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Preparation, thermal, antimicrobial efficiency and spectroscopic characterizations of Ce(III), Gd(III), Nd(III), Tb(III) and Er(III) eosin yellow complexes.

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ABSTRACT

The $[\text{Ce}_2(\text{Cl})_4(\text{H}_2\text{O})_6(\text{L})]$, $[\text{Gd}_2(\text{Cl})_4(\text{H}_2\text{O})_6(\text{L})]$, $[\text{Nd}_2(\text{Cl})_4(\text{H}_2\text{O})_6(\text{L})]$, $[\text{Tb}_2(\text{Cl})_4(\text{H}_2\text{O})_6(\text{L})]$ and $[\text{Er}_2(\text{Cl})_4(\text{H}_2\text{O})_6(\text{L})]$ which resulted from the interaction between Ce(III), Gd(III), Nd(III), Tb(III) and Er(III) ions and sodium salt of eosin yellow ligand (Na_2L) were interpretative using elemental analysis (%C and %H), molar conductivity, (infrared, electronic and ¹H-NMR spectra) and thermogravimetric analysis to achieve the speculated suitable formula. The observed and calculated data of the percentage of the carbon, hydrogen and metal(III) ions content are in a good agreement with each other and with the predicted structures of Ce(III), Gd(III), Nd(III), Tb(III) and Er(III) complexes.

Keywords: eosin yellow; complexes; spectroscopic; thermogravimetric; lanthanides; biological.

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INTRODUCTION

Eosin Yellow Fig. 1 is a tetra bromo derivative of fluorescein and it has been used for the spectrophotometric determination of many pharmaceutical compounds either through the formation of binary complexes [1-6] or ternary complexes in the presence of a metal ion [7,8]. On the other hand, 2,4-dinitrofluorobenzene (FDNB) or Sanger's reagent, the active aryl halide, is known to react with thiol, phenolic and amino group bearing compounds giving yellow colored products thus allowing their spectrophotometric determination [9]. In fact, literature contains several methods utilizing FDNB for the determination of drugs bearing primary [10] or secondary amino groups [11,12].

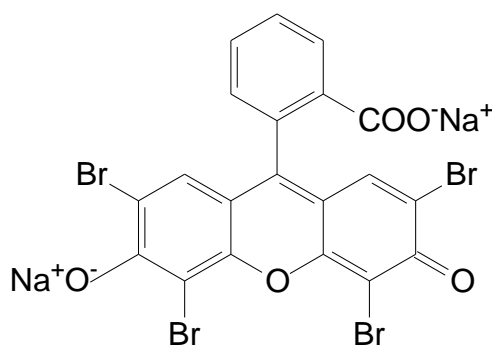


Fig 1: Structure of eosin yellow (ESY).

In this work, the coordination mode of sodium salt of eosin yellow (Na_2L) coordinated to Ce(III), Gd(III), Nd(III), Tb(III), and Er(III) metal ions have been investigated. The antibacterial and antifungal activities of the prepared complexes also were evaluated.

EXPERIMENTAL

Materials

All chemicals used in this investigation were of analytical grade and used without further purification (Merck). Sodium salt of eosin yellow dye, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ were used to prepare the corresponding target complexes. Melting points were determined on a digital apparatus. Carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer CHN 2400. The metal content was found gravimetrically by converting the compounds into their corresponding oxides.

Apparatus and experimental conditions

IR spectra were recorded on Brüker FT-IR spectrophotometer ($4000\text{-}400\text{ cm}^{-1}$) in KBr pellets. The UV-Vis spectra were studied in the DMSO solvent with concentration (10^{-3} M) for sodium salt of eosin yellow dye and its complexes by help of Jenway 6405 spectrophotometer with 1 cm quartz cell, in the range 200-800 nm. Molar conductivities of freshly prepared 10^{-3} mol/L DMSO solutions were measured using Jenway 4010 conductivity meter. ^1H NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer using DMSO-d_6 as solvent. Thermogravimetric analysis (TG and DTG) was carried out in dynamic nitrogen atmosphere (30 ml/min) with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ using a Schimadzu TG 50 H thermal analyzer.

Microbiological investigation

The investigated isolates of bacteria and fungi seeded in tubes with nutrient broth (NB) and Dox's broth (DB), respectively. The seeded (NB) for bacteria and (DB) for fungi (1 ml) were homogenized in the tubes with 9 ml of melted ($45\text{ }^\circ\text{C}$) nutrient agar (NA) for bacteria and (DA) for fungi. The homogeneous suspensions poured into Petri dishes. The holes (diameter 0.5 cm) done in the cool medium. After cooling in these holes, $100\text{ }\mu\text{l}$ of the investigated compounds applied using a micropipette. After incubation for 24 h in an incubator at $37\text{ }^\circ\text{C}$ and $28\text{ }^\circ\text{C}$ for bacteria and fungi, respectively, the inhibition zone diameters were measured and

expressed in cm. The antimicrobial activities of the investigated compounds were tested against Escherichia Coli as (Gram –ve) and Bacillus subtilis as (Gram +ve) as well as some kinds of fungi; Aspergillus niger and Penicillium rotatum activities. In the same time with the antimicrobial investigation of the complexes, the pure solvent also tested as a blank test. The concentration of each solution was 10^{-3} mol/L. Commercial DMSO was employed to dissolve the tested samples.

Preparation of eosin yellow dye solid complexes

For all preparations, doubly distilled water was employed as solvent. All used reagents were of analytical grade and employed without further purifications. Ce(III), Gd(III), Nd(III), Tb(III) and Er(III) chlorides (2 mmol) were dissolved in 10 ml 99% methyl alcohol A.R and then the prepared solutions were slowly added to a solution of eosin yellow (Na_2L) (1 mmol; in 20 ml methyl alcohol A.R), with molar ratios (2:1). The pH was adjusted at 8-9 using 0.1 M NaOH. The resulting solutions were stirred and refluxed on a hot plate at 60-70 °C for one hour and left to evaporate slowly at room temperature overnight. The obtained precipitates were filtered off, washed several times by minimum amounts of hot methanol and dried under vacuum over anhydrous CaCl_2 .

RESULTS AND DISCUSSION

Molar conductivities of metal chelates:

The low values of molar conductivity for the Ce(III), Gd(III), Nd(III), Tb(III) and Er(III) complexes of eosin yellow in DMSO solvent (10^{-3}M) were found to be in the range $50\text{-}68 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, indicating the complexes are non electrolytes Table 1. Conductivity measurements have frequently used in elucidation of structure of metal chelates (mode of coordination) within the limits of their solubility. They provide a method of testing the degree of ionization of the complexes, the molecular ions that a complex liberates in solution in case of presence of anions outside the coordination sphere, the higher will be its molar conductivity and vice versa [13,14]. Hence the molar conductance values indicate that no ions are present outside the coordination sphere, so Cl^- ions may exist inside the coordination sphere or absent. The obtained results were strongly matched with the elemental analysis data where Cl^- ions were existed inside the coordination sphere of Ce(III), Gd(III), Nd(III), Tb(III) and Er(III) complexes after decomposition of these complexes with nitric acid followed by addition of AgNO_3 solutions.

Table 1: Elemental analyses and physical data of eosin yellow and its complexes

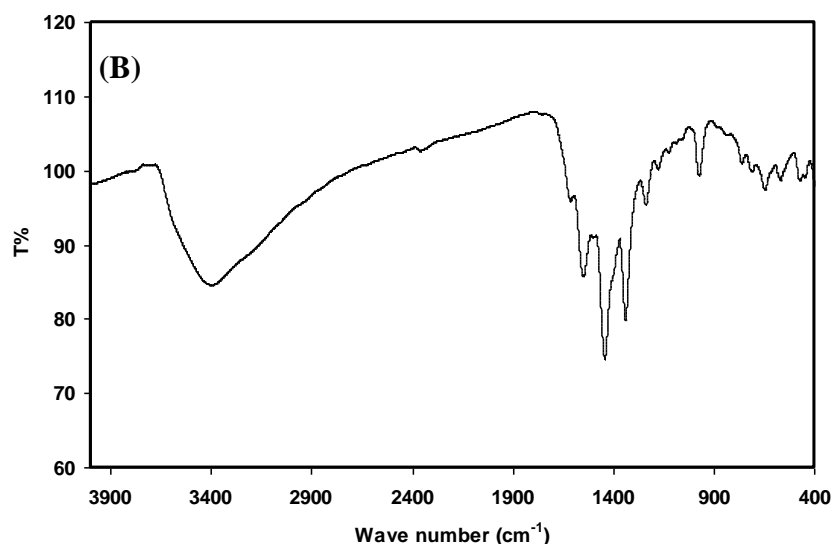
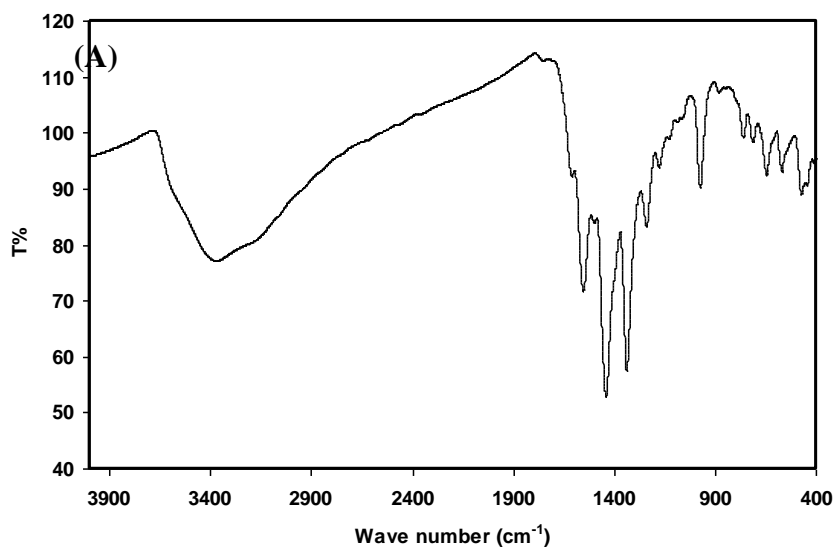
Complexes	Color	M.wt (g/mol)	Content ((calculated) found)			Λ_M $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	M.P. (°C)
			% C	% H	% M		
$[\text{Ce}_2(\text{Cl})_4(\text{H}_2\text{O})_6(\text{L})]$	Yellowish brown	1176	(20.07) 20.40	(1.19) 1.53	(24.02) 23.80	68	250
$[\text{Gd}_2(\text{Cl})_4(\text{H}_2\text{O})_6(\text{L})]$	Orange	1210	(19.67) 19.83	(1.66) 1.48	(26.52) 26.09	56	230
$[\text{Nd}_2(\text{Cl})_4(\text{H}_2\text{O})_6(\text{L})]$	Brown	1184	(19.85) 20.27	(1.31) 1.52	(24.09) 24.32	50	300
$[\text{Tb}_2(\text{Cl})_4(\text{H}_2\text{O})_6(\text{L})]$	Deep Yellow	1214	(19.81) 19.76	(1.26) 1.48	(26.82) 26.19	59	280
$[\text{Er}_2(\text{Cl})_4(\text{H}_2\text{O})_6(\text{L})]$	Reddish brown	1230	(18.85) 19.51	(1.34) 1.46	(27.44) 27.18	57	260

IR spectral studies

The infrared spectra of eosin yellow (Na_2L) and its binuclear complexes under investigation are shown in Fig. 2 and Table 2. The spectra are similar but there are some differences which could give indication on the type of coordination. The infrared spectra of eosin yellow complexes reveal a broad bands observed at $3380\text{-}3407 \text{cm}^{-1}$. These bands can be assigned to the $\nu(\text{OH})$ stretching vibration of the coordinated H_2O molecules. The spectra of the complexes show two characteristic bands at 1339-1554, 1341-1550, 1342-1555, 1343-1545,

and 1344-1556 cm^{-1} for Ce(III), Gd(III), Nd(III), Tb(III) and Er(III) complexes, respectively, assigned to symmetric and asymmetric stretching vibrations of $\nu(\text{COO}^-)$ carboxylate group, respectively.

