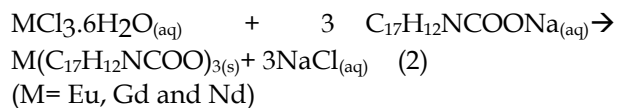
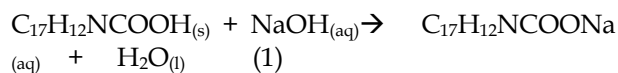
0.1307 g (2.948×10^{-4} mole) of $Er(NO_3)_3 \cdot 5H_2O$ was dissolved in 10.0 mL of water and to it three equivalents of sodium 2,6 -Diphenylisonicotinate salt prepared as above was added drop by drop while stirring at room temperature. A white precipitate formed instantly which was left to stir for few more hours. The product was filtered, washed three times with distilled water and three times with methanol and dried under vacuum at room temperature. 0.2987 g (97.1%) of the product was isolated

RESULTS AND DISCUSSIONS

Synthesis

2, 6-Diphenylisonicotinic acid is insoluble in distilled water, but when treated with an equivalent amount of sodium hydroxide, it dissolves forming the sodium 2,6 -Diphenylisonicotinate salt. The pH of the light brown solution was maintained between 6 and 7 because if the pH is higher than 7, it leads to the formation of the undesired lanthanide (III) hydroxide precipitate that can affect the elemental analysis results. Three equivalents of this sodium salt solution were added drop by drop to one equivalent aqueous solution of the lanthanide ion at room temperature. White or white-gray precipitates were formed immediately. The

reactions that took place could be represented by the following equations.



The precipitates formed from reactions in equations 2 and 3 were filtered and dried under

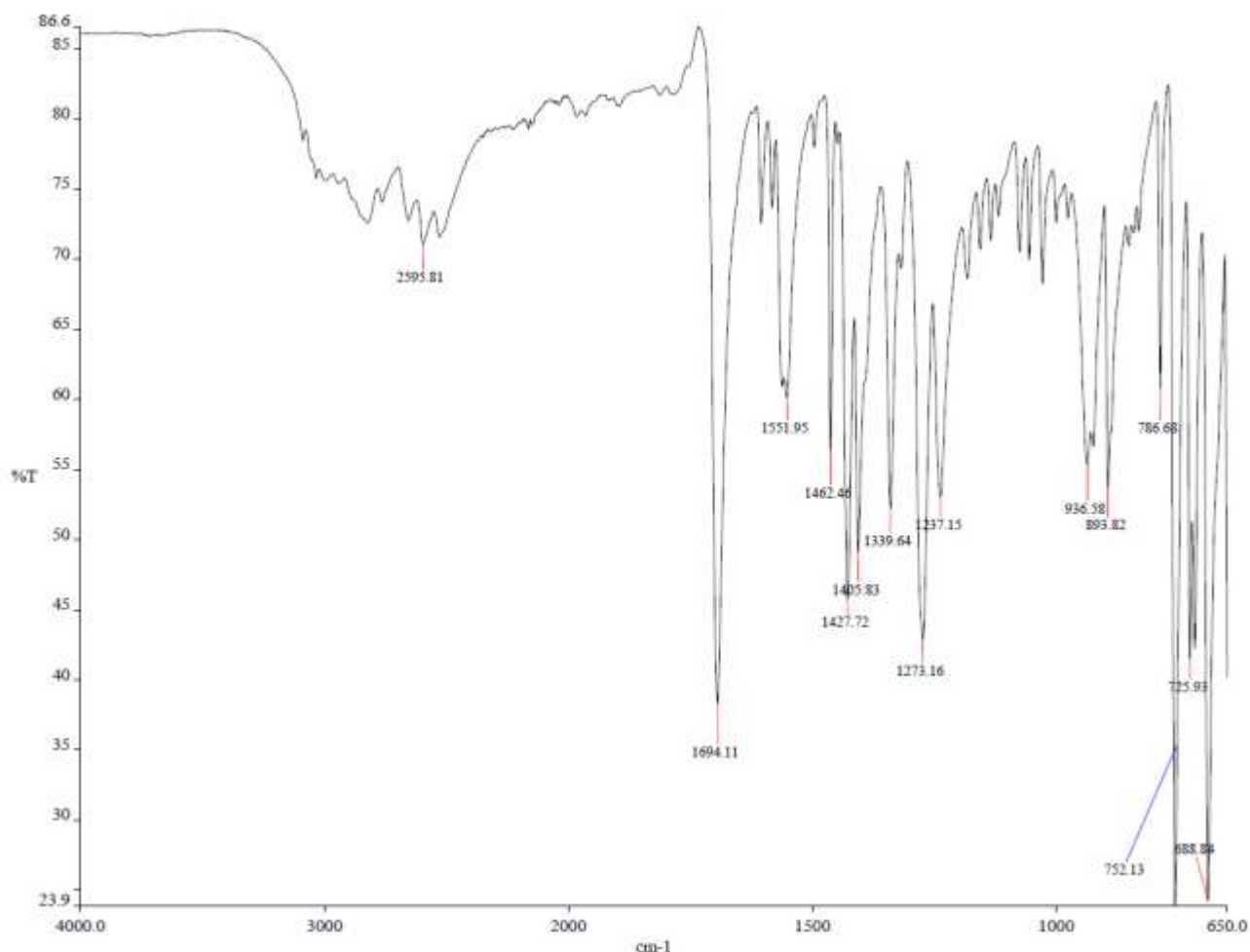
vacuum first and in an oven at 110 °C for two days. These were characterized by spectroscopic methods and CHN analysis. All the complexes synthesized were thermally stable and did not melt at high temperature (360°C).

