



SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND BIOLOGICAL ACTIVITIES OF Sm(III) AND Dy(III) COMPLEXES WITH SCHIFF BASE DERIVED FROM 2-HYDROXY-1-NAPHTHALDEHYDE AND 2-AMINOBENZOIC ACID

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ABSTRACT

A tridentate Schiff base, L, 2-((2-hydroxynaphthalen-1-yl) methyleneamino)benzoic acid was prepared by condensation of 2-aminobenzoic acid with 2-hydroxy-1-naphthaldehyde. The prepared ligand was used to synthesize Sm(III) and Dy(III) complexes $[Ln(NO_3)_2]NO_3 \cdot 2H_2O$, (Ln=Sm(III) and Dy(III)). The ligand and its lanthanide (III) complexes were characterized by elemental analysis, molar conductivity, thermal analysis and IR spectroscopy. The elemental and spectral analysis show that ligand coordinate to the central lanthanide(III) ion by its imine nitrogen, phenolic oxygen and carboxylic oxygen in 1:1 stoichiometry. The complexes were found to be electrolytic in nature on basis of their molar conductance values. The thermal analysis data provided an evidence for the present of uncoordinated water in all complexes. It was found that the complexes exhibit higher antioxidant activity than that of its corresponding ligand.

Keywords: Complex, ligand, Schiff base, spectroscopy.

INTRODUCTION

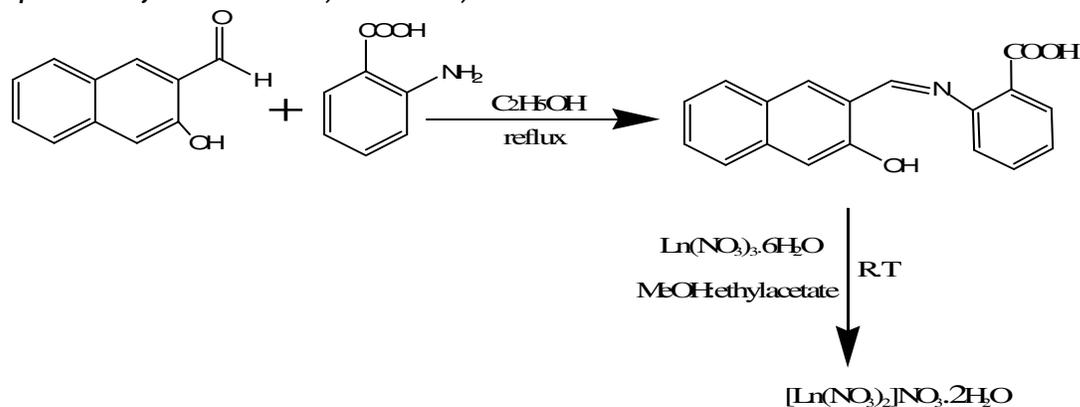
Schiff base ligands have played an essential role in the development of coordination chemistry due to their ability to form a stable complexes with different transition metal ions and lanthanide metal ions in a various oxidation state through nitrogen and oxygen atoms (Nataraja *et al.*, 2002). Transition metal complexes have become increasingly interested in the last few years because of their diverse applications in different areas such as catalysis and manufacture of many valuable drugs, for instance iron (III) and cobalt (III) complexes have been used as catalyst and anticancer respectively (Comby *et al.*, 2007). However, in the recent years the chemistry of lanthanide metal complexes have attracted much attention due to their unique properties and valuable applications in biological system, magnetic resonance imaging agent, sensor laser material and optical telecommunication (Alexander, 1995). In view of the numerous application of lanthanide complexes, we have synthesized and characterized the Schiff base ligand {2-((2-hydroxynaphthalen-1-yl) methylene amino) benzoic acid and its lanthanide complexes. The characterization was done by elemental analysis, conductivity measurement, spectral and thermal analyses.

MATERIALS AND METHODS

The reagents and solvents used in this work were of analytical grade. The Infrared spectra (IR) were recorded on a JASCO FT-IR model 470 spectrophotometer in the region of 4000-400 cm^{-1} in KBr pellets, Molar conductivities were measured in DMF solution, using WTW LF 318 conductivity meter. The Microanalysis for carbon, hydrogen and nitrogen was performed on Euro EA elemental analyzer 3000. The metal content of the complexes was determined by titration with EDTA (Ethylenediamine tetraacetic acid disodium salt) using xylenol orange as an indicator and acetic acid as buffer. and Thermal analysis was performed on a PCT-2A thermobalance analyzer operating at a heating rate of 10 °C per minute in the range of ambient temperature up to 900 °C under N_2 . The free radical scavenging activity of Schiff base ligand and its lanthanides complexes were determine by measuring the change in the absorbance of DPPH at 517nm spectrophotometrically.

