

Spectroscopic and Fluorescence Studies on the Trivalent Ce, Eu, Nd and La Metal Ions Rhodamine C Fluorescent Dye Complexes

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Abstract The four isolates solid complexes: $[\text{La}(\text{RHC})(\text{NO}_3)_2] \cdot 3\text{H}_2\text{O}$, $[\text{Nd}(\text{RHC})(\text{NO}_3)_2] \cdot 4\text{H}_2\text{O}$, $[\text{Eu}(\text{RHC})(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$, and $[\text{Ce}(\text{RHC})(\text{NO}_3)_2] \cdot 5\text{H}_2\text{O}$ that obtained by the reaction of the nitrate salts of the Ce(III), Eu(III), Nd(III) and La(III) ions and rhodamine C (RHC) ligand were interpretative using elemental analysis (C, H and N), molar conductivity, infrared, electronic, fluorescence and ¹H-NMR spectra to achieve the speculated suitable formula. The low molar conductance values of the synthesized RHC complexes concluded the non-electrolytic behavior. The infrared spectra recorded the absence of stretching vibration $\nu(\text{OH})$ of the $-\text{COOH}$ and presence of two new vibration bands at $1597\sim 1601$ and $1383\sim 1399$ cm^{-1} which were assigned to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$. The difference between them revealed that the carboxylate group acts as a bidentate ligand. ¹H-NMR spectra of Europium and lanthanum(III) complexes were supported the FTIR results based on the absent of proton of the carboxylic group. Therefore, the microanalytical and spectroscopic results deduced that RHC acts as a monobasic bidentate ligand, and coordinated to the central metal(III) ions via the two oxygen atoms of deprotonated carboxylic group. Fluorescence studies were performed on the metal complexes of Ce^{3+} , Tb^{3+} , Th^{4+} , Gd^{3+} and La^{3+} , that referred a quenching in the fluorescence intensity of rhodamine C in the aqueous state after complexation. The antimicrobial assessment against some kind of bacteria and fungi were also checked and recorded enhancement in case of their complexes.

Keywords Rhodamine C; Chelation; Spectroscopic; Thermogravimetric; Lanthanides

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Introduction

Laser dyes are very versatile^[1]. Owing to the high fluorescence quantum yield, broad fluorescence in the visible region, and high absorption coefficient of rhodamine dyes, they are widely used as fluorescent probes^[2]. Fluorescents are basic for researches in the clinical diagnosis of diseases,

the assurance of food safety, environmental quality, the development of new drugs, and in the biological science^[3-4].

Many researchers have prepared and designed several derivatives used as rhodamine-labeled oligonucleotides^[5], probe in a biological environment^[6], fluorescent peptides^[7], induces, inhibitors^[8] and protease substrates^[9]. Rhodamine dyes are used in many applications including spectroscopy, medicine, analysis, biophysical probes, and chemical

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sensors^[10-14]. Refat et al.,^[15] had designed and synthesized complexes of rhodamine 640 perchlorate and rhodamine C with Cu(II), Co(II) and Mn(II) ions to learn more about the thermal stability of these dyes compared with their metal complexes. The present work aimed to learn more about the structural, spectral and antimicrobial properties of rhodamine C and its Ce(III), Eu(III), Nd(III) and La(III) metal chelates.

1 Experimental

1.1 Instrumental analyses

Rhodamine C (Fig. 1) was purchased from Aldrich Company. Melting points were determined on a digital apparatus. The elemental analysis of C, N, and H were carried out with a Perkin-Elmer CHN 2400. Molar conductivities of solutions in SMSO solvent ($10^{-3} \text{ mol} \cdot \text{L}^{-1}$) were determined with a Jenway 4010 conductivity meter. The electronic absorption spectra of solutions in DMSO solvent ($10^{-3} \text{ mol} \cdot \text{L}^{-1}$) were measured with a Jenway 6405 spectrophotometer in the range 200 ~ 800 nm using 1 cm quartz cell. The infrared spectra of the products were collected on a Brüker FT-IR spectrophotometer within the range of 4 000 ~ 400 cm^{-1} using KBr discs. ^1H NMR spectra were obtained using a Varian Gemini 200 MHz spectrometer at room temperature using tetramethylsilane (TMS) as the internal reference and dimethylsulfoxide, d_6 (DMSO- d_6) as the solvent. The metal content was obtained gravimetrically by converting the metal complexes to their corresponding metal oxides.