Deacon and Phillips [15] have studied the criteria that can be used to distinguish between the three binding states of the carboxylate complexes. These criteria are: (a) $\Delta\nu > 200 \text{ cm}^{-1}$ (where $\Delta\nu = [\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)]$), this relation was found in case of monodentate carboxylate complexes, (b) bidentate or chelating carboxylate complexes exhibit $\Delta\nu$ significantly smaller than ionic values ($\Delta\nu < 100 \text{ cm}^{-1}$), and finally, (c) bridging complexes show $\Delta\nu$ comparable to ionic values ($\Delta\nu \sim 150 \text{ cm}^{-1}$). Therefore, the difference value $\Delta\nu$ is a useful character for determining the coordination mode of the carboxylate group of the ligands. The observed $\Delta\nu$ for Ce(III), Gd(III), Nd(III), Tb(III), and Er(III) complexes (Table 2) fall in the range 202-215 cm^{-1} , indicating a monodentate coordination mode of the carboxylate group [16,17]. According to the IR data, the eosin yellow (Na_2L) is coordinated to the metal ions through two centers of donation via the monodentate carboxylate and phenolic-oxygen atoms, these facts are clearly supported by the formation of MO-bonds as shown in Table 2.



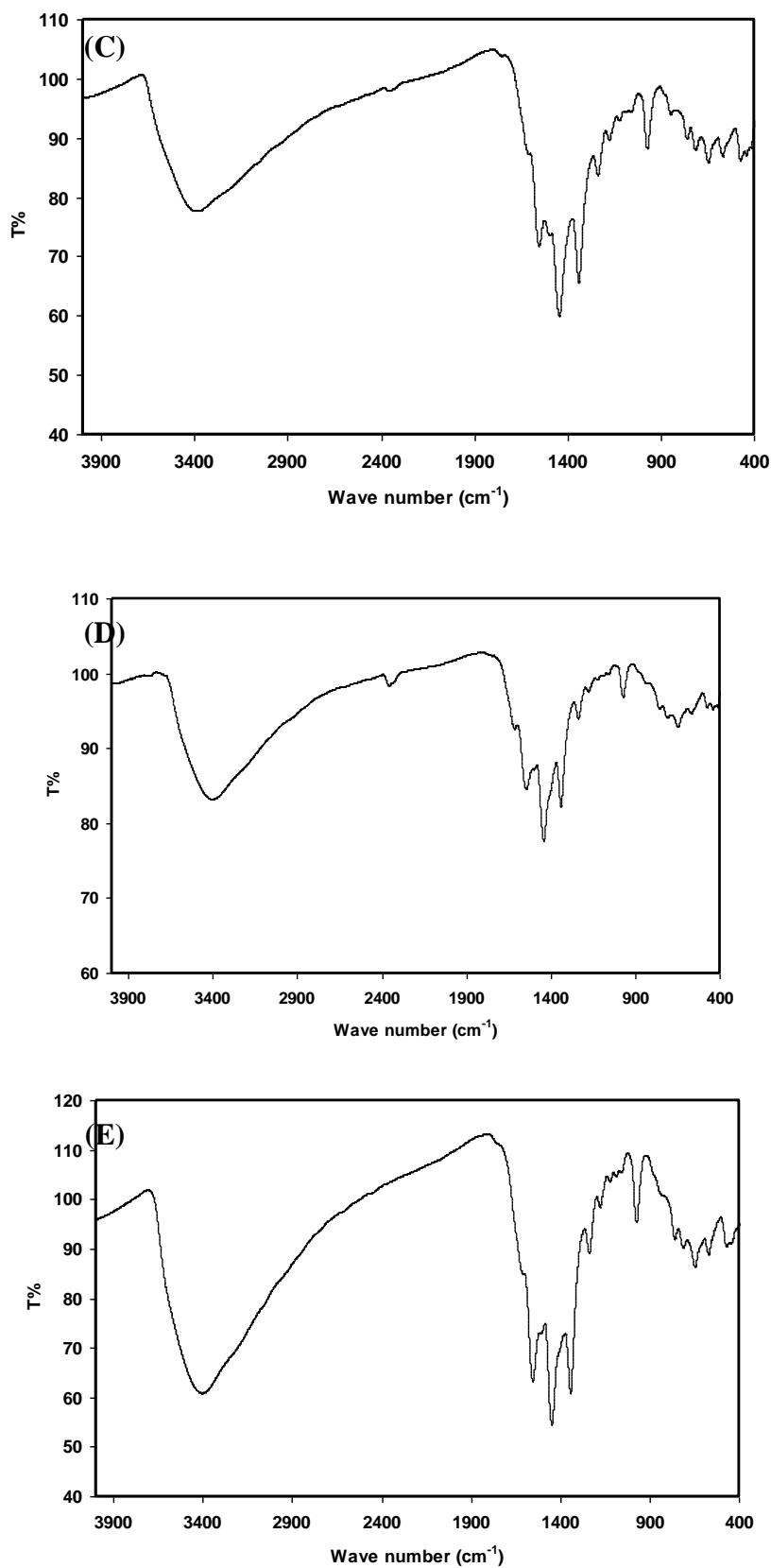


Fig 2: IR spectra of: (A) Ce(III) complex of eosin yellow (B) Gd(III) complex of eosin yellow (C) Nd(III) complex of eosin yellow (D) Tb(III) complex of eosin yellow (E) Er(III) complex of eosin yellow

Table 2: IR frequencies (4000-400 cm⁻¹) of eosin yellow (Na₂L) and its binuclear Ce(III), Gd(III), Nd(III), Tb(III) and Er(III) complexes.

Complexes	$\nu(\text{O-H})$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\Delta\nu$	$\nu(\text{C-O});$	$\nu(\text{M-O})$
Eosin yellow	---	1558	1345	213	1231	---
Ce(III) complex	3380	1554	1339	215	1241	569, 474, 411
Gd(III) complex	3400	1550	1341	209	1240	569, 471, 410
Nd(III) complex	3388	1555	1342	213	1239	570, 474, 444
Tb(III) complex	3406	1545	1343	202	1239	569, 478, 443
Er(III) complex	3407	1556	1344	212	1239	571, 472, 415

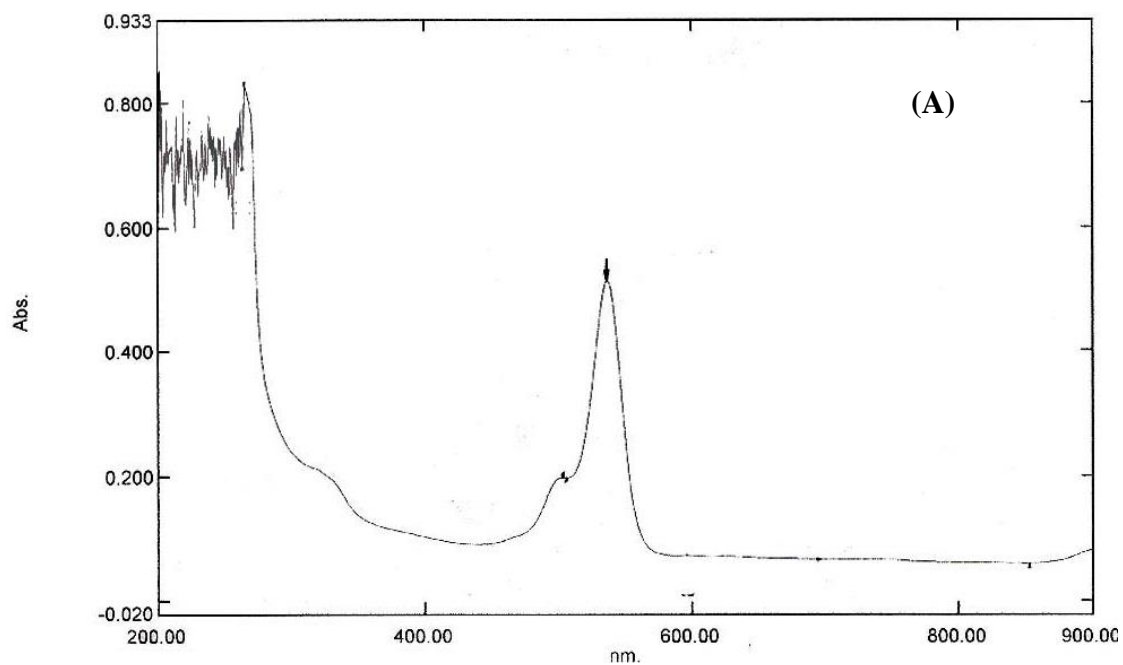
Electronic absorption spectra of eosin yellow complexes