Synthesis of Schiff base Ligand and its Lanthanide Complexes

The Schiff base was prepared by condensation reaction of 2-aminobenzoic acid with 2-hydroxy-1-naphthaldehyde in 1:1 molar ratio. The lanthanide complexes were synthesized by treating the ligand with $Ln(NO_3)_3 \cdot 6H_2O$ (Ln=Sm(III) and Dy(III)) as shown in Scheme 1.



Where: Ln=Sm and Dy

Scheme.1 Synthetic route for the synthesis of the Schiff base ligand L, Dy(III), and Sm(III) complexes.

RESULTS AND DISCUSSION

The isolated complexes were stable in air, non-hygroscopic powders, insoluble in water, slightly soluble in methanol, ethylacetate and completely soluble in DMSO and DMF. The elemental analyses data of the Schiff base ligand and the two Lanthanide complexes are presented in the Table 1. The data obtained are in consistent with their proposed molecular formulae. The analytical data show that all the complexes have 1:1 metal to ligand

stoichiometry. The molar conductivity (Λ_m) data for the lanthanide (III) complexes in DMF solution at room temperature are presented in Table 1. The conductivity values are in the range of 98-100 $\text{Scm}^2\text{mol}^{-1}$ indicating that all the metal complexes are in 1:1 electrolyte (Geary, 1971). These values intimate the coordination of two nitrate groups to the lanthanide (III) ion and it is in good agreement with the results obtained from IR and TGA studies.

Table 1 Analytical data and molar conductance values for the Schiff base and its complexes.

Compound	F.wt.	C (%) found(calc.)	H (%) found (calc.)	N (%) found (calc.)	Ln (%) found (calc.)	Yield (%)	Λ_m ($\text{Scm}^2\text{mol}^{-1}$)
L	291.29	73.48(74.22)	5.39 (4.50)	4.49 (4.81)	-	95	-
[SmL(NO ₃) ₂] ₂ NO ₃ ·2 H ₂ O	661.69	33.48(32.67)	3.52 (3.48)	8.38 (8.47)	23.02 (22.72)	90	98.75
[DyL(NO ₃) ₂] ₂ NO ₃ ·2H ₂ O	673.83	32.12(32.08)	2.16 (2.24)	8.42 (8.31)	24.08 (24.12)	85	99.37

Calc :calculated

The thermal analysis of the Schiff base ligand, L, and its Lanthanide complexes were carried out by TGA and DTGA techniques, to determine the thermal behaviour and amount of the water present in the ligand and the complexes within the temperature range of 25-900 °C under N₂flow. The TGA and DTGA curves of Schiff base ligand, L, are presented in Figure 1. This figure clearly show that the ligand decomposed in one step, from 251-314 °C with an estimate mass loss of 92%. The remaining mass may be due to some ashes. The TGA-DTGA curves of the Dysprosium complex show that the complex underwent three steps decomposition (Fig.1). The first step of decomposition occurred in temperature between 67°C and

118°C with an estimate mass loss of 6.61%, it correspond to the lost of two uncoordinated water molecule (physic-sorbed water) (Goswami, *etal.*,2012).The second and third steps with peak temperature at 341 °C and 499 °C are accompanied with mass loss of 19% and 22% respectively, it correspond to the elimination of the nitrate and Schiff base ligand. The decomposition was completed at 900 °C. The thermal decomposition behaviour of Sm(III) complex show a similar pattern to that of Dysprosium complex, [DyL(NO₃)₂]₂NO₃·2H₂O . The result obtained from thermal study are in good agreement with the elemental analysis result.