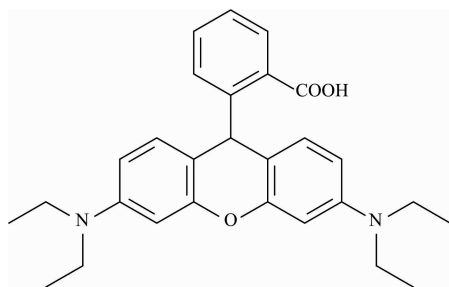


Fig. 1 Structure of Rhodamine C (RHC)

1.2 Microbiological investigation

The isolates of fungi and bacteria were seeded in tubes containing nutrient Dox's broth (DB) and broth (NB), respectively. One ml of the seeded (DB) for fungi was homogenized in a tube containing 9 mL of melted nutrient agar (DA) at 45 °C, while 1 mL of the seeded (NB) for bacteria was homogenized in a tube containing 9 mL of melted nutrient agar (NA) at 45 °C. The resultant suspensions were poured into Petri dishes, and the dishes were left to cool. After cooling, holes with a diameter of 0.5 cm were done, then 100

μL of the investigated complexes were added to these holes using a micropipette. The dishes were incubated in an incubator at 28 °C for fungi and 37 °C for bacteria for 24 hours. Diameters of the inhibition zone were obtained and expressed in cm. The antimicrobial activities of the investigated metal complexes as well as the pure solvent as a blank test were tested against two kinds of fungi; *Aspergillus niger* and *Penicillium rotatum*, and two kinds of bacteria; *Escherichia Coli* as (Gram - ve) and *Bacillus subtilis* as (Gram +ve).

1.3 Syntheses

The Ce(III), Eu(III), Nd(III) and La(III) nitrates (1 mmol) were dissolved in 10 mL 99% methyl alcohol A. R. The nitrate solutions were added slowly to a solution containing 1 mmol of RHC in 20 ml methyl alcohol. The pH was adjusted at pH 7 ~ 9 using 0.1 $\text{mol} \cdot \text{L}^{-1}$ NH_4OH solution. The mixtures were stirred on a magnetic stirrer with refluxing at 60 ~ 70 °C for one 60 minutes. Then, the mixtures were left to evaporate slowly at room temperature to produce the products. The formed products were filtered off, washed with hot solvent several times to obtain pure products, and dried under vacuum over anhydrous CaCl_2 .

2 Results and discussion

2.1 Molar conductivity

The formation mechanism of RHC complexes can be summarized as following: $\text{M}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O} + \text{RHC}(\text{HL}) + \text{NH}_4\text{OH} \rightarrow [\text{M}(\text{L})(\text{NO}_3)_2] \cdot n\text{H}_2\text{O} + \text{NH}_4\text{NO}_3 + n\text{H}_2\text{O}$ (where, $\text{M} = \text{Eu}(\text{III}), \text{La}(\text{III}), \text{Nd}(\text{III})$ and $\text{Ce}(\text{III})$; $n = 2, 3, 4$ and 5 , respectively).

Values of the molar conductivity for the Ce(III), Eu(III), Nd(III) and La(III) complexes of rhodamine C in DMSO solvent ($10^{-3} \text{ mol} \cdot \text{L}^{-1}$) are listed in Table 1. The values are in the range from 9 to 19 $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, which indicate the synthesized complexes are non-electrolytes^[16-17].

2.2 IR spectral studies

The main infrared bands are summarized in Table 2. The very strong absorption band located at 1 704 cm^{-1} in the IR spectrum of free Rhodamine C, is assigned to the $\nu(\text{C}=\text{O})$ for the free ketone of the carboxylic group. This band was no longer observed in the spectra of the Ce(III), Eu(III), Nd(III) and La(III) complexes. In the IR spectra of the complexes, the bands observed at the range of 1 597 ~ 1 601 and 1 383 ~ 1 399 cm^{-1} are assigned to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, respectively. The shift in the frequency values of $\nu_{\text{s}}(\text{COO}^-)$ and $\nu_{\text{as}}(\text{COO}^-)$ concerning the free carboxylate ion depends on the coordination mode of the (COO^-) group with the metal ion^[18] has assured that if coordination is

