Rare Earth Nitrate Complexes with an ONO Schiff Base Ligand: Spectral, Thermal, Luminescence and Biological Studies

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ABSTRACT: Five rare earth complexes lanthanum(III), praseodymium(III), neodymium(III), samarium(III) and europium(III) have been synthesized from Schiff base ligand (N,N-bis (2-hydroxy-1-naphthylidene) acetylhydrazone). The complexes were characterized based on elemental analysis, molar conductance, ultraviolet, infrared, mass, thermogravimetric and powder X-ray diffraction studies. Infrared spectra suggest ligand act as a neutral tridentate ligand. The Schiff base ligand coordinating through the naphtholic oxygen without proton displacement, azomethine nitrogen atom and hydrazone carbonyl oxygen atoms of the ligand to the lanthanide ion. The conductivity and thermal decomposition studies indicate the presence of two coordinated nitrate ion acts as bidentate fashion. Powder X-ray diffraction studies reveal the neodymium complex has an orthorhombic system with different unit cell parameters. Europium, samarium, neodymium and praseodymium complexes exhibit the characteristic luminescence. Further, the in vitro antimicrobial activities of the metal complexes exhibited greater activity as compared with the ligand.

KEYWORDS: Ln complexes; Powder X-ray diffraction; Fluorescence; Biological activities.

INTRODUCTION

Synthesis of luminescent lanthanide complexes has been of considerable interest because of their potential applications, such as fluorescent labeling reagents, imaging agents, and emitter materials in Organic Light-Emitting Diodes (OLEDs) [1-3] Generally, complexes of Eu(III), Tb(III) and Sm(III) have been extensive applications in biological medicine, especially in the fluorescence imagery cancer radiation treatment[4,5]

Metal complexes of both acyl- and aroyl-hydrazones have been motivated wide verity of therapeutic activity. In particular, novel chelators with high Fe mobilization efficiency for the treatment of Fe overload disease [6], overload disease[6], Eg. methyl pyrazinylketone isonico tinoyl hydrazone[7] and diaroylhydrazines[8,9]. Although Ln(III) complexes of acetyl/benzoyl hydrazone are reported in the literature [10,11], spectral and luminescence characteristics of ONO ligand Ln(III) complexes with such important ligands are not reports so far.

In the light of the above and in continuation of our ongoing research work[11,12] on metal complexes of Schiff base ligand, we have investigated La(III), Pr(III), Nd(III),Sm(III) and Eu(III) complexes with (N,N-bis(2-hydroxy-1-naphthylidene) acetylhydrazone (HL) Schiff base ligand. In addition, the in vitro anti-microbial

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activities of the complexes have been evaluated against gram +ve and gram -ve bacteria.

EXPERIMENTAL SECTION

Materials and Methods

All the reagents used in the synthesis of ligand viz. 2-hydroxy-1-napthaladehyde, acetylhydrazide and lanthanide nitrates were purchased from Sigma-Aldrich chemical and used without further purification. All other solvents and reagents were of analytical grade.

Physical measurements

Elemental analysis was carried out on a Perkin-Elmer 2400 CHN elemental analyzer. Molar conductivities were measured in DMF solution, concentration of 10⁻⁴M, at 25°C using ELICO conductivity meter equipped with CM162 conductivity cell. Infrared spectra were recorded on a Perkin-Elmer FT-IR model 100 spectrophotometer in the region of 4000-400 cm⁻¹ using KBr pellets. UV-visible spectra were recorded in DMF solution, concentration of 10⁻⁵M, at 25°C using a UV-Lamda 50 Perkin-Elmer UV-visible spectrophotometer. Fluorescence spectra (scanned from 200 to 900 nm, with a spectral resolution of 0.2 nm, slit widths ~2.5nm) were recorded instrument model Perkin Elmer precisely LS-55 fluorescence spectrophotometer with 1 cm quartz cell at room temperature. The light source and detectors were 450Wxenon lamp and R955 photomultiplier tube, respectively. The thermal analysis were performed on a Perkin-Elmer Pyris STA 6000 thermo balance analyzer operating at a heating rate of 10°C/min in the range of ambient temperature up to 900°C under N₂. X-ray diffractometer (XRD) Philips: PW1830. Electron ionization-mass spectrometer, model: AUTOSPEC-M, Micromass, UK.