Characterization

FTIR-spectra.

The FTIR spectra of the ligand and the metal complexes synthesized were collected from 4000-650 cm^{-1} using PerkinElmer FTIR equipped with ATR crystal. The spectra of 2, 6-Diphenylisonicotinic acid and the Eu (III) complex are shown on figure 1 as **A** and **B** respectively.

(A)



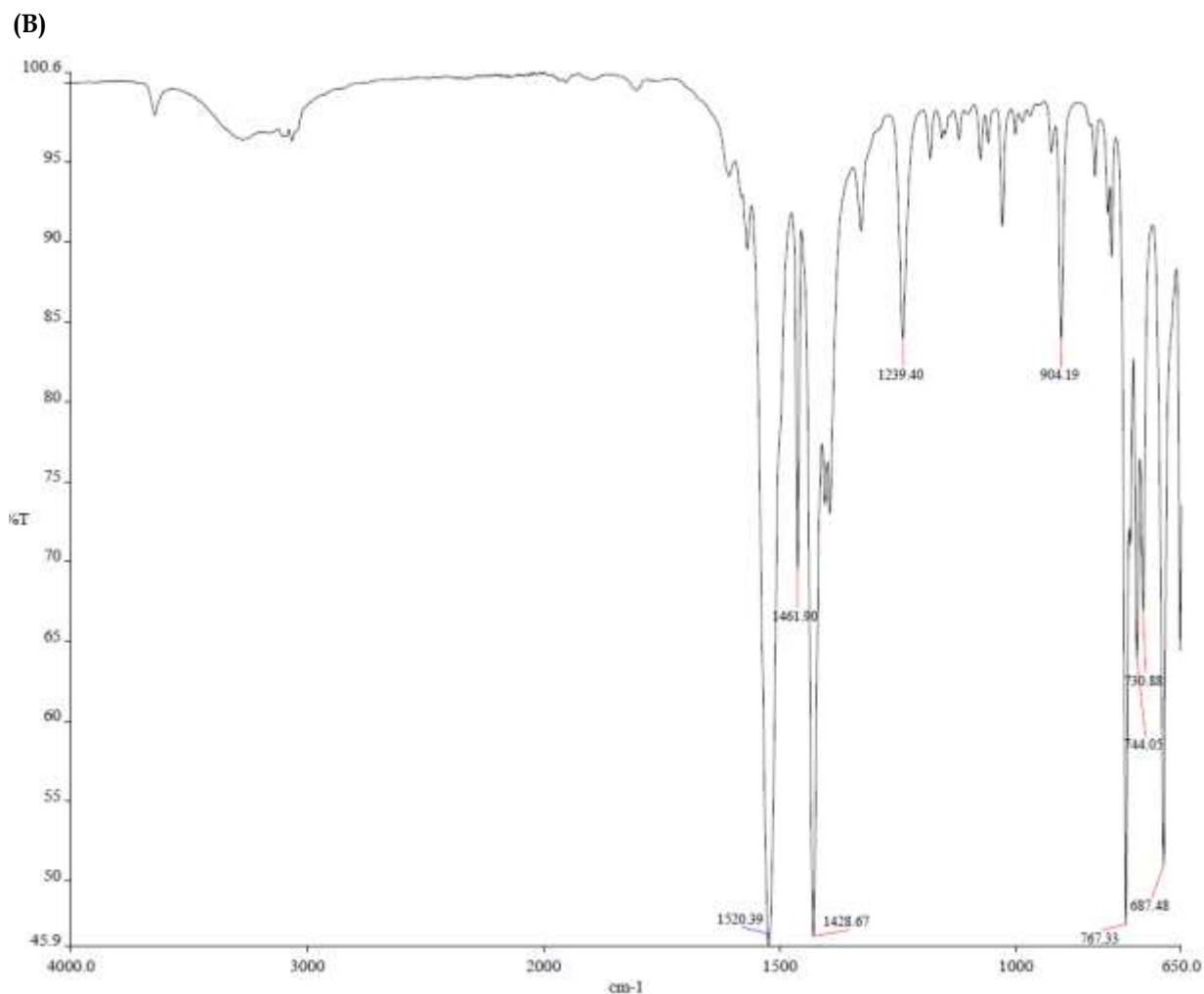


Figure 1. FTIR Spectrum of 2,6-Diphenylisonicotonic acid (A) and Europium (III) complex (B).

The IR spectrum of 2,6-Diphenylisonicotonic acid shows a broad medium band in the region of 2800-2500 cm⁻¹ due to hydrogen bonded carboxylic acid (Skoog, et. al.,2017), and a very strong sharp peak at 1694 cm⁻¹ which is associated with the asymmetric stretching vibration of the carboxylate $\nu_{as}(-COO^-)$ group. The symmetric vibration $\nu_s(-COO^-)$ is observed at 1427 and 1339 cm⁻¹. The peaks 1237-1339 cm⁻¹ could be due to O-H bending vibration. However, in the complexes formed, the broad band (2800-2500 cm⁻¹) that was seen in the acid is not visible indicating that bonding to the metal center has taken place through the carboxylate group. Additionally, the asymmetric and symmetric stretching of COO⁻ shifted to lower

wavenumbers, 1535 -1520 cm⁻¹ and 1427-1239 cm⁻¹ respectively. Such shifts with a difference of about 100-170 cm⁻¹ in the asymmetric and symmetric vibrations of the complex indicate that the carboxylate acts as a bidentate ligand when coordinating to the lanthanide metal center (Tanase, S.; et.al). Similar shifts to a lower wavenumber in stretching frequencies of other metal carboxylate complexes were observed (Du, Ren, Zhang,2022). The medium band around 904 cm⁻¹ is attributed to bending vibration, $\delta(O-C-O)$ of the carboxylate group. As can be seen from the spectra of the ligand and complexes, the strong peaks 1400-1000 cm⁻¹ in the acid are not all observed or have become weaker in the spectra of

(B)