monodentate, the $\nu_s(\text{COO}^-)$ and $\nu_{\text{as}}(\text{COO}^-)$ will be moved to lower and higher frequencies, respectively. But, if the coordination is bridging bidentate or chelating bidentate, the frequencies of $\nu_s(\text{COO}^-)$ and $\nu_{\text{as}}(\text{COO}^-)$ will move in the same direction. Therefore, the obtained metal complexes have chelating bidentate structure. Also, the complexes show new bands at $1\,312\sim 1\,344\text{ cm}^{-1}$ due to NO_3^- ion which support

the bidentate coordinated nature of the NO_3^- ion^[18]. The new bands located in the range of $532\sim 568$ and $496\sim 476\text{ cm}^{-1}$ are attributed to $\nu(\text{M}-\text{O})$ of carboxylate-O and coordinated nitrate groups, respectively. These data indicate that RHC behaves as monobasic bidentate ligand, and complexed to the metal (III) ions through the deprotonated carboxylate-O atoms.

Table 1 Elemental and physical data of Rhodamine C metal complexes

Complexes	Color	Content ((calculated) found)				$\Delta_M/(\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1})$
		%C	%H	%N	%M	
[Ce(RHC)(NO ₃) ₂] · 5H ₂ O	Bright yellow	(41.94) 41.36	(4.36) 4.41	(6.99) 6.36	(17.47) 17.90	19
[Eu(RHC)(NO ₃) ₂] · 2H ₂ O	Dark yellow	(44.26) 44.50	(4.61) 4.49	(7.37) 7.23	(20.02) 20.42	15
[Nd(RHC)(NO ₃) ₂] · 4H ₂ O	Orange	(42.69) 42.88	(4.44) 4.23	(7.11) 7.21	(18.55) 18.41	9
[La(RHC)(NO ₃) ₂] · 3H ₂ O	Reddish brown	(43.97) 43.33	(4.58) 4.28	(7.32) 7.69	(18.19) 18.57	14

Table 2 IR Frequencies of RHC and the Ce(III), Eu(III), Nd(III), and La(III) complexes

Complexes	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_s(\text{COO}^-)$	Δ	$\nu(\text{C}=\text{O}), \text{COOH}$	$\nu(\text{M}-\text{O})$
RHC	1 588	1 338	250	1 704	—
Ce(III) complex	1 601	1 399	202	—	476, 550
Eu(III) complex	1 597	1 385	212	—	568, 496
Nd(III) complex	1 599	1 383	216	—	532, 474
La(III) complex	1 598	1 383	215	—	564, 480

2.3 Electronic absorption spectra

The complexes exhibit two characteristics absorption peaks at the ranges $350\sim 500$ and $215\sim 340\text{ nm}$, which are attributed to $n-\pi^*$ and $\pi-\pi^*$ transitions of the organic rhodamine C moiety, respectively. The synthesized complexes exhibit a bathochromic shift in their spectra compared with the free ligand within $n-\pi^*$ transition region. This shift is due to the change in the electronic configuration and the place of complexation for the obtained complexes.

2.4 ¹H-NMR spectra

The ¹H-NMR spectra of the Eu(III) and Nd(III) complexes, respectively. The signal of the carboxylate OH which observed at $\delta = 11\text{ ppm}$ in the spectrum of the free ligand, was disappeared in the spectra of the [Eu(RHC)

(NO₃)₂] · 2H₂O and [La(RHC)(NO₃)₂] · 3H₂O complexes, indicating that the coordination between the RHC ligand and the M(III) ions taking place via the deprotonated carboxylic O group. The aromatic protons signals located at $\delta = 6.00\sim 8.00\text{ ppm}$ are present with decreasing intensities, due to different chemical environments. The signals at $\delta = 3.58, 3.46\text{ ppm}$ [H, H₂O] can be assigned for the water molecules of hydration.