Synthesis of Ln(III) complexes

The Schiff base ligand (HL) was prepared as reported earlier [11]. A 0.7 m mole of HL was dissolved in 20 mL of hot ethanol. To this solution, metal salt [Ln(NO₃)₃.6H₂O, Where, Ln = La, Pr, Nd, Sm, Eu] solution (0.350 m mole) in 10 mL acetonitrile was added. The reaction mixture was refluxed for 4h. On cooling microcrystalline precipitate was formed. The complex was collected by filtration, washed with ethanol and dried in *vacuo*. The complex was recrystallized by slow diffusion of diethyl ether into a methanol solution of the complex. Yield: 60%.

Antimicrobial activity

Antibacterial activity of lanthanides complexes was determined initially by using an agar diffusion method [13]. Petri-dishes(90mm) were prepared containing 20 ml of Mueller-Hinton agar. The inoculum density of all bacterial isolates was standardized with 0.5 Mc Farland turbidity standards. Once cooled a bacterial lawn was prepared by spreading 100 μ L of bacterial culture onto the surface of the dried Mueller-Hinton agar plates using sterile swabs. Wells 6 mm in diameter were punched into the agar and filled with 100 μ L of the lanthanide complexes at a concentration of 1 μ g/mL[14]. The plates were incubated at 37°C for 24h. Zones of inhibition were measured using a caliper.

RESULTS AND DISCUSSIONS

All the complexes were synthesized by reacting [Ln $(NO_3)_3.XH_2O$] (where Ln = La, Pr, Nd, Sm, and Eu) with the ligand yielded a series of complexes corresponding to the formula of [Ln(HL)₂(NO₃)]. The complexes are stable at room temperature, non-hygroscopic, insoluble in water and diethyl ether, but slightly soluble in methanol, ethanol, ethyl acetate, chloroform, and benzene and readily soluble in dimethylformamide and DMSO. The elemental analysis, compound formula, weight, yield%, and molar conductivity data of the complexes are given in Table 1.

Molar conductance

Molar conductivity data for all complexes in DMF solution at 25° C, are given in Table 1, The values in the range of 110-122 cm²/ Ω .mol indicate that these complexes are 1:1 electrolytes [15]. The values suggest that the two nitrates are present within co-ordination sphere and one nitrate as counter anion *via* ionic bond.

UV-Visible spectroscopy

The UV- visible absorption spectra of all the Ln(III) complexes and Schiff base ligand $(1.0\times10^{-5}\text{M}\text{ in DMF})$ are listed in Table 2. The ligand(HL) shows very strong absorption bands in the ultraviolet region, two maxima at 321 and 368 nm, due to the $\pi\to\pi^*$ transitions within the aromatic ring and $n\to\pi^*$ naphthalene ring and the imine function of hydrazone moiety respectively[16]. The M \to L charge transfer transitions are more clearly observed in the electronic spectrum, as strong peak

Table 1: Elemental analytical data and molar conductivity values for the Ln complexes.

Compound	F.wt.	C(%) Found(Calc.)	H(%) Found(Calc.)	N(%) Found(Calc.)	Yield(%)	$\Lambda_{\rm m} ({ m cm}^{ m Y} / \Omega.{ m mol})$
HL	228	68.40(68.42)	5.22(5.26)	12.26(12.28)	60	-
[La(HL) ₂ (NO ₃) ₂]NO ₃	780.09	37.93(39.95)	1.96(3.07)	12.34(12.54)	50	112
[Pr(HL) ₂ (NO ₃) ₂]NO ₃	782.09	37.83(39.85)	1.95(3.06)	12.26(12.51)	62	114
[Nd(HL) ₂ (NO ₃) ₂]NO ₃	786.24	37.66(39.68)	1.94(3.05)	12.21(12.46)	65	122
[Sm(HL) ₂ (NO ₃) ₂]NO ₃	792.36	37.35(39.37)	1.91(3.02)	12.11(12.36)	60	118
[Eu(HL) ₂ (NO ₃) ₂]NO ₃	793.97	37.27(39.29)	1.91(3.02)	12.09(12.34)	60	116

Calc. means calculated values

Table 2: Important IR bands (cm-1) and UV-visible absorption bands for the Ln complexes.