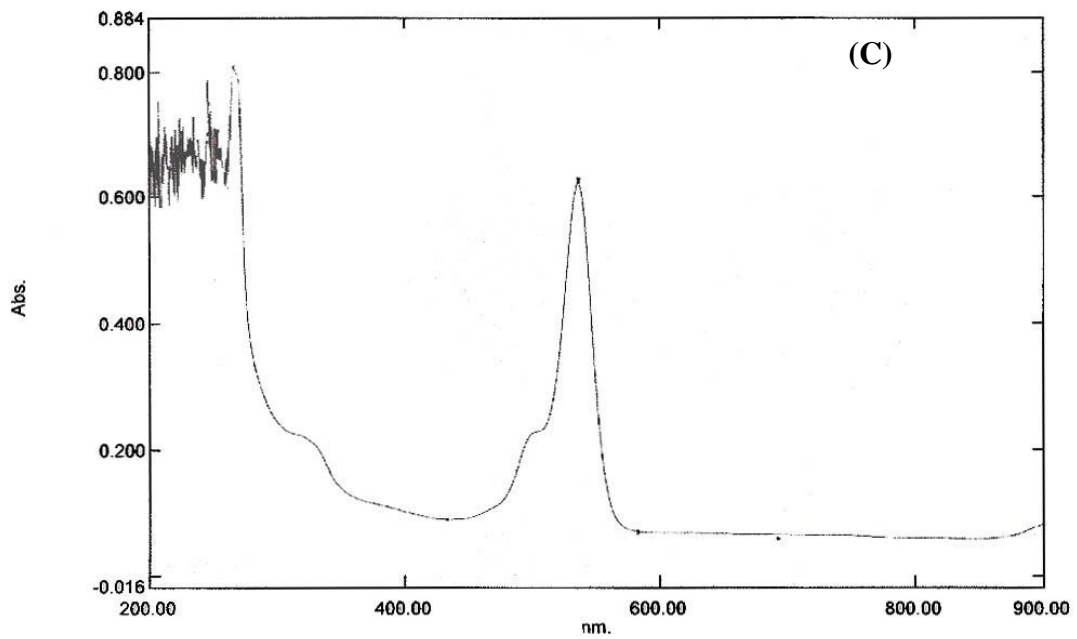
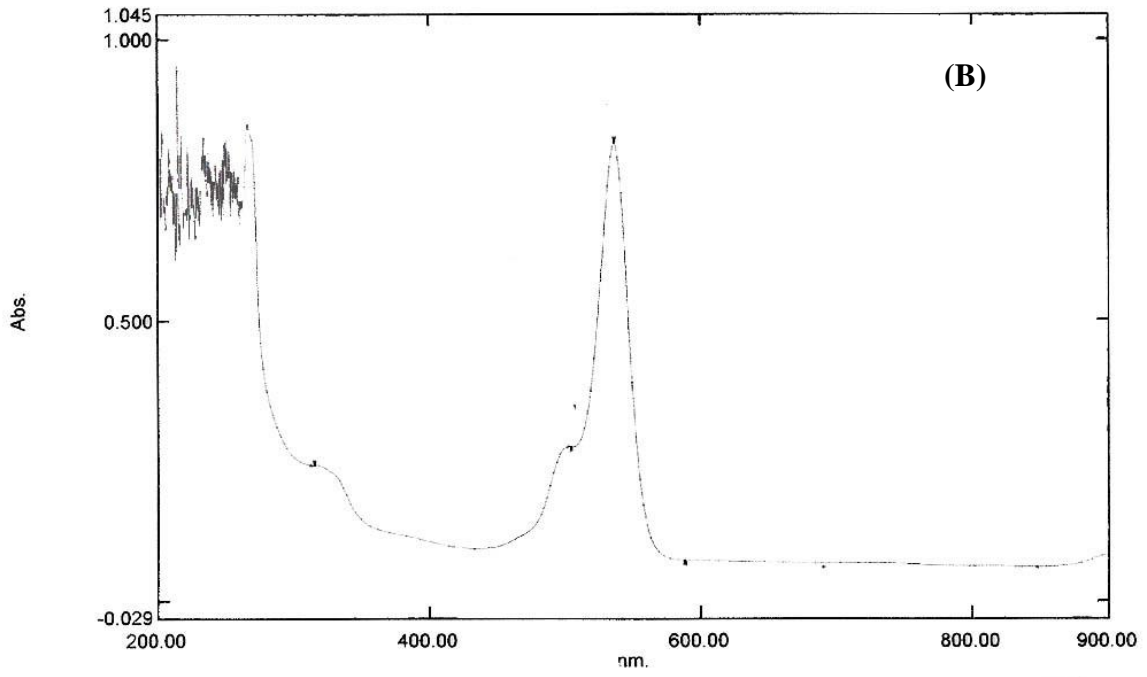
The formation of the binuclear Ce(III), Gd(III), Nd(III), Tb(III), and Er(III) complexes with eosin yellow (Na₂L) was also confirmed by UV-Vis spectra. The UV-Vis spectra of eosin yellow (Na₂L) and its binuclear complexes in DMSO exhibit and detect peaks which are tabulated in Table 3 and shown in Fig. 3. There are two absorption maxima peaks at 280 nm and 330 nm, which are assigned to π - π^* and n - π^* transitions within the organic moiety of eosin yellow (Na₂L) ligand, respectively. These transitions occur in case of unsaturated hydrocarbons, which contain carbon atom connected with oxygen atoms as in carboxylic and phenolic groups. These two bands of free eosin yellow are clearly hypsochromically affected (blue shifted). This hypsochromic change in the spectra of eosin yellow binuclear complexes indicates that the carboxylic and phenolic groups are involved in the complexation. These results are clearly in accordance with the results of FT-IR and ¹H-NMR spectra.

Table 3: Electronic spectral data of eosin yellow and its metal complexes

Compound	λ_{max} (nm)	ϵ (M ⁻¹ cm ⁻¹)	Assignment
Ce(III) complex	611	73	π - π^* trans.
	536	515	n - π^* trans.
	503	199	n - π^* trans.
	265	829	n - π^* trans.
	238	791	n - π^* trans.
	223	768	n - π^* trans.
	852	59	π - π^* trans.
	595	72	π - π^* trans.
	506	198	n - π^* trans.
	435	91	π - π^* trans.
	263	698	n - π^* trans.
	228	602	n - π^* trans.
	Gd(III) complex	536	815
502		275	n - π^* trans.
315		243	n - π^* trans.
266		845	n - π^* trans.
847		60	π - π^* trans.
588		72	π - π^* trans.
502		274	n - π^* trans.
432		93	π - π^* trans.
313		243	n - π^* trans.
227		651	n - π^* trans.
Nd(III) complex	535	622	n - π^* trans.
	266	809	n - π^* trans.
	253	696	n - π^* trans.
	847	59	π - π^* trans.
	583	71	π - π^* trans.
	432	90	π - π^* trans.
	260	615	n - π^* trans.

	243	591	n- π^* trans.
Tb(III) complex	534	206	n- π^* trans.
	500	115	n- π^* trans.
	266	742	n- π^* trans.
	248	781	n- π^* trans.
	852	61	π - π^* trans.
	503	115	n- π^* trans.
	445	89	π - π^* trans.
	261	615	n- π^* trans.
	221	579	n- π^* trans.
	Er(III) complex	535	345
268		733	n- π^* trans.
233		734	n- π^* trans.
713		66	π - π^* trans.
439		89	π - π^* trans.
258		613	n- π^* trans.
224		605	n- π^* trans.





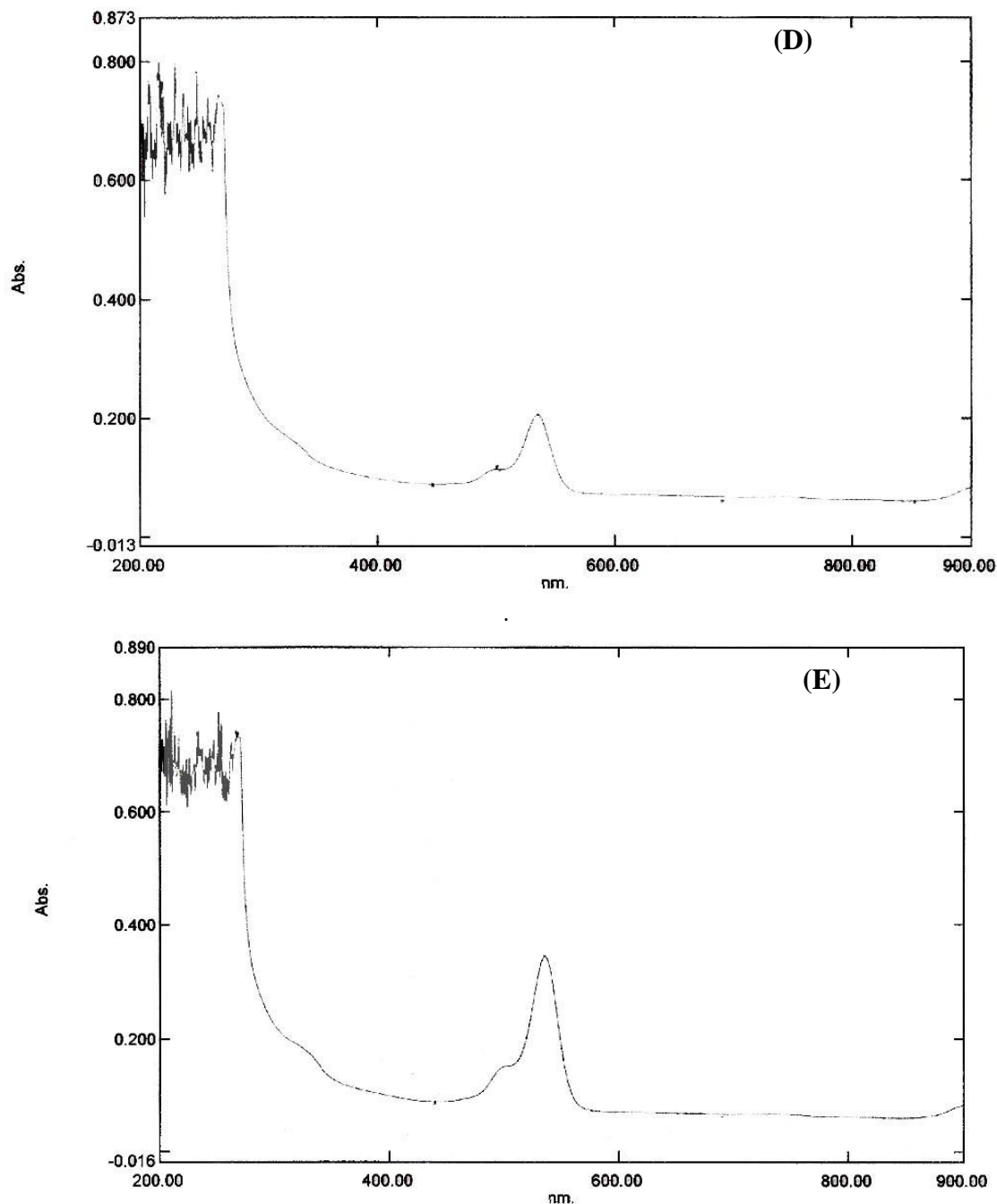


Fig 3: UV-Vis spectra of: (A) Ce(III) complex of eosin yellow (B) Gd(III) complex of eosin yellow (C) Nd(III) complex of eosin yellow (D) Tb(III) complex of eosin yellow (E) Er(III) complex of eosin yellow

¹H-NMR spectra

The ¹H-NMR spectra presented the persuasive confirmation of the coordination modes. Thus, the ¹H-NMR spectra of free eosin yellow (Na₂L) and its binuclear Gd(III) complex, as an example, are listed in Table 4 and shown in Fig. 4. On comparing with those of spectrum of the free eosin yellow (Na₂L), it is clear that eosin yellow ligand from two sides, one through carboxylate group and the other through phenolic-oxygen to form binuclear complex. In case of binuclear Gd(III) complex, due to different chemical environments, the signals of aromatic protons at $\delta = 7.00\text{--}8.00$ ppm are present with increasing intensities, this was expected due to the high symmetry between ligand and complex. ¹H-NMR spectrum for binuclear Gd(III) complex shows signal at $\delta = 3.34$ ppm, this signal is not observed in the free ligand spectrum and can be assigned to the protons of H₂O

molecules, supporting the binuclear complex formula. The overall changes of the $^1\text{H-NMR}$ spectrum of the binuclear Gd(III) complex are indicative of coordination of eosin yellow ligand to the metal through two potential sites, one via phenolic-oxygen atom and the other via carboxylate oxygen atom. This suggested coordination is in a good agreement with that obtained by elemental analyses and IR spectra.