2.5 Biology

The results of the antibacterial and the antifungal activities of the synthesized complexes are presented in Table 3, and Fig. 2. All the complexes have no biological activity against *E. coli*, but in case of *Aspergillus niger*, La(III) complex is more active than Nd(III) complex. On the other

Table 3 Antimicrobial activity of the synthesized complexes

Tested compounds	Diameter of inhibition zone/cm			
	<i>B. subtilis</i>	<i>E. coli</i>	<i>P. rotatum</i>	<i>A. niger</i>
Control (DMSO)	0	0	0	0
Ce(III) complex	1.5	0	0.7	0
Eu(III) complex	0.5	0	0.3	0
Nd(III) complex	0.7	0	0.5	0.6
La(III) complex	0.6	0	0.4	1.2

hand, Ce(III) and Eu(III) complexes have no effect against *Aspergillus niger*. Generally, the orders of antimicrobial activity against *B. subtilis* and *Penicillium rotatum* for the different complexes are: Eu(III) < La(III) < Nd(III) < Ce(III).

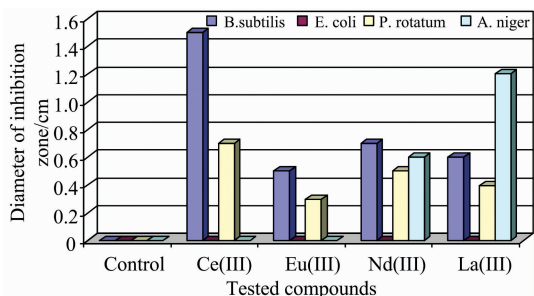


Fig. 2 Statistical representation for antibacterial and antifungal activities of the synthesized complexes

2.6 Proposed structure of the synthesized complexes

The structures of the synthesized complexes of RHC ligand with Ce(III), Eu(III), Nd(III) and La(III) ions have been established from the molar conductance, elemental analyses, UV-Vis, IR, and $^1\text{H-NMR}$ spectra. Based on these techniques, octahedral geometries are proposed for the synthesized complexes as represented in Fig. 3.

2.7 Fluorescence studies

Excitation and emission spectra of rhodamine C were recorded (Fig. 4).

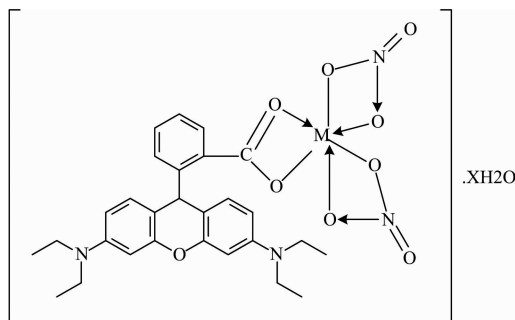


Fig. 3 Modes of the chelation of RHC complexes (where M = Eu(III), La(III), Nd(III) and Ce(III), and X = 2, 3, 4 and 5, respectively)

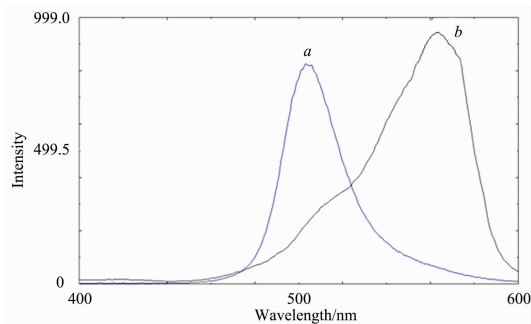


Fig. 4 Excitation and emission spectra of rhodamine C

a: Excitation spectrum ($\lambda_{em} = 508 \text{ nm}$);
b: Emission spectrum ($\lambda_{ex} = 550 \text{ nm}$)

Metal ions of Ce^{3+} , Tb^{3+} , Th^{4+} , Gd^{3+} and La^{3+} were found to quench the fluorescence intensity of rhodamine C in the aqueous state. The experimental results showed that the metal ions quench the fluorescence intensity of rhodamine C by forming dye-metal complexes (Figs. 5–9). It was found that static quenching was the main reason of fluorescence quenching. Quenching can occur by a variety of molecular interactions, viz. excited-state reactions, molecular rearrangement, energy transfer and ground state complex formation (static quenching).