Complex	ν(О-Н)	ν(C=O)	ν(C=N)	ν(NO ₃ -)				ν(Ln-O)	ν(Ln-N)	(λ _{max}) nm		
				ν_1	ν2	ν3	ν4	ν1-4	ν ₀			
HL	3437	1625	1581	-	-	-	-	-	-	-	-	321ª, 368 ^b
[La(HL) ₂ (NO ₃) ₂]NO ₃	3403	1616	1578	1466	1018	833	1314	152	1384	667	470	330 ^a ,429 ^b ,409 ^c
[Pr(HL) ₂ (NO ₃) ₂]NO ₃	3404	1618	1579	1464	1025	833	1319	145	1384	669	468	330 ^a ,429 ^b ,409 ^c
[Nd(HL) ₂ (NO ₃) ₂]NO ₃	3403	1620	1580	1465	1028	834	1323	142	1384	667	470	330 ^a ,428 ^b ,409 ^c
[Sm(HL) ₂ (NO ₃) ₂]NO ₃	3404	1622	1582	1466	1030	833	1320	146	1384	669	469	330 ^a ,429 ^b ,409 ^c
[Eu(HL) ₂ (NO ₃) ₂]NO ₃	3403	1622	1582	1467	1031	833	1324	143	1384	668	470	330°,429°,409°

 $a\pi \rightarrow \pi^*$; $bn \rightarrow \pi^*$; cLMCT

observed at 330,429 and 409 nm was corresponding to the electron transfer from coordinate Schiff base lanthanide metal ion[17]. This change is essentially variant for each of the lanthanide complexes La(III) Pr(III), Nd(III), Sm(III) and Eu(III) and is attributed to metal coordination by the ligand. Spectra are shown in Fig.1. The higher energy band in the free ligand is observed as a single band upon complexation without much shift in frequency. Based on analytical and spectral data a general structure Fig. 2 is tentatively assigned to the lanthanide complexes.

Infrared Spectroscopy

IR spectra of Eu complex are shown in Fig 3. Important IR spectral data of complexes are presented in Table 2. The IR spectrum of the free Schiff base ligand exhibit a broad band at 3340cm⁻¹, which is attributed to stretching frequencies of naptholic v(O-H) group of Schiff base involved in intermolecular hydrogen bonds [18]. On other hand, in the IR spectrum of the Ln complexes, this band is shifted to high frequency (3403-3405 cm⁻¹) due to coordination of naptholic v(O-H) to the Ln(III)

ion without a proton displacement. The IR spectrum of the free ligand show strong band at 1625 cm⁻¹, which is assigned to stretching vibrations of the carbonyl group v(C=0). The vibrational band at 1581 cm⁻¹ can be assigned to the v(C=N) of azomethine. In the IR spectra of lanthanide(III) complexes, the $\nu(C=O)$ and $\nu(C=N)$ shift by 3-9, 2-3 cm⁻¹. The shift of the $\nu(C=O)$ and $\nu(C=N)$ show a medium intensity bands towards lower wave numbers on complexation. This observation indicates participation of carbonyl oxygen and azomethine nitrogen in coordination to the metal ion [19]. In the IR spectrum of Schiff base ligand, the band at 3196 cm⁻¹ can be assigned to the v(N-H). The v(N-H) band is observed in the range 3154-3224 cm⁻¹ for the complexes. The observance of v(C=O) and v(N-H)bands observed in the IR spectrum of complexes indicate that HL acts as neutral to tridentate ligand in the complex formation[20]. The binding of the metal to the ligand through nitrogen and oxygen atom is further supported by the appearance of new bands in 468-470 cm⁻¹ and 667-669 cm⁻¹ rages due to v(Ln-N) and v(Ln-O) respectively, in the spectra of all the Ln complexes [21].

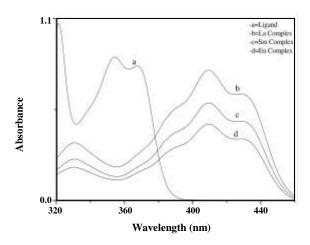


Fig. 1: UV-Visible absorption spectra for the Ln complexes.

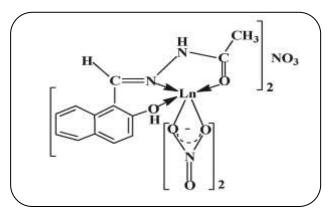


Fig.2: Proposed structure for the rare earth complexes (Ln = La, Pr, Nd, Sm and Eu)

The absorption bands assigned to the coordinated nitrate groups (C2v) are observed at about 1464-1467 cm⁻¹(v_1), 1314-1324cm⁻¹(v_4),1018-1031cm⁻¹(v_2),833-834 cm⁻¹(v_3) [22] for the nitrate complexes. The frequency separation [$\Delta v = v_1 - v_4$] between the asymmetric and symmetric stretching of this group made to distinguish between these binding state. Separation between the two bonds is from 142 to 152 cm⁻¹. These observations suggest that NO₃-acts as bidentate ligand. The vibrational band is present at 1384 cm⁻¹(v_0) in IR spectra of complexes indicate the presence of free ionic nitrate (D_{3h} symmetry), which is in agreement with the results of the conductivity experiments. Similar data are obtained for all Ln complexes.