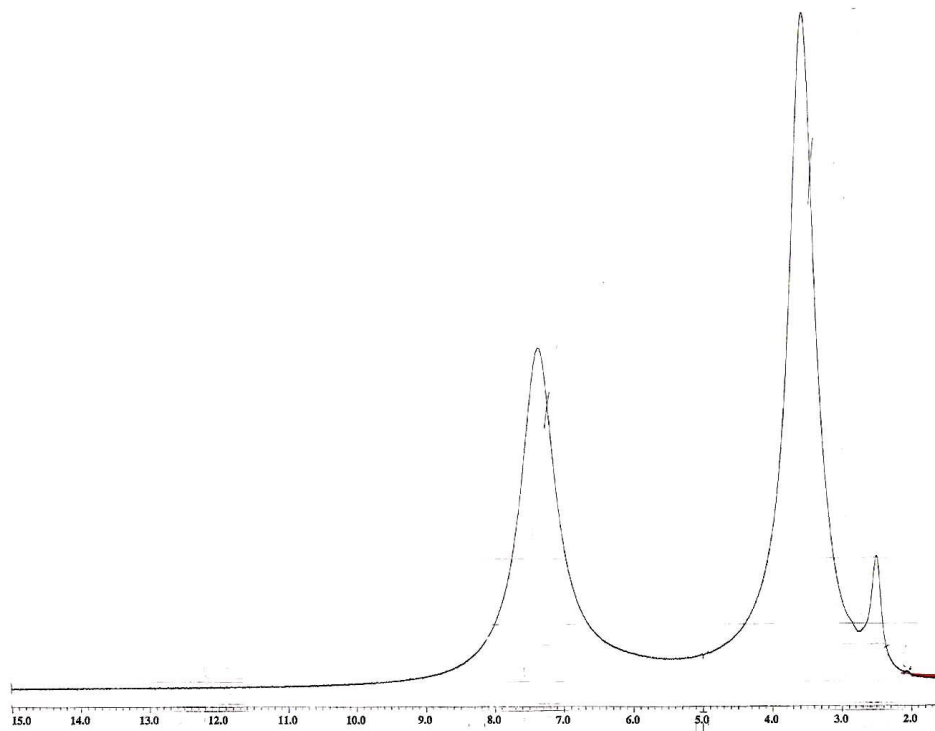


Fig 4: $^1\text{H-NMR}$ spectrum of binuclear Gd(III) complex of eosin yellow.

Table 4: $^1\text{H-NMR}$ spectral data of eosin yellow (Na_2L) and its binuclear Gd(III) complex.

Compound	δ ppm of hydrogen	
	H; OH_2	H; aromatic
Eosin yellow	---	7.14 - 7.80
Gd(III) complex	3.34	7.38 - 7.96

Thermal analyses of eosin yellow complexes

The results showed that the complexes lost its hydration water below 573 K. Within the temperature range 573-653 K, the coordinated water molecules were liberated. The anhydrous complexes displayed the decomposition of the organic ligand within the temperature range 673-1073 K leading to formation of metal oxide. The metal contents were calculated from the residue and results of elemental analyses. In the present investigation, the general thermal behavior of the eosin yellow complexes in terms of stability ranges, peak temperatures and kinetic parameters is shown in Table 5 and Fig. 5.

The $[\text{Ce}_2(\text{Cl})_4(\text{H}_2\text{O})_6(\text{L})]$ complex was thermally decomposed in two successive decomposition steps. The first decomposition step (obs.= 9.21%, calc.= 9.8%) within the temperature range 323-423 K, may be attributed to the liberation of six hydrated water molecules. The rest of the molecule was removed on the second step within the temperature range 623-773 K (obs. = 61.5%, calc.= 62.3%) which are reasonably accounted by the removal of C_6H_6 , 2Br_2 , 4HCl , 4CO_2 and $4\text{C}_2\text{H}_2$ molecules. The decomposition of the ligand molecule ended with a final oxide residue and contaminated with residual carbon (Ce_2O_3 and 2C residue).

The $[\text{Gd}_2(\text{Cl})_4(\text{H}_2\text{O})_6(\text{L})]$ complex was thermally decomposed in four successive decomposition steps. The first decomposition step (obs.= 8.8%, calc.= 8.9%) within the temperature range 313-453 K may be

attributed to the liberation of six hydrated water molecules. The second decomposition step found within the temperature range 473-603 K (obs.= 3.0%, calc.= 3.0%), which are reasonably accounted by the removal of HCL molecule. The third decomposition step found within the temperature range 623-773 K (obs.= 26.2%, calc.= 27.2%), which are reasonably accounted by the removal of CO₂, Br₂, 2HCL and 3H₂O molecules. The rest of the molecule was removed on the fourth step within the temperature range 773-1073 K (obs. = 12.6%, calc.= 13.2%) which are reasonably accounted by the removal of HCL, Br₂ and 3H₂O molecules. The decomposition of the ligand molecule ended with a final oxide residue and contaminated with residual carbon (Gd₂O₃ and 19C residue).

The [Nd₂(Cl)₄(H₂O)₆(L)] complex was thermally decomposed in four successive decomposition steps. The first decomposition step (obs.= 9.29%, calc.= 9.12%) within the temperature range 303-423 K may be attributed to the liberation of six hydrated water molecules. The second decomposition step found within the temperature range 473-723 K (obs.= 22.5%, calc.= 22.6 %), which are reasonably accounted by the removal of 2HCL, Br₂ and 2H₂O molecules. The third decomposition step found within the temperature range 773-1073 K (obs.= 7.6%, calc.= 8.4%), which are reasonably accounted by the removal of HCL and 0.5Br₂ molecules. The rest of the molecule was removed on the fourth step within the temperature range 773-1073 K (obs. = 12.0%, calc.= 11.8%) which are reasonably accounted by the removal of HCL , 0.5Br₂, 5H₂O and 0.5O₂ molecules. The decomposition of the ligand molecule ended with a final oxide residue and contaminated with residual carbon (Nd₂O₃ and 20C residue).

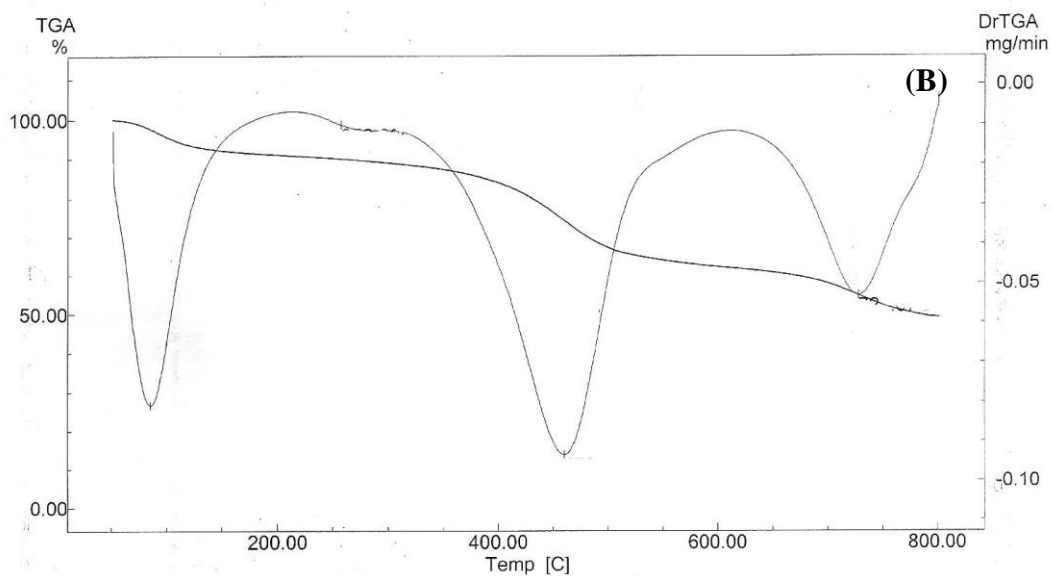
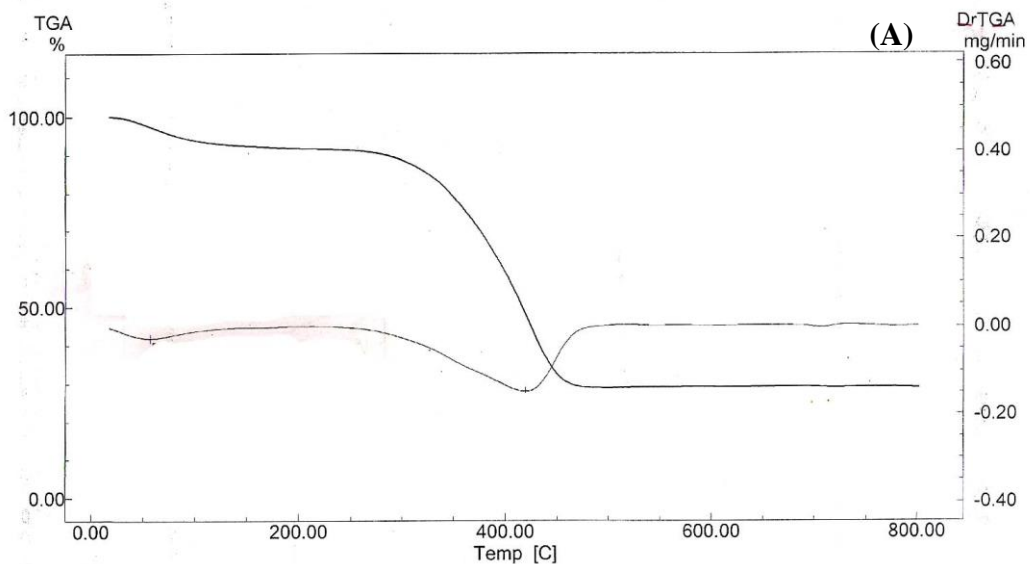
The [Tb₂(Cl)₄(H₂O)₆(L)] complex was thermally decomposed in three successive decomposition steps. The first decomposition step (obs.= 26.4%, calc.= 27.2%) within the temperature range 323-423 K may be attributed to the liberation of CO₂, 2HCL, Br₂ and 3H₂O molecules. The second decomposition step found within the temperature range 473-723 K (obs.= 15.3%, calc.= 14.2%), which are reasonably accounted by the removal of 3H₂O, HCL, 0.5Br₂ and H₂ molecules. The rest of the molecule was removed on the third step within the temperature range 773-1073 K (obs. = 9.2%, calc.= 9.5%) which are reasonably accounted by the removal of HCL and 0.5Br₂ molecules. The decomposition of the ligand molecule ended with a final oxide residue and contaminated with residual carbon (Tb₂O₃ and 19C residue).