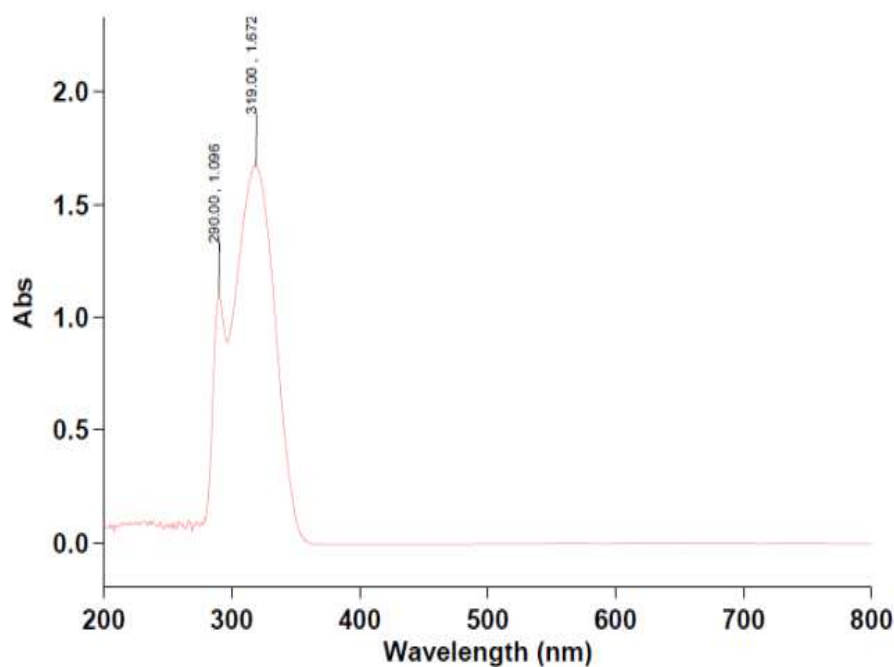


Figure 2. UV- Spectrum of 2,6-Diphenylisonicotinic acid (A) and Europium(III) complex (B) in DMSO.

For 2,6-Diphenylisonicotinic acid, the absorption band at 293 nm corresponds to $\pi\pi^*$ transition and the one at 330 nm is probably attributed to $n\pi^*$ transition of the $-\text{COO}^-$ group (Xu, et. al.,2011). The absorption bands of the Eu (III) and the other complexes are similar in shape to that of the ligand. However, the Eu(III) complex shows a slight blue shift to 290 and 319 nm respectively. Similar trend is observed for the other complexes. The shift to lower λ of the $\pi\pi^*$ and $n\pi^*$ transition of the complexes indicates the coordination of the ligands to the metal center through the $-\text{COO}^-$ end of the ligand.

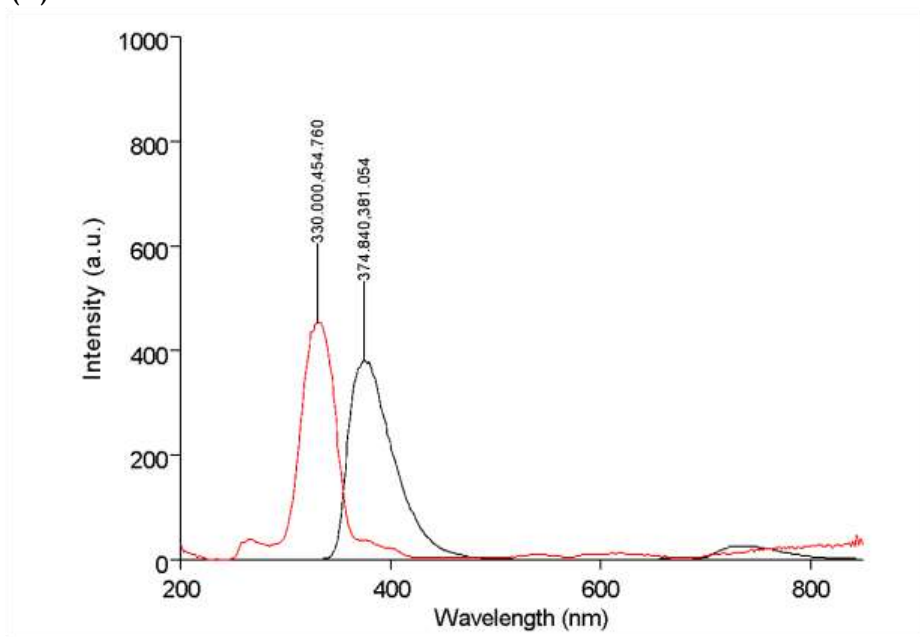
Table 2. UV-Absorption Peaks.