Mass spectroscopy

In the present investigation, the EI-MS spectrum of HL showed the formation of a molecular ion peak at

m/z: 228 (Sodium ion base peak m/z: 251) corresponding to the formation of [M+Na]⁺ ion. The molecular ion peak is not detected in the recorded mass spectra of the discussed lanthanide (III) complexes. The obtained mass spectra were relatively complex and exhibited a large number of peaks possibly due to extensive fragmentation.

Thermal studies

Thermo Gravimetric (TG) and Differential Thermo Gravimetric Analysis (DTGA) were carried out for the ligand(HL), and its corresponding Ln(III) complexes in nitrogen atmosphere at a heating rate 10°C/min. Thermogram reveals that the ligand is thermally stable up to 280°C and its decomposition starts at 290°C and finishes at 500°C with one decomposition step. The TGA curve of La(III) complex is shown in Fig. 4 . Decomposition occurs in three major steps. In TG analysis, no weight loss observed in the temperature range, 100-300°C. In the first stage (300-325 °C), weight loss of 27.2%((Calcd.25.3%) is due to removal of lattice nitrate. The coordinated nitrates are lost in the 2nd stage(325-400°C)

In the third stage (400-750 °C), the loss is due to elimination and/or decomposition of ligand moiety and formation of stable La_2O_3 with a weight loss of 37.2% (Calcd.38.6 %). On continued heating up to 900 °C, the most stable La_2O_3 oxide id formed which is in agreement with the calculated values. Based on these data, a general structure (Fig.2) is proposed for complexes.

X-ray powder diffraction studies

X-ray diffraction studies of the powder sample were carried out as it was not possible to grow crystals suitable for single crystal X-ray analysis. The observed interplanar spacing values ('d' in A°), have been measured from the diffractogram (Fig.5) of the $[Nd(HL)_2(NO_3)_2]NO_3$ complex with respect to major peaks having relative intensity at wavelength = 1.54178 and the Millar indices, h, k, l have been assigned to each d value and 2θ angles are reported. Data are given in Table 3. The system belongs to 'Orthorhombic' form. The direct unit cell dimensions determined are:

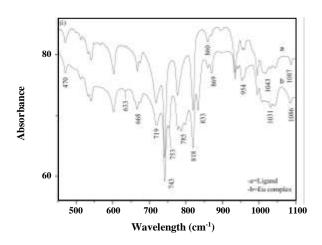
 $a = 8.1412 \text{ A}^{\circ}$

 $b = 9.1064 \text{ A}^{\circ}$

 $c = 10.548 \text{ A}^{\circ}$

 $V = 781.9827(A^{\circ})^3$

 $\alpha = \beta = \gamma = 90^{\circ}$



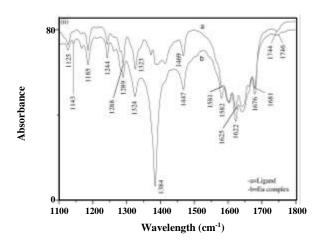
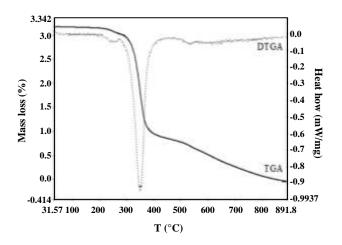


Fig. 3: Infrared spectra in the 1800-400 cm⁻¹ region for the Eu complex.



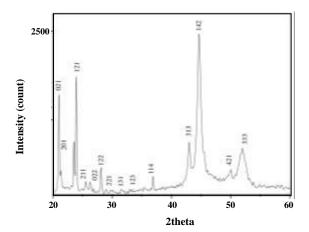


Fig. 4: Differential thermal gravimetric analysis cures for the La complex.

Fig. 5: Powder X-ray diffraction spectrum for the Nd complex.