The [Er₂(Cl)₄(H₂O)₆(L)] complex was thermally decomposed in four successive decomposition steps. The first decomposition step (obs.= 8.9%, calc.= 8.7%) within the temperature range 323-423 K may be attributed to the liberation of six hydrated water molecules. The second decomposition step found within the temperature range 473-733 K (obs.= 7.8%, calc.= 6.5 %), which are reasonably accounted by the removal of CO₂ and HCL molecules. The third decomposition step found within the temperature range 623-823 K (obs.= 19.9%, calc.= 20.4%), which are reasonably accounted by the removal of 2HCL, Br₂ and H₂O molecules. The rest of the molecule was removed on the fourth step within the temperature range 773-1073 K (obs. = 12.6%, calc.= 13.0%) which are reasonably accounted by the removal of HCL, Br₂, 5H₂O and H₂ molecules. The decomposition of the ligand molecule ended with a final oxide residue and contaminated with residual carbon (Er₂O₃ and 19C residue).

Table 5: Thermal data of eosin yellow (Na₂L) and its complexes.

Compound	Steps	Temp range (°C)	DTG peak (°C)	TG weight loss (%)		Assignments
				Calc.	Found	
[Ce ₂ (Cl) ₄ (H ₂ O) ₆ (L)]	1	50-150	60°C	9.18	9.21	6H ₂ O.
	2	350-500	420°C	62.3	61.5	C ₆ H ₆ , 2Br ₂ , 4HCL, 4CO ₂ , and 4C ₂ H ₂ . Ce ₂ O ₃ and 2C residue.
[Gd ₂ (Cl) ₄ (H ₂ O) ₆ (L)]	1	40-180	85°C	8.9	8.8	6H ₂ O.
	2	200-330	260°C	3.0	3.0	HCL.
	3	350-500	460°C	27.2	26.2	CO ₂ , Br ₂ , 2HCL and 3H ₂ O.
	4	500-800	730°C	13.2	12.6	HCL, Br ₂ and 3H ₂ O. Gd ₂ O ₃ and 19C residue.
[Nd ₂ (Cl) ₄ (H ₂ O) ₆ (L)]	1	30-150	80°C	9.12	9.29	6H ₂ O.

	2 3 4	200-450 500-800 500-800	415°C 570°C 785°C	22.6 8.4 12.0	22.5 7.6 11.8	2HCL, Br ₂ and 2H ₂ O. HCL and 0.5Br ₂ . HCL , 0.5Br ₂ , 5H ₂ O and 0.5O ₂ . Nd ₂ O ₃ and 20C residue.
[Tb ₂ (Cl) ₄ (H ₂ O) ₆ (L)]	1 2 3	50-150 200-450 500-800	55°C 440°C 530°C	27.2 14.2 9.5	26.4 15.3 9.2	CO ₂ , 2HCL, Br ₂ and 3H ₂ O. 3H ₂ O, HCL, 0.5Br ₂ and H ₂ . HCL and 0.5Br ₂ . Tb ₂ O ₃ and 19C residue.
[Er ₂ (Cl) ₄ (H ₂ O) ₆ (L)]	1 2 3 4	30-150 200-460 350-550 500-800	80°C 430°C 510°C 785°C	8.7 6.5 20.4 13.0	8.9 7.8 19.9 12.6	6H ₂ O. CO ₂ and HCL. 2HCL, Br ₂ and H ₂ O. HCL, Br ₂ , 5H ₂ O and H ₂ . Er ₂ O ₃ and 19C residue.



(C)

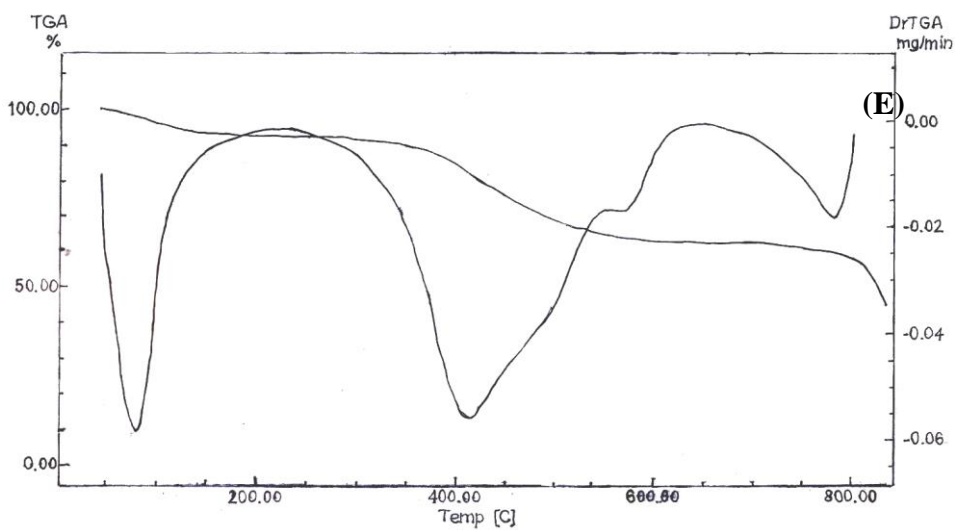
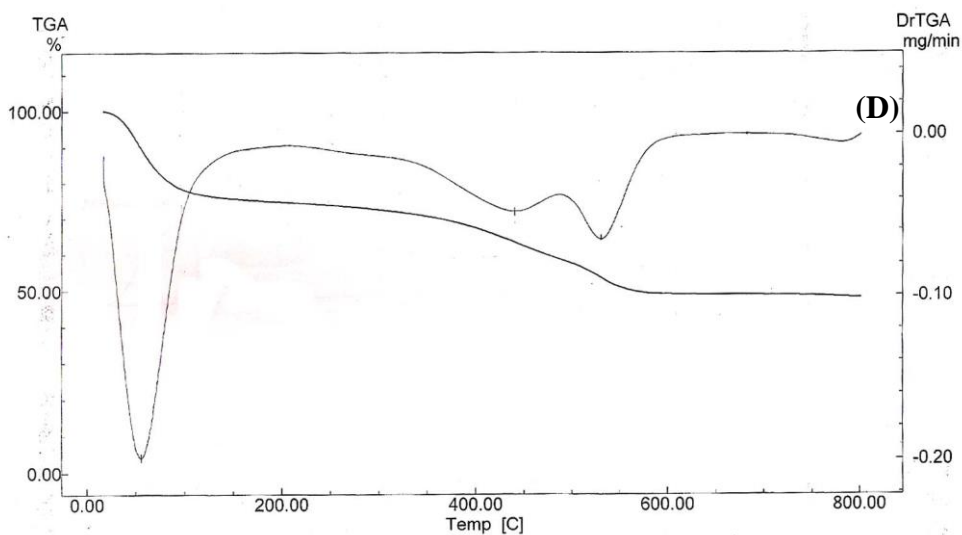
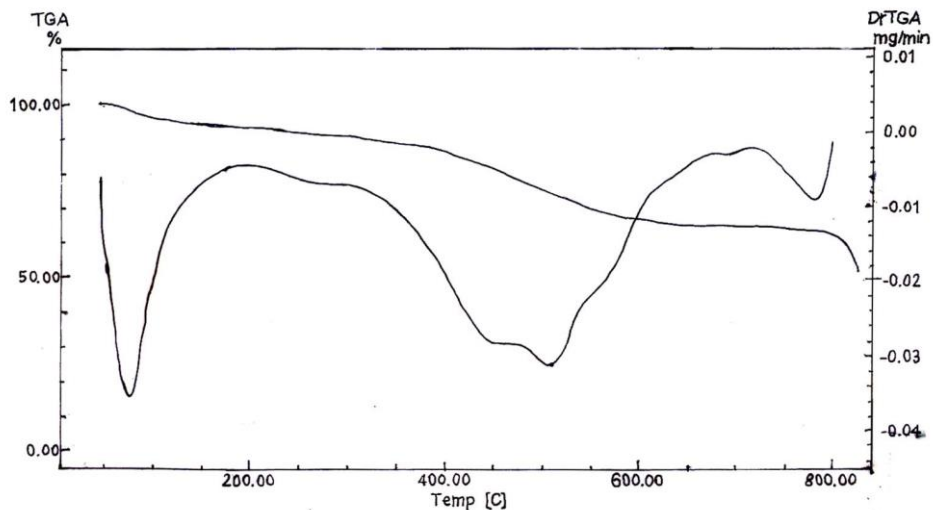


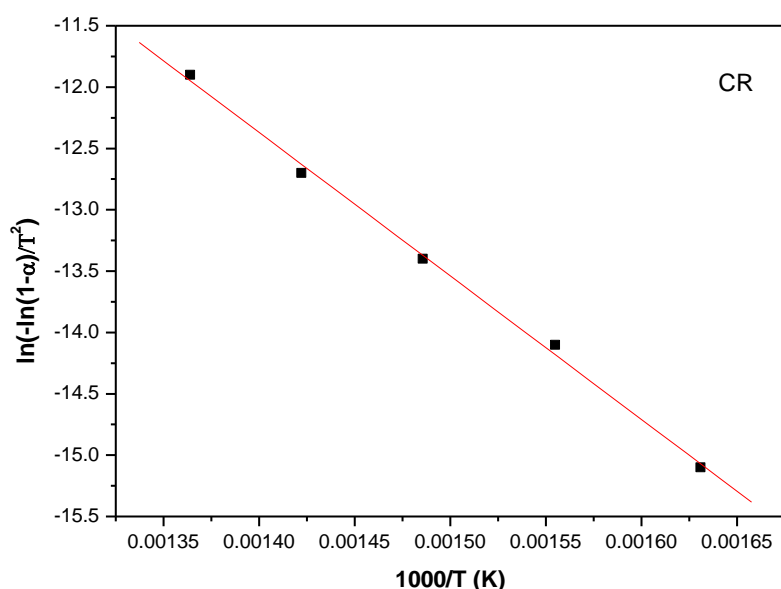
Fig 5: TG/DTG curves of: (A) Ce (III) complex of eosin yellow (B) Gd(III) complex of eosin yellow (C) Nd(III) complex of eosin yellow (D) Tb(III) complex of eosin yellow (E) Er(III) complex of eosin yellow