Compound	λ_{max} (nm)
2,6-Diphenylisonicotinic acid	293, 330
Eu(C ₁₈ H ₁₂ NO ₂) ₃ ·3H ₂ O	289, 319
Gd(C ₁₈ H ₁₂ NO ₂) ₃ ·3H ₂ O	289, 318
Er(C ₁₈ H ₁₂ NO ₂) ₃ ·3H ₂ O	289, 319
Nd(C ₁₈ H ₁₂ NO ₂) ₃ ·3H ₂ O	288, 320

Excitation-Emission spectra

The excitation and emission spectra of 2,6-Diphenylisonicotinic acid and the lanthanide complexes were measured in DMSO solution at a concentrations of about 10^{-5} M. Figure 3 shows the results obtained for the ligand (A) and the Eu(III) complex (B). The other complexes show similar excitation and emission spectra as that of the Eu complex. The results obtained indicate that there is no significant difference in the spectrum of the ligand and the complexes synthesized. However, the slight difference in the excitation and emission wavelengths indicate the formation of the complexes due to reactions between the metals and the ligand. Additionally, the results show that the excitation and emission wavelengths of the complexes might have originated from the ligand only thereby suggesting that it is not possible to conclude if the ligand has sensitization ability of the complexes formed. We plan to conduct further studies to see if the ligand has an antenna effect by scanning the emission spectrum at a fixed excitation wavelength in the solid state.

(A)



(B)

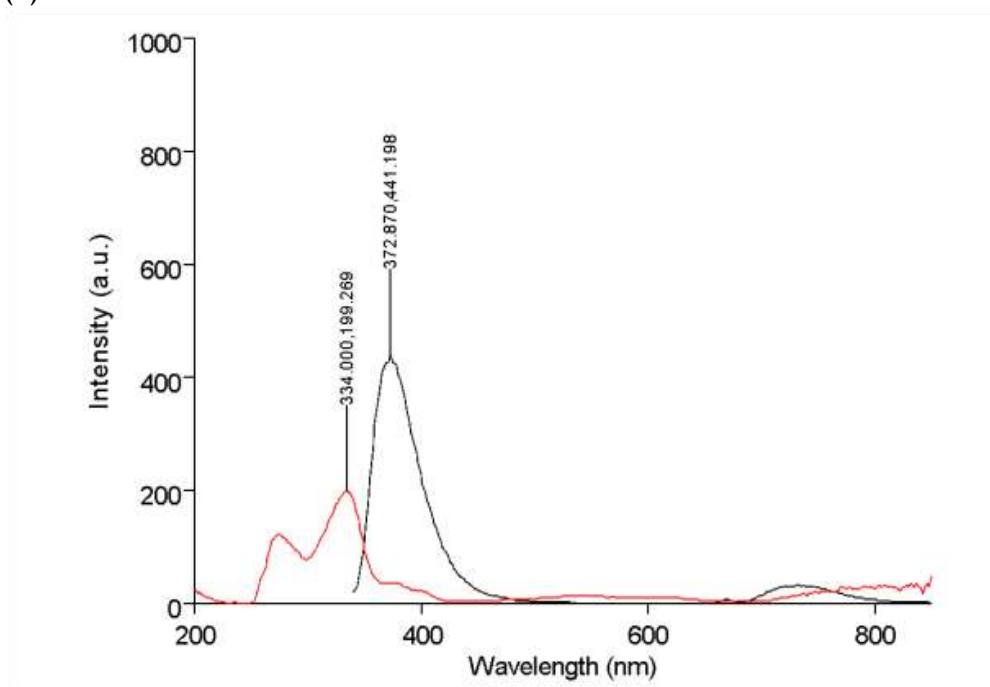


Figure 3. Excitation and Emission Spectrum of 2,6-Diphenylisonicotinic Acid (A) and Europium(III) complex (B) in DMSO.