Based on the experimental evidences, the average crystallite or grain size varies from 22 to 34 nm. The system exhibits nano crystallite phase.

Luminescence spectroscopy

The room temperature excitation and emission spectra of all the Ln³+ complexes and Schiff base hydrazone ligand (1.0 × 10-5 M in DMF solution) has been recorded as show in Fig.6 data are given in Table 4. The emission spectrum excitation wavelength was fixed at 321 nm of the free ligand HL exhibits to $\pi \rightarrow \pi^*$ transitions [22-24]. Inspection of Eu³+,Sm³+,Nd³+and Pr³+ complexes shows characteristic emission spectral band at 330 nm is assigned to $\pi \rightarrow \pi^*$ transition, respectively.

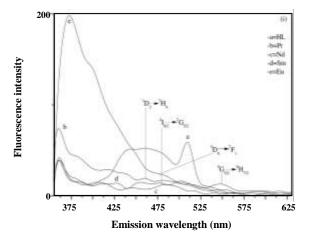
Europium complex e, the emission spectrum excited

at 330 nm shows Fig.6 three luminescence bands corresponding to $S_0 \rightarrow S_1$ at 367 nm, ${}^5D_0 \rightarrow {}^7F_1$ at 475 nm, ${}^5D_0 \rightarrow {}^7F_2$ at 669 nm transitions respectively. The excitation spectrum was obtained by monitoring the 669 nm intensity peak of the ${}^5D_0 \rightarrow {}^7F_2$ emission. It can be seen that the organic chromophore $(S_0 \rightarrow S_1)$ excitation band is less intense than the ${}^5D_0 \rightarrow {}^7F_2$ (669 nm) emission band. This indicates that the sharp emission peak is characteristic of the hypersensitive transition for europium-containing luminescence materials[10, 22-24].

The emission spectrum of samarium complex ${\bf d}$ displays three luminescence bands assigned to the $S_0{\rightarrow} S_1$ transition at 367 nm, ${}^4G_{5/2}{\rightarrow}^6H_{9/2}$ at 658 nm and ${}^4G_{5/2}{\rightarrow}^6H_{7/2}$ at 549 nm transitions, respectively. It contains a very intense broadband that corresponding

h	k	1	2θ(Exp.)	2θ(Calc.)	2θ(Diff.)	d (Exp.)	d (Calc.)	Intensity (Exp.)
0	2	1	21.002	21.213	-0.211	4.2266	4.2148	79.4
2	0	1	23.554	23.753	-0.199	3.7741	3.7512	45.9
1	2	1	23.951	23.643	0.308	3.7123	3.7325	90.9
2	1	1	25.209	25.123	0.086	3.4890	3.4751	15.8
0	2	2	26.238	26.236	0.002	3.3937	3.3725	16.0
1	2	2	28.160	28.074	0.086	3.1663	3.1712	25.2
2	2	1	30.580	30.425	0.155	2.9211	2.9074	9.3
1	3	1	32.502	32.712	-0.210	2.7526	2.7485	9.6
1	3	2	34.026	34.117	-0.151	2.6326	2.6425	9.9
1	1	4	36.910	36.543	0.367	2.4333	2.4344	18.1
3	1	3	43.008	43.186	-0.178	2.1014	2.1256	37.1
1	4	2	44.632	44.494	0.138	2.0286	2.0112	100.0
4	2	1	50.034	50.008	0.026	1.8215	1.8458	22.7
3	3	3	51.956	51.634	0.322	1.7585	1.7495	34.6

Table 3: Powder X-ray diffraction data for the Nd complex.



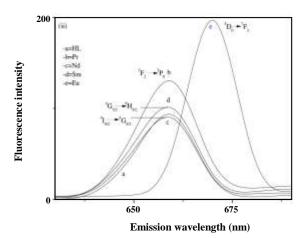


Fig. 6: Fluorescence spectrum excited and emission for the Ln complexes (i and ii).

to the excitation of the organic-localized ($S_0 \rightarrow S_1$) transition. The emission sharp peak transition centered to the more hypersensitive $^6H_{9/2}$ (658 nm) than the $^6H_{7/2}$ (549 nm) level [10,24]

The intense broadband that corresponding to the excitation of the organic chromophore $(S_0 \rightarrow S_1)$ transition. The emission spectrum of praseodymium \mathbf{b} and neodymium \mathbf{c} complexes displays three luminescence bands $\pi \rightarrow \pi^*$ at 362, 460 483 and 658 nm corresponding to the $^1D_2 \rightarrow ^3H_4, ^3P_0 \rightarrow ^3F_2$ for Pr(III) and

 $^4I_{9/2} \rightarrow ^2G_{5/2}, ^4I_{9/2} \rightarrow ^4G_{5/2}$ for Nd(III) transition respectively. The intensity sequence of the peaks is $I_{3P0} \rightarrow {}_{3F2} > I_{4!9/2} \rightarrow {}_{4G5/2}$ transition, respectively [24].