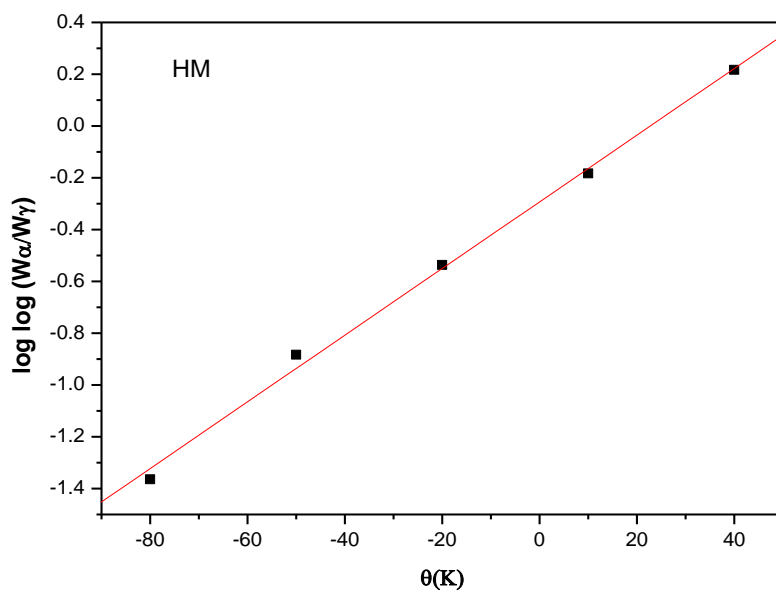
Kinetic studies

The kinetic studies of the thermal decomposition of the eosin yellow metal complexes were carried out. The second stage was taken for the kinetic studies of decomposition of the complexes (Fig. 6). The kinetic parameters are summarized in the Table 6. On the basis of thermal decomposition, parameters such as activation energy (E^*), pre-exponential factor (A), entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and free energy of activation (ΔG^*) were calculated by using the Coats–Redfern [18] and Horowitz–Metzger [19] equations. The high values of the activation energies reflect the thermal stability of the complexes. The complexes have negative entropy, which indicates that the decomposition reactions proceed with a lower rate than the normal ones. The negative value of entropy also indicates that the activated complexes have a more ordered and more rigid structure than the reactants or intermediates. The negative values of the entropies of activation are compensated by the values of enthalpies of activation, leading to the same values for the free energy of activation [20,21].

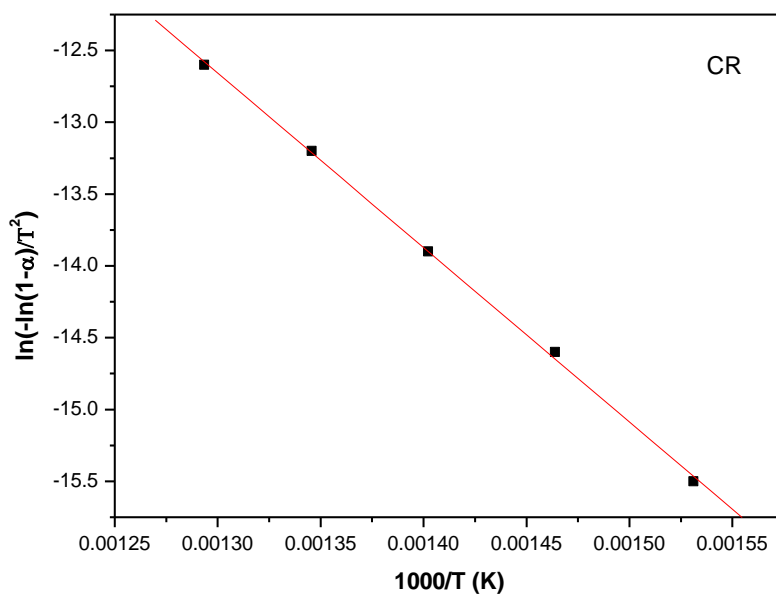
Table 6: Thermodynamic parameters of the thermal decomposition of Eosin Yellow complexes

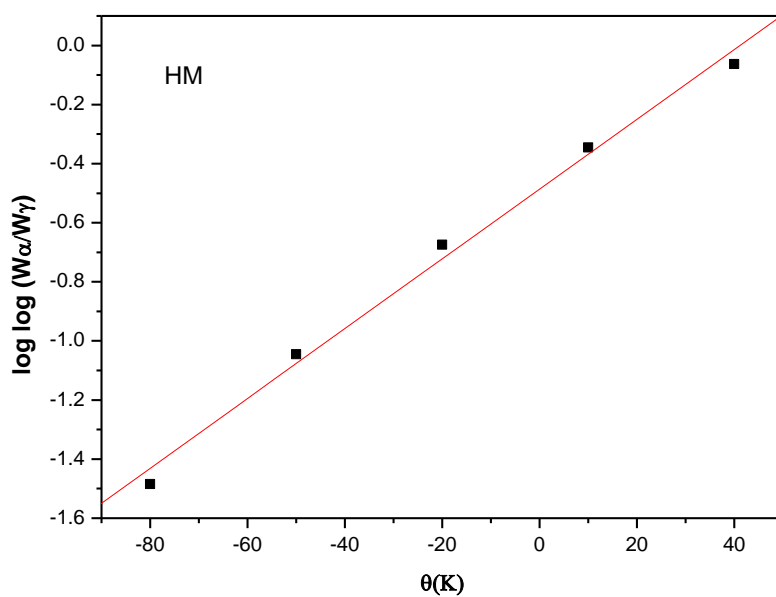
Complex	Method	Parameter					r
		E (J mol ⁻¹)	A (s ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔH (J mol ⁻¹)	ΔG (J mol ⁻¹)	
Ce(III) complex	CR	9.73E+04	1.61E+05	-1.52E+02	9.15E+04	1.97E+05	0.9987
	HM	1.18E+05	6.20E+06	-1.22E+02	1.13E+05	1.97E+05	0.9983
Gd(III) complex	CR	1.01E+05	6.95E+04	-1.60E+02	9.49E+04	2.12E+05	0.9996
	HM	1.22E+05	3.11E+06	-1.28E+02	1.15E+05	2.09E+05	0.9963
Nd(III) complex	CR	8.65E+04	1.13E+04	-1.74E+02	8.08E+04	2.01E+05	0.9980
	HM	1.05E+05	5.92E+05	-1.41E+02	9.90E+04	1.96E+05	0.9938
Tb(III) complex	CR	1.93E+05	2.21E+10	-5.51E+01	1.86E+05	2.30E+05	0.9904
	HM	1.99E+05	8.58E+10	-4.38E+01	1.93E+05	2.28E+05	0.9909
Er(IV) complex	CR	1.48E+05	4.27E+07	-1.07E+02	1.41E+05	2.25E+05	0.9972
	HM	1.60E+05	3.94E+08	-8.84E+01	1.53E+05	2.22E+05	0.9962