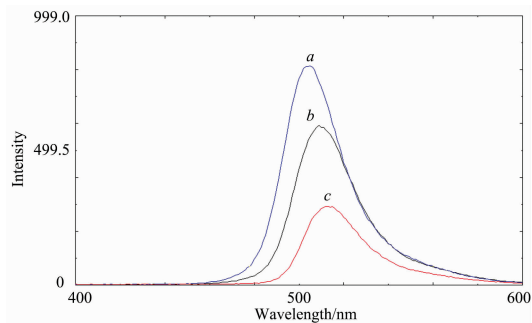


Fig. 5 Fluorescence spectra of rhodamine C in absence and presence of varying concentration of Gd^{3+} ($\lambda_{ex} = 550 \text{ nm}$)
a: Without Gd^{3+} ; b: $2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-2}$; c: $4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$

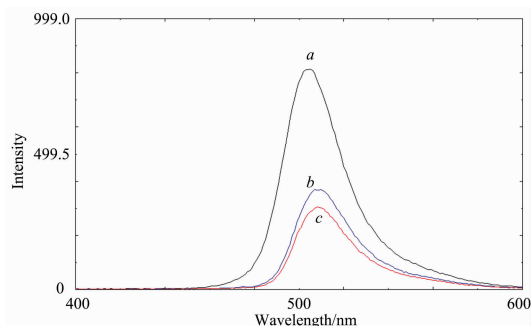


Fig. 6 Fluorescence spectra of rhodamine C in absence and presence of varying concentration of La^{3+} ($\lambda_{ex} = 550 \text{ nm}$)
a: Without La^{3+} ; b: $2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-2}$; c: $4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$

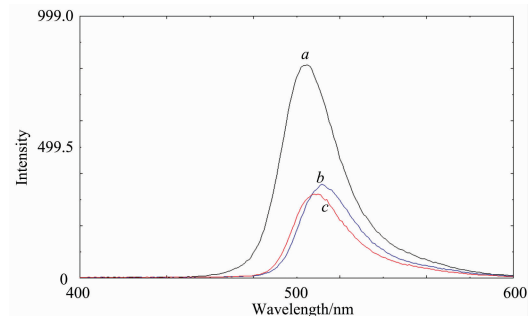


Fig. 7 Fluorescence spectra of rhodamine C in absence and presence of varying concentration of Ce^{3+} ($\lambda_{ex} = 550 \text{ nm}$)
a: Without Ce^{3+} ; b: $2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-2}$; c: $4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$

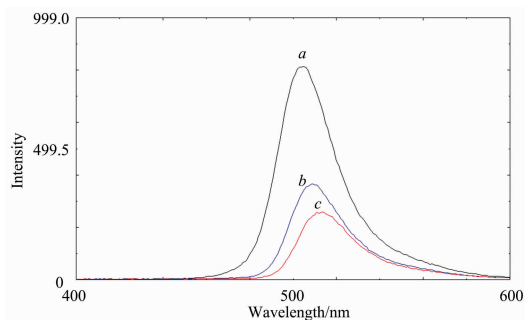


Fig. 8 Fluorescence spectra of rhodamine C in absence and presence of varying concentration of Tb^{3+} ($\lambda_{ex} = 550$ nm)

a: Without Tb^{3+} ; *b*: 2×10^{-5} mol \cdot L $^{-2}$; *c*: 4×10^{-5} mol \cdot L $^{-1}$

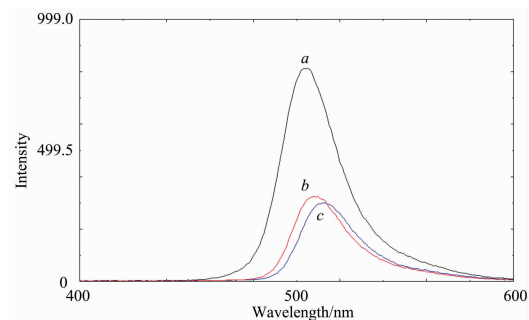


Fig. 9 Fluorescence spectra of rhodamine C in absence and presence of varying concentration of Th^{4+} ($\lambda_{ex} = 550$ nm)

a: Without Th^{3+} ; *b*: 2×10^{-5} mol \cdot L $^{-2}$; *c*: 4×10^{-5} mol \cdot L $^{-1}$

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