The above four Schiff base complexes was sensitized by its chelating organic ligand, which was acting as photosensitizer. The characteristic luminescence of the lanthanides can be used by the efficiency energy transfer from Schiff base ligand HL to the Ln(III) ions. The Eu(III), Pr(III), Nd(III) complexes show stronger luminescence intensities than those of Sm(III) complex.

Table 4: Luminescence data for the Ln complexes.

Compound	$\lambda_{\rm ex}$ (nm)	ν(cm ⁻¹)	$\lambda_{\rm em}$ (nm)	ν(cm ⁻¹)	Intensity	Assignments	
HL	321	31,152	362(broad)	27,624	37.812	π→π*	
nL	321	31,132	658(broad)	15,197	93.003		
$[La(HL)_2(NO_3)_2]NO_3$	330	31,303	363(broad)	27,548	72.481	π→π*	
			362(broad)	27,624	72.492	$S_0 \rightarrow S_1$	
$[Pr(HL)_2(NO_3)_2]NO_3$	330	30,303	460(broad)	21,739	18.881	$^{1}D_{2} \rightarrow ^{3}H_{4}$	
			658(sharp)	15,197	130.317	${}^{3}F_{2} \rightarrow {}^{3}P_{0}$	
	330	30,303	362(broad)	27,624	41.742	$S_0 \rightarrow S_1$	
$[Nd(HL)_2(NO_3)_2]NO_3$			483(broad)	20,703	12.587	${}^{4}I_{9/2} \rightarrow {}^{2}G_{5/2}$	
			658(sharp)	15,197	101.938	${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$	
			361(broad)	27,700	38.831	$S_0 \rightarrow S_1$	
$[Sm(HL)_2(NO_3)_2]NO_3 \\$	330	30,303	549(sharp)	16,025	15.587	$^{4}G_{5/2} \rightarrow ^{6}H_{7/2}$	
			658(sharp)	18,214	89.856	$^{4}G_{5/2} \rightarrow ^{6}H_{9/2}$	
			367(broad)	27,247	197.639	$S_0 \rightarrow S_1$	
$[Eu(HL)_2(NO_3)_2]NO_3 \\$	330	30,303	475(broad)	21,052	26.669	$^{5}D_{0} \rightarrow ^{7}F_{1}$	
			669(sharp)	14,947	196.572	$^{5}D_{0}\rightarrow^{7}F_{2}$	

Table 5: Antibacterial activity for the Ln complexes.

Gram(-)	bacteria	Gram(+)bacteria		
Ec	Pa	Sa	Bs	
+	+	+	+	
++	++	++	+++	
++	+++	++	++	
+++	++	+++	+++	
+++	+	++	+++	
++	+	++	+++	
-	-	-	-	
	Ec + ++++++++++++++++++++++++++++++++++	+ + + + + + + + + + + + + + + + + + +	Ec Pa Sa + + + + + + + + + + + + + + + + + +	

Key: (-) = no inhibition zone = inactive; 9-10 mm(+) = less active; 10-11 mm(++) = moderately active; 11-13 mm(+++) = highly active.

Therefore, the efficiency of the intermolecular energy transfer between the triplet level of the ligand and emitting level of the lanthanide ions.

Antimicrobial activity

The antimicrobial activity results expressed as the diameter of the growth inhibition area are data given in Table 5. The results show that the three complexes exhibited highly good activities when compared with standard antibiotics, evaluated against gram-nagative (Eschereshia coli, Pseudomonas aeruginosa), grampositive(Staphylococcus aureus, Bacillus subtilis) using an agar disc diffusion method[25] Fig.7. While the DMF and the free ligand exhibit low anti-bacterial activities. Beside, the metal complexes of neodymium complex highly active against (Eschereshia coli, Staphylococcus aureus, Bacillus subtilis), moderately active Pr(III), La(III), less active Sm(III) and Eu(III) complexes are aginst (Pseudomonas aeruginosa) activity indicated that the free ligand have less activity than the complexes.