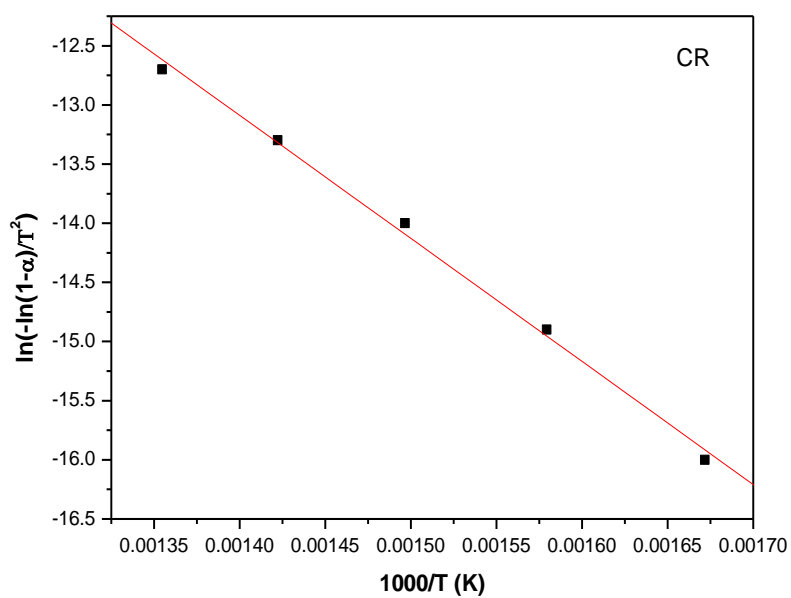


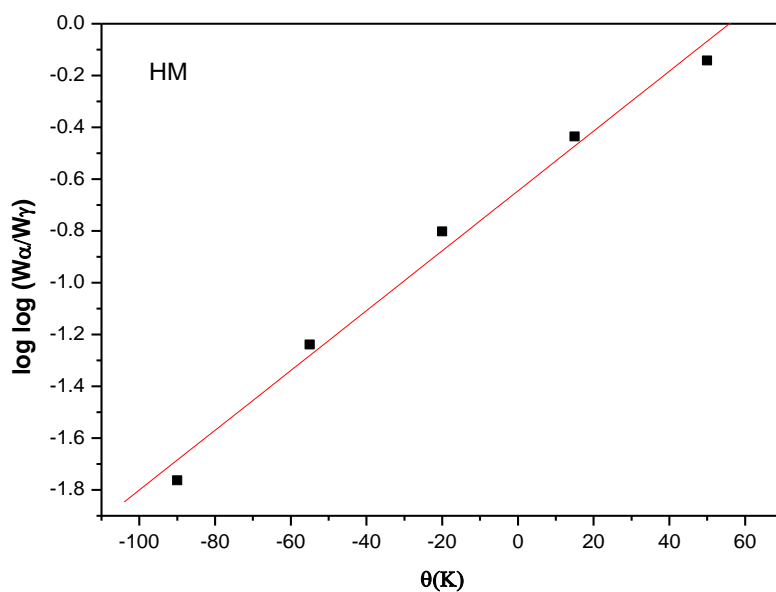
Ce(III) complex



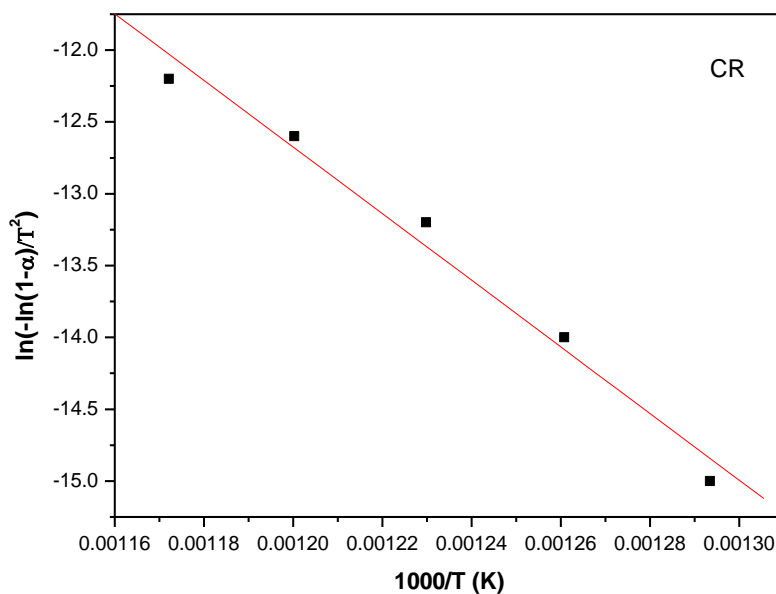


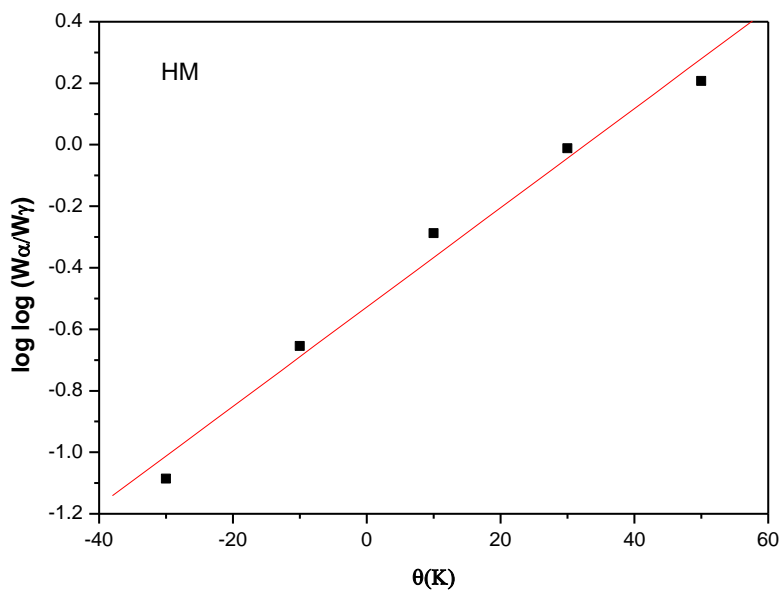
Gd(III) complex



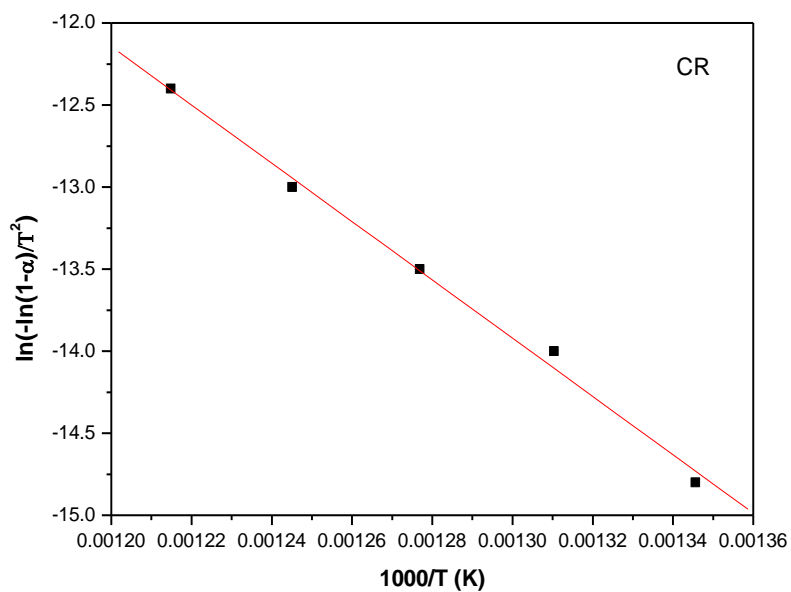


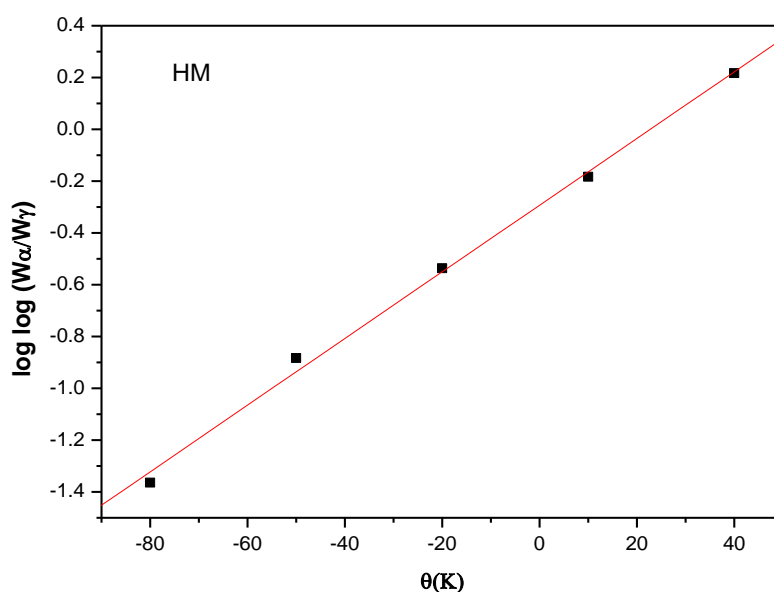
Nd(III) complex





Tb(III) complex





Er(III) complex

Fig 6: Coat-Redfern (CR) and Horowitz and Metzger (HM) curves for eosin yellow complexes.

Antimicrobial activity of eosin yellow complexes

Antibacterial and antifungal activities of the eosin yellow ligand and its complexes were carried out against *Escherichia coli* (Gram –ve), *Bacillus subtilis* (Gram +ve) and antifungal (*Aspergillus* and *Penicillium* activities). The results of antimicrobial activities (bacteria and fungi) in vitro of free eosin yellow ligand and its binuclear metal complexes to the adopted method of Gupta et al., [22] are listed in Table 7 and shown in Figs. 7 and 8. The ligand and its complexes have no activity against *Escherichia coli*, but Nd(III)/eosin yellow is more active rather than Ce(III)/eosin yellow, Er(III)/eosin yellow and Gd(III)/eosin yellow complexes against *Penicillium*.

Table 7: Antimicrobial activity of eosin yellow (Na₂L) and its binuclear metal 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	0.7	0	0.6	0.9
Gd(III) complex	0.9	0	0.4	0.7
Nd(III) complex	0.5	0	0.7	0.8
Tb(III) complex	0	0	0	0.4
Er(IV) complex	0.6	0	0.5	0.5

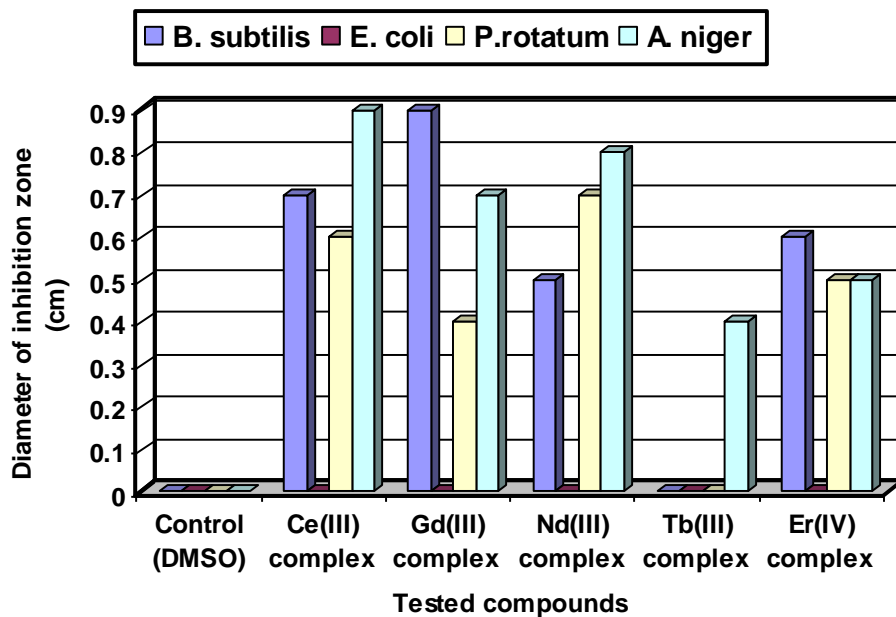


Fig 7: Statistical representation for biological activity of eosin yellow complexes.

Antibacterial activity

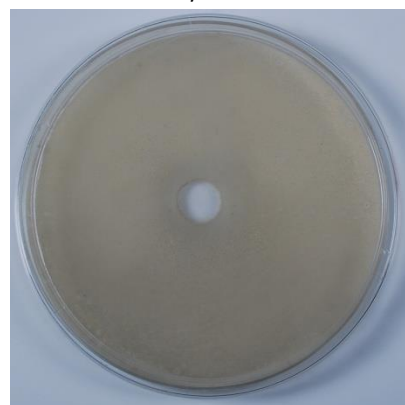
Bacillus subtilis (Gram +ve)



Ce³⁺/ EOSIN YELLOW



Gd³⁺/ EOSIN YELLOW



Nd³⁺/ EOSIN YELLOW

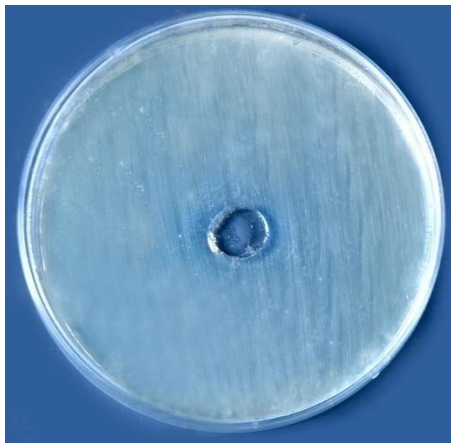


Tb³⁺/ EOSIN YELLOW

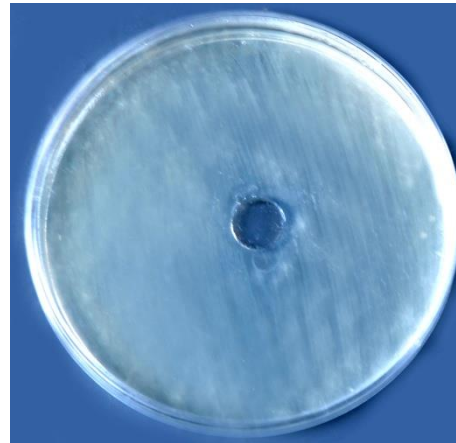


Er⁺³/ EOSIN YELLOW

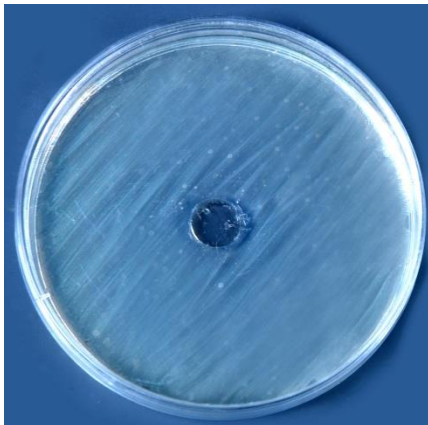
Escherichia coli (Gram -ve)