Table 3. Excitation and Emission wavelength of the ligand and the complexes.

Sample	λ_{Ex}	λ_{Em}
2,6-Diphenylisonicotinic Acid	330	375
Eu(C ₁₈ H ₁₂ NO ₂) ₃ ·3H ₂ O	260, 334	373
Gd(C ₁₈ H ₁₂ NO ₂) ₃ ·3H ₂ O	334	375
Er(C ₁₈ H ₁₂ NO ₂) ₃ ·3H ₂ O	334	375
Nd(C ₁₈ H ₁₂ NO ₂) ₃ ·3H ₂ O	335	380

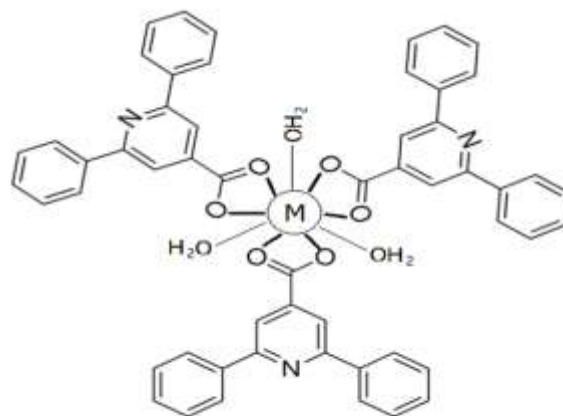
CHN-Analysis

Elemental analysis of carbon, hydrogen and nitrogen were done on PerkinElmer 2400 series II CHNSO analyzer. The instrument was calibrated with a high-purity Acetanilide and 2.00-3.00 mg of each sample was analyzed twice. The table below shows the found and calculated percentage of CHN in each complex. These results reveal that the complexes have the molecular formula,

M(C₁₈H₁₂NO₂)₃·3H₂O. Based on spectroscopic data and elemental analysis, we suggest that the complexes have the molecular structure shown in figure 4. The coordination number around the metal is nine and resulted from the bonding of three 2, 6-Diphenylisonicotinate ligands that serve as bidentate ligand and three water molecules. Lanthanide complexes with nine or more coordination number are very common and most of them achieve high coordination numbers by adding three or more water molecules in the coordination sphere of the metal (Hussain, et. al., 2019; Hussain, et. al., 2015a; Hussain, et. al., 2015b; Hussain, et. al., 2014; Hussain, et. al., 2018; Xu, Li, Shi, Chen, 2011).

Table 4. CHN- Analysis.

Complexes	Found (Calculated)		
	%Carbon	%Hydrogen	%Nitrogen
Eu(C ₁₈ H ₁₂ NO ₂) ₃ ·3H ₂ O	62.58(63.04)	3.59(4.09)	3.91(4.09)
Gd(C ₁₈ H ₁₂ NO ₂) ₃ ·3H ₂ O	61.83(62.61)	3.66(4.05)	3.93(4.05)
Er(C ₁₈ H ₁₂ NO ₂) ₃ ·3H ₂ O	61.68(62.13)	3.59(4.03)	3.96(4.03)
Nd(C ₁₈ H ₁₂ NO ₂) ₃ ·3H ₂ O	62.85(63.53)	3.42(4.12)	3.94(4.12)



M = Eu, Gd, Er, Nd

Figure 4. Suggested molecular structure of the complexes formed.

CONCLUSION

Four lanthanide (III) complexes bearing carboxylate donor ligand derived from 2,6-Diphenylisonicotinic acid were synthesized and characterized by spectroscopic methods and CHN analysis. Spectroscopic and elemental analysis results proved the formation of M(C₁₈H₁₂NO₂)₃·3H₂O, nine coordinate complexes. The complexes are insoluble in most organic solvents, but slightly soluble in DMSO. All the complexes were found to be thermally stable and do not melt when heated to 360°C. In the future we will thoroughly investigate the photoluminescence of the complexes in the solid state and evaluate the sensitization ability of the ligand.

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