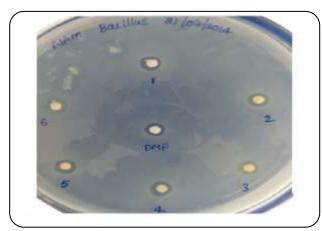


Fig.7: Antibacterial activity for the Ln complexes (+) bacteria (Bacillus subtilis).

Such increased activity of the metal chelate can penetrate the bacterial cell membrane by coordinate of Schiff base metal ion through oxygen or nitrogen donor atom to lipopolysaccharide(LPS), which leads to the damage of outer cell membrane and consequently inhibits growth of the bacteria.

CONCLUSIONS

In this work, Schiff base ligand and its lanthanide [Ln(HL)₂(NO₃)₂]NO₃ complexes were synthesized and characterized on the basis of physico-chemical and spectral (UV-visible,IR, Mass) studies. The HL ligand is good organic neutral tridentate coordinating lanthanide complexes with (Ln:L=1:2). Central Ln(III) complexes, spectral, molar conductance and thermal data showed that the two coordinate nitrate group sphere acts as inner bidentate manner. In addition, the participation of molecules in coordination number of 10. Thus, the present Schiff base lanthanide nitrate complexes as a good luminescent and laser materials. The PXRD patterns of the neodymium (III) nitrate complex were recorded and the particle size of the metal complex was calculated. Antibacterial activity indicated that the free ligand have less activity than the complexes, especially neodymium (III) complex possessed effective and selective antibacterial activity.

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REFERENCES

- [1] Frias J.C., Bobba G., Cann M.J., Hutchinson C.J., Parker D., Luminescent Nonacoordinate Cationic Lanthanide Complexes as Potential Cellular Imaging and Reactive Probes, *Org. Biomol. Chem.*, 21: 905-907 (2003).
- [2] Diaz-Garcia M.A., De Avila S.F., Kuzyk M.G., Energy Transfer From Organics to Rare-Earth Complexes, *Appl.Phys.Lett.*, **81**: 3924-3926 (2002).
- [3] Duan J.-P., Sun P.-P., Cheng C.-H., New Iridium Complexes as Highly Efficient Organic-Red Emitters in Organic Light Emitting Diodes, *Adv.Mater.*, **15**: 224-228 (2003).
- [4] Mathis G., Rare Earth Cryptates and Homogeneous Fluoroimmuno Assays with Human Sera, *Clini. Chem.*, **39**: 953-959 (1993).
- [5] DeNardo G.L., Mirick G.R., Kroger L.A., O Donnel R.T., Meares C.F., DeNadro S.J., Antibody Responses to Macrocycles in Lymphoma, J. Nucl. Med., 37: 451-456 (1996).
- [6] Richardson D.R., Ponka P., Development of Iron Chelators to Treat Iron Overload Disease and Their Use as Experimental Tools to Probe Interacellular Iron Metabolism, Am. J. Hematol., 58: 299-305 (1998).
- [7] Kalinowski D.S., Sharpe P.C., Bernhardt P.V., Richardson D.R., Structure-Activity Relationships of Novel Iron Chelators for the Treatment of Iron Overload Disease the Methyl Pyrazinylketone Isonicotinoyl Hydrazone Series, J. Med. Chem., 51: 331-344 (2008).
- [8] Bernhardt P.V., Chin P., Sharpe P.C., Wang J.-Y.C., Richardson R.D., Novel Diaroylhydrazine Ligands as Iron Chelators: Coordination Chemistry and Biological Activity, J. Biol. Inorg. Chem., 10: 761-777 (2005).
- [9] Adrian-Mihail Stadler., Jack Harrowfield., Bis-Acyl-/aroyl-hydrazones as Multidentate Lgands, *Inorg. Chimi. Acta.*, **362**: 4298-4314 (2009).