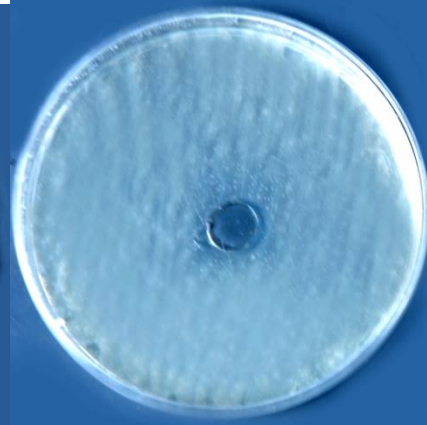
Ce⁺³/ EOSIN YELLOW



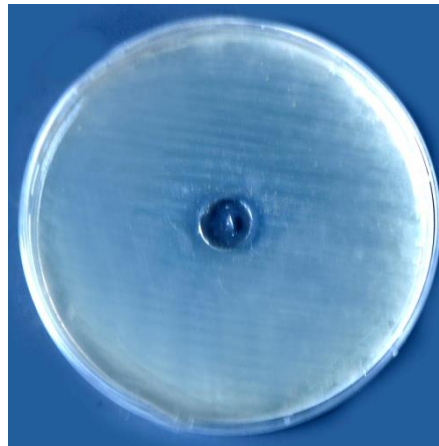
Gd⁺³/ EOSIN YELLOW



Nd⁺³/ EOSIN YELLOW



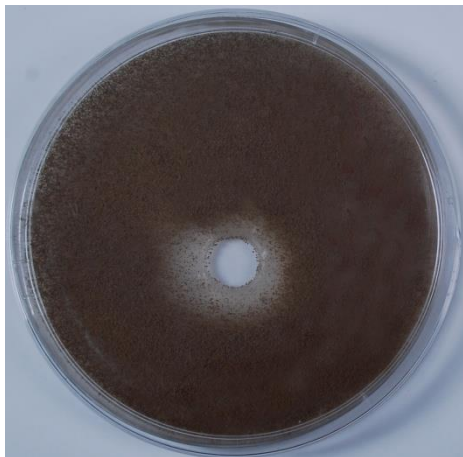
Tb⁺³/ EOSIN YELLOW



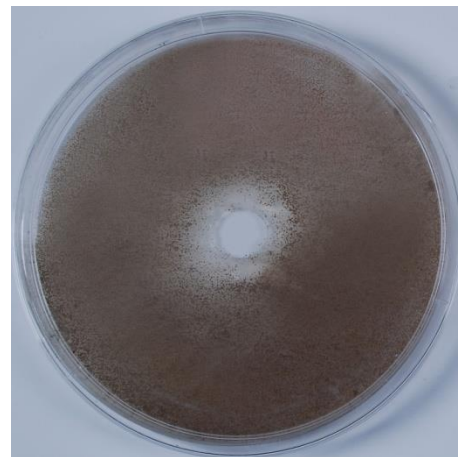
Er⁺³/ EOSIN YELLOW

Antifungal activity

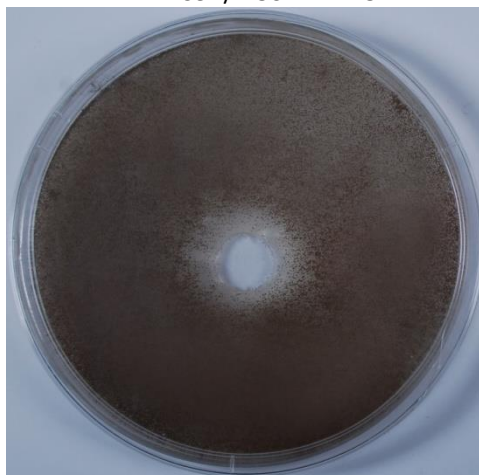
Aspergillus niger



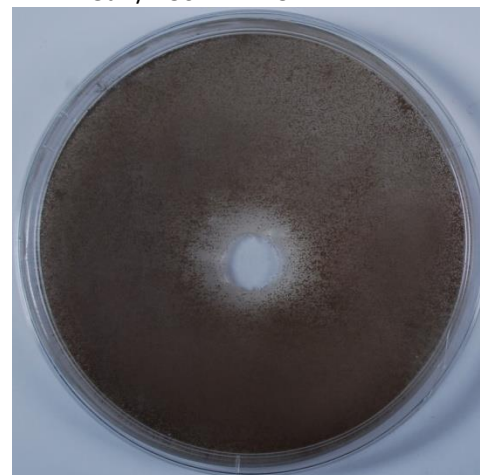
Ce⁺³/ EOSIN YELLOW



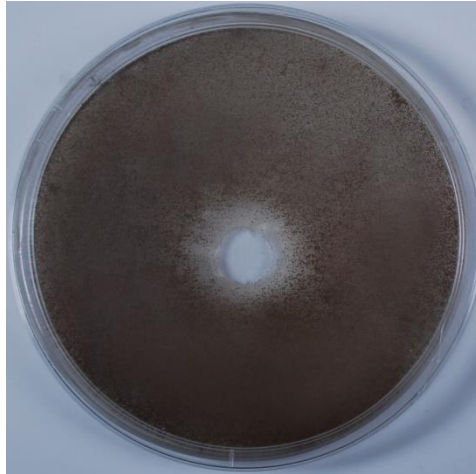
Gd⁺³/ EOSIN YELLOW



Nd⁺³/ EOSIN YELLOW



Tb⁺³/ EOSIN YELLOW

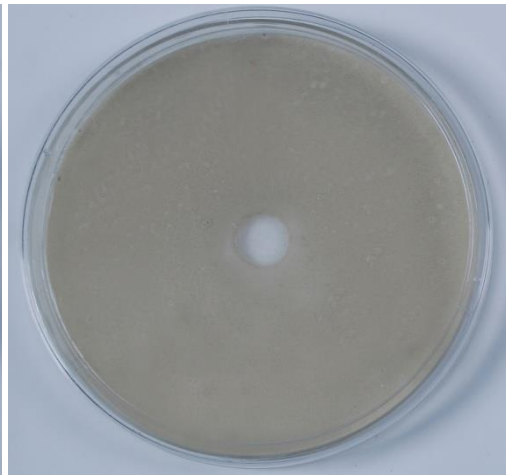


Er⁺³/ EOSIN YELLOW

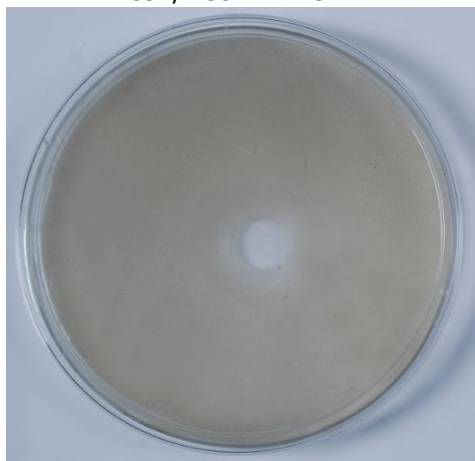
Penicillium notatum



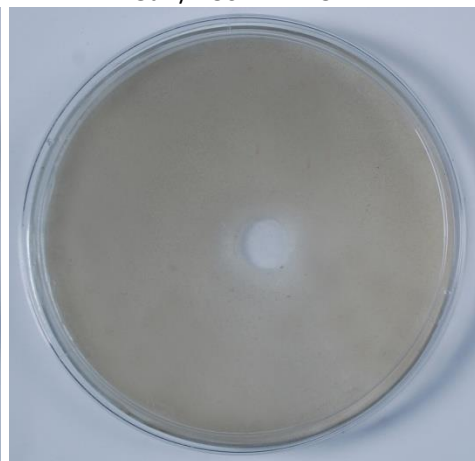
Ce⁺³/ EOSIN YELLOW



Gd⁺³/ EOSIN YELLOW



Nd⁺³/ EOSIN YELLOW



Tb⁺³/ EOSIN YELLOW

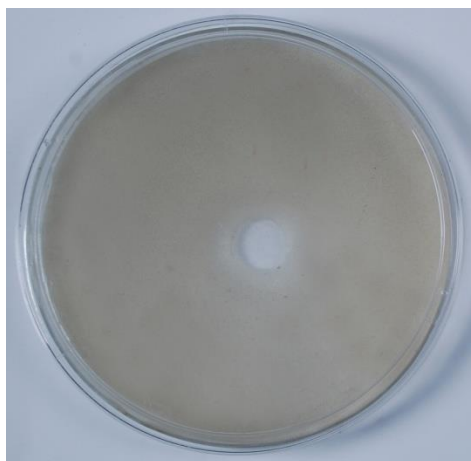
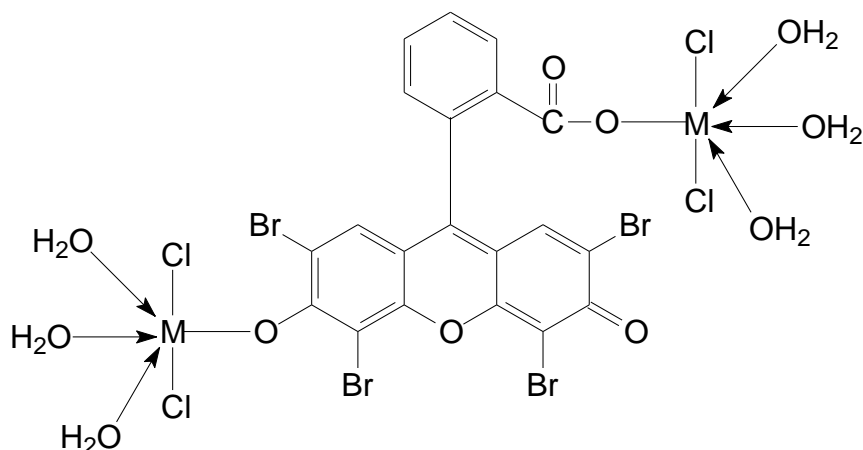

 Er³⁺/ EOSIN YELLOW

Fig 8: Biological activity of EOSIN YELLOW metal complexes

Structure of the eosin yellow complexes

The structures of the complexes of eosin yellow with Ce(III), Gd(III), Nd(III), Tb(III) and Er(III) ions have been confirmed from the elemental analysis, IR, molar conductance, UV-V is ¹H-NMR spectra and thermal analysis data. Thus, on the basis of the above studies, octahedral geometries are suggested for the investigated eosin yellow complexes and represented in Fig. 9.


Fig 9: Structure of Ce, Tb, Gd, Nd and Er(III) complexes of eosin yellow

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