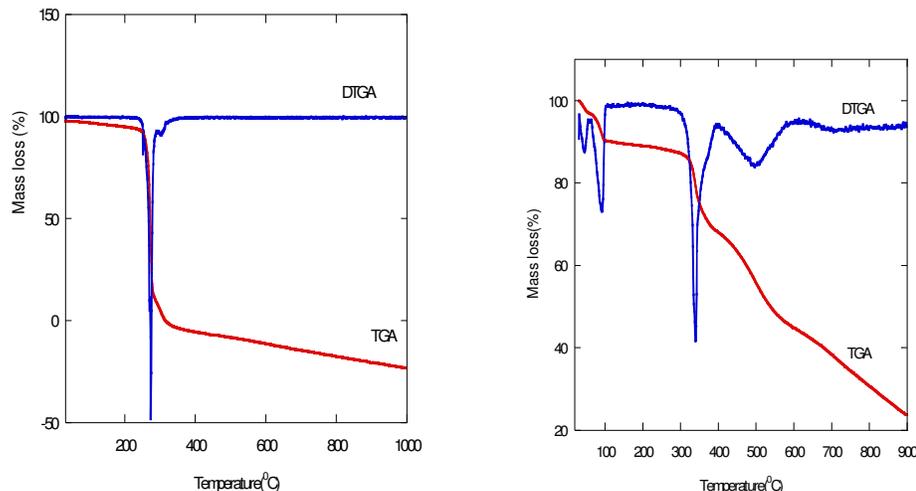


Figure 1 TGA-DTGA thermogram for the Schiff base ligand and Dy(III) complex.

Infrared Spectroscopy

The essential IR bands for the Schiff base ligand, L, Dy(III) and Sm(III) complexes together with their assignments are reported in Table 2. The IR spectra of Sm(III) and Dy(III) complexes were compared with the spectrum of the free Schiff base ligand. The IR spectrum of the free ligand showed a strong band at 1613cm^{-1} which may be attributed to the azomethine(C=N) stretching vibration (Goswami, *et al.*, 2012). This band was slightly shifted to higher wave number by 9cm^{-1} upon complexation with Sm(III), indicating the involvement of the azomethine nitrogen atom in coordination to the Sm(III) ion. This supposition was further supported by the appearance of the medium intensity band at 496cm^{-1} which may be assigned to $\nu(\text{Sm}-\text{N})$ (Taha, *et al.*, 2011). The IR spectrum of the ligand shows a phenolic vibration $\nu(\text{OH})$ band at

3421cm^{-1} which gets shifted to lower wave number in the Sm(III) complex by 33cm^{-1} this may be due to intramolecular hydrogen bond that occur between phenolic oxygen and azomethine proton.

The appearance of $\nu(\text{OH})$ in the Sm(III) complex indicates that phenolic hydroxyl oxygen is coordinated to the Sm(III) ion without proton displacement (Ajlouni, *et al.*, 2012). The absorption band at 1329cm^{-1} is assigned to $\nu(\text{Ar}-\text{O})$ stretching vibration in the spectrum of the ligand, this shifted to lower frequency at 1320cm^{-1} on complex formation indicating that the coordination of Sm(III) ion occur via oxygen atom of the hydroxyl naphthalene of the Ligand. This was supported by the appearance of medium intensity band at 540cm^{-1} which is assigned to $\nu(\text{Sm}-\text{O})$ vibration (Lekha, *et al.*, 2014).

Table 2. Major infrared spectral data for the Schiff base ligand L, and its complexes (cm^{-1}).

Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{Ar}-\text{O})$	$\nu(\text{NO}_3^-)$						$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
					ν_1	ν_2	ν_3	ν_4	ν_{1-4}	ν_6		
L	3421	1613	1711	1329	-	-	-	-	-	-	-	-
[SmL(NO ₃) ₂] ₂ NO ₃ .2H ₂ O	3388	1622	1669	1320	1470	1034	818	1281	189	1385	540	496
[DyL(NO ₃) ₂] ₂ NO ₃ .2H ₂ O	3389	1620	1672	1319	1471	1036	817	1281	188	1385	540	495

A band observed at 1711cm^{-1} in the IR spectrum of the free ligand may attributed to $\nu(\text{C}=\text{O})$ stretching vibration, this band shifted to lower wave number 1669cm^{-1} in the

corresponding Sm(III) complex indicating the participation of the carbonyl group in the complexation (Goswami, *et al.*, 2012).

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The IR spectrum of Sm(III) complex displayed several non-ligand absorption bands at 1465 cm^{-1} (ν_1), 1035 cm^{-1} (ν_2), 815 cm^{-1} (ν_3) and 1281 cm^{-1} (ν_4) which are assigned to the coordinated nitrate ion (C_{2v}). The separation between two strongest frequencies ν_1 and ν_4 is almost 184 cm^{-1} , indicating that the coordinated nitrate ion in the Sm(III) complex is a bidentate Ligand(Laussac *et al.*,2002). The appearance of the band at 1385 cm^{-1} in the spectrum of the Sm(III) complex indicates the existent of the

non-coordinated nitrate group (D_{3h}) (Nakamoto, 1986). Dy(III) complex showed a similar IR spectra to that of Sm(III) complex, indicating that it has a similar coordination structure (table 2).