- [10] Xishi Tai., Huigin Wang., Xiaozheng Sun., Minyu Tan., Synthesis and Spectral Characterization of Methyl-2- Pyridyl Ketone Benzoyl Hydrazone and Its Complexes with Rare Earth Nitrates, Spectroscopy Letters., 38: 497-504 (2005).
- [11] Raja K., Suseelamma A., Hussain Reddy K., Synthesis, Spectral Properties, DNA Binding Interactions and DNA Cleavage Studies of Lanthanide(III) Complexes of 2- Acetylpyridine Acetylhydrazone: The X-Ray Crystal Structure of 10-Coordinate Ce(III) and Sm(III) Complexes, *J. Iran. Chem. Soc.*, 12: 1473-1486 (2015).
- [12] Vidyasagar Babu.S., Hussain Reddy K., Spectral and DNA Binding Properties of Lanthanide Complexes with Tetradentate Ligand, *Inorganic and Nano-Metal Chemistry.*, **47**: 456-461(2017).
- [13] Perez C., Pauli M., Bazerque P., An Antibiotic Assay by Agar-Well Diffusion Method, *Acta .Biol. Med. Exp.*, **15**: 113-115 (1990).
- [14] Ter Laak E.A., Noordergraaf J.H., Verschure M.H., Susceptibilities of Mycoplasma Bovis, Mycoplasma Dispar, and Ureaplasma Diversum Strains to Antimicrobial Agents in Vitro, Antimicrob. Agents. Chemotherapy., 37: 317-321 (1993).
- [15] Geary W.J., The Use of Conductivity Measurements in Organic Solvents for the Characterisation of Coordination Compounds, Coord. Chem. Rev., 7: 81-122(1971).
- [16] Guo L., Wu S., Zeng F., Zhao J., Synthesis and Fluorescence Property of Terbium Complex with Noval Schiff-Base Macromolecular Ligand, *Eur. Polym. J.* **42**: 1670-1675(2006).
- [17] Felicio R.C., Cavalheiro E.T.G., Dockal E.R., Preparation, Characterization and Thermo Gravimetric Studies of [N,N-cis1,2-Cyclohexylenebis (Salicylideneaminato) Cobalt(III) and [N,N-(±)Trans-1,2-Cyclo-Hexylenebis (Salicylideneaminato) Cobalt(III), Polyhedron., 20: 261-268 (2001).
- [18] Ajlouni A.M., Taha Z.A., AI.Momani W., Hijazi M., Ebqa A.K., Synthesis, Characterization, Biological Activities and Luminescent Properties of Lanthanide Complexes with N,N-bis-(2-hydroxy-1-napthylidene)- 1,6- Hexadiimine, *Inorg. Chimi. Acta.*, **388**:120-126 (2012).

- [19] Ajlouni A.M., Taha Z.A., A1-Hassan K.A., Abu-Anzeh A.M., Synthesis, Characterization, Luminescence Properties and Antioxidant Activity of Ln(III) Complexes with A New Arylamide Bridge Ligand, *J. Lumin.*, **132**:1357-1363 (2012).
- [20] Kaczmarek S.M., Leniec G., EPR and IR Investigations of Some Chromium(III) Phosphate(V) Compounds, J. Non-Cryst. Solids., 355: 1289-1438 (2009).
- [21] Yan P., Sun W., Li G., Nie C., Gao T., Yue Z., Synthesis, Characterization and Fluorescence of Lanthanide Schiff-Base Complexes, *J. Coord. Chem.*, **60**:1973-1982 (2007).
- [22] Sun W.B., Yan P.F., Li G.M., Xu Hui., Zhang J.W., N,N-bis(salicylidene)propane-1,2diamine Lanthanide(III) Coordination Polymers: Synthesis, Crystal Structure and Luminescence Properties, J. Solid. State. Chemistry., 182: 381-388 (2009).
- [23] Li Y., Yang Z., Rare Earth Complexes with 3-Carbaldehyde Chromone(benzoyl) Hydrazone: Synthesis, Characterization, DNA Binding Studies and Antioxidant Activities, *J. Fluoresc.*, **20**: 329-342 (2010).
- [24] Regulaco M.D., Pablico M.H., Vasquez J.A., Myers P.N., Gentry S., Prushan M., Tam-Chang, Sun-Wah., Stoll S.L., Luminescence of Ln(III) Dithiocarbamate Complexes(Ln) La, Pr, Sm, Eu, Gd, Tb, Dy, Inorg. Chem., 47: 1512-1523 (2008).
- [25] Osowole A.A., Kolawole G.A. ,Fagade O.J., Synthesis, Characterization and Biological Studies on Unsymmetrical Schiff-Base Complexes of Nickel(II), Copper(II) and Zinc(II) and Adducts with 2,2'-Dipyridine and 1,10-Phenanthroline, Coord. Chem., 61:1046-1055 (2008).