Based on these results, it could be concluded that the ligand coordinated to the Sm(III) and Dy ions through carboxylic oxygen, azomethine nitrogen and the phenolic oxygen as depicted in figure.2

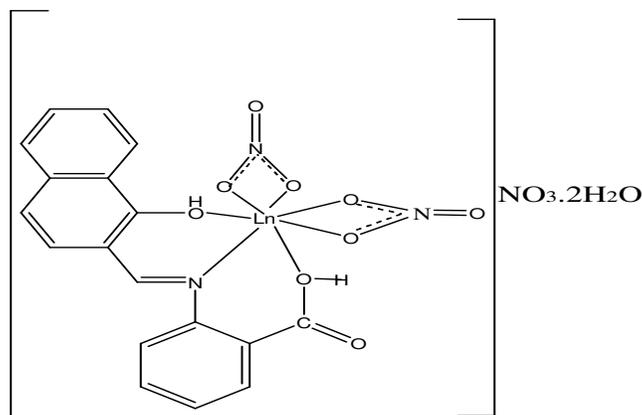


Figure. 2The proposed structure of the $[LnL(NO_3)_2]NO_3 \cdot 2H_2O$ complexes.

DPPH - Radical Scavenging Assay

This method was developed to investigate the antioxidant activity of Schiff base ligand and its lanthanide metal complexes using stable 2, 2-diphenyl-2-picrylhydrazyl (DPPH) radical as described in the literature (Matthaus, 2002).The antioxidant activity of the tested compounds was recorded spectrophotometrically at 517 nm. It was observed that the scavenging activity is increases with increase in concentration of the tested compound (Table 3). The lanthanide metal complexes displayed a higher antioxidant scavenging activities than that of the Schiff base ligand (table 3.) which is consistent with previously reported data for other

elements(Xu,*et al.*, 2007). This could be attributed to the reaction of hydroxyl group of the naphthaldehyde with DPPH radical via hydrogen atom transfer (HAT) mechanism (Takasaki, 1993). In addition to that, the positively charge lanthanide ion withdrawn an electron toward itself, thereby making O-H bond more polarized as such the hydrogen atom has greater tendency to ionize than that in the free ligand (Foti *et al.*, 2004).Among the complexes tested for DPPH scavenging activities, Dy(III) complex exhibit lowest scavenging activity while Sm(III) complex displayed highest scavenging activity which may be related to the ionic size effect.

Table 3.Antioxidant scavenging activity data of the Schiff base ligand, L, and its complexes.

Tested Compounds.	Concentration(μM)				
	62.5	125.0	187.5	250.0	321.5
L	3.46 \pm 0.31	5.48 \pm 0.70	9.52 \pm 0.4	10.97 \pm 0.21	11.98 \pm 0.59
$[SmL(NO_3)_2]NO_3 \cdot 2 H_2O$	32.90 \pm 0.21	34.05 \pm 0.20	35.93 \pm 0.85	37.81 \pm 1.42	47.19 \pm 0.93
$[Dy L(NO_3)_2]NO_3 \cdot 2 H_2O$	27.83 \pm 0.44	33.24 \pm 0.99	35.23 \pm 0.24	38.37 \pm 0.67	43.78 \pm 1.45

CONCLUSION

In this research a tridentate Schiff base ligand, L {2-((2-hydroxynaphthalenyl) methylene amino) benzoic acid} and its corresponding lanthanide complexes [LnL(NO₃)₂] NO₃.2H₂O were synthesized and characterized by elemental analysis, TGA-DTGA and spectral analysis. The analytical and spectral data show that the ligand coordinate to the central lanthanide ion by its imine nitrogen, phenolic oxygen and carboxylic oxygen with 1:1 stoichiometry. The molar conductance data revealed that two nitrate ions are present inside the coordination sphere while other

nitrate is in the outer coordination sphere of the complexes. The IR spectral data also show that the two nitrate ions are bidentately bonded to the lanthanide metal ions in all complexes. Based on these observations the coordination number of seven is suggested for metal ion in these lanthanide (III) nitrate complexes. The thermal analysis data are in consistent with the proposed formula of the synthesized compounds and provided an evidence for the uncoordinated water in all complexes. We were found that the complexes exhibit higher antioxidant activity than that of its corresponding ligand.

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