



Synthesis, Spectral Characterization and Photoluminescence Properties of Europium(III) and Terbium(III) Complexes with Schiff bases Derived from 5-(phenyl/substituted phenyl)-2-hydrazino-1,3,4-thiadiazoles and Benzyl/Diacetyl

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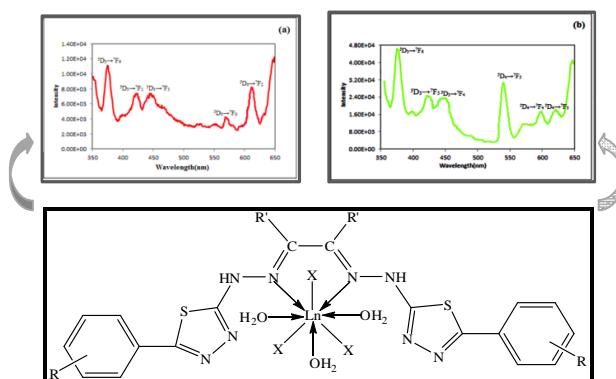
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ABSTRACT

A novel class of europium(III) and terbium(III) complexes with Schiff bases derived by the condensation of 5-(phenyl/substituted phenyl)-2-hydrazino-1,3,4-thiadiazoles and benzyl/ diacetyl have been prepared in ethanol. The structures of the complexes have been proposed on the basis of elemental analysis, electrical conductance, magnetic moment, spectroscopic measurements (IR, UV spectra), X-ray diffraction studies and photoluminescence properties such as emission spectra of the complexes were investigated. Emission spectra of the europium(III) and terbium(III) complexes exhibit strong characteristic emission in red and green regions, respectively.

Graphical Abstract



(Where, Ln= Eu, Tb; X= Cl in case of Eu and OAc in case of Tb)

Highlights:

- Ligands act as bidentate chelating agent and have “antenna effect”.
- X-ray diffraction pattern shows that the particles are in the range of 09-20 nm.
- The characteristic peaks of Eu(III) and Tb(III) show the strong red and green emission at ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_4 \rightarrow {}^7F_5$ transitions, respectively.

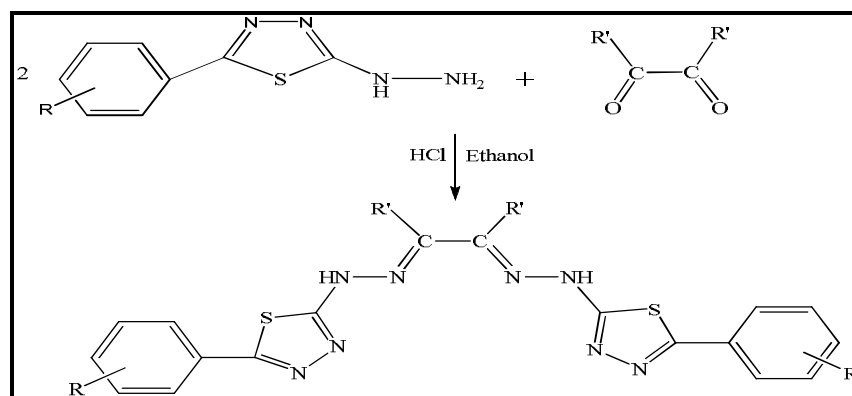
Keywords: Europium(III), Terbium(III), IR, Luminescence.

INTRODUCTION

The derivatives of 1,3,4-thiadiazole Schiff bases possess an extensive variety of biological activity and have been extensively investigated in the field of pesticides and medicines [1, 2] such as anti-inflammatory, antitumor and antimicrobial [3-6], antiviral [7], antifungal [8], antiparasitic [9], antibacterial [10], anti-HIV [11] and anticancer properties [12]. Some other main applications are in solar cell [13], conducting polymer [14, 15], sensor [16, 17], energy storage [18], electrodes [19], enzymatic application [20], anxiolytic activity [21]. The europium(III) and terbium(III) complexes display a high affinity for organophosphate pesticides [22]. In recent times, the coordination chemistry of such ligands arises due to their some specific properties such as magnetism, selective gas adsorption, gas storage, molecular recognition, catalysis, luminescence, etc. [23-30]. Recently, terbium(III) complexes play an important role in the development of a highly sensitive and selective fluorescent sensor towards Ca^{2+} ions [31]. The complexes of rare earth frequently show optical properties particularly due to their large Stokes shift, emission bandwidth and long luminescence lifetimes [32, 33] and they have been widely used in biomedical and functional material [34] such as lasers materials [35], analytical and structure probe [36, 37] and light emitting diodes [38, 39]. In this paper, we report the synthesis of a series of novel Eu(III) and Tb(III) complexes and their spectral and luminescent properties. This work might provide an allusion for the development of the luminescent materials.

MATERIALS AND METHODS

All the reagents and solvents were used of analytical grade. Europium(III) chloride was purchased from Sigma Aldrich and terbium(III) acetate was purchased from Alfa Aesar "A Johnson Matthey company". The ligands were prepared according to the earlier report [40]. 5-(phenyl/substituted phenyl)-2-hydrazino-1,3,4-thiadiazoles and benzil/diacetyl in 2:1 molar ratio respectively, then it was condensed in ethanol containing few drops of concentrated hydrochloric acid for 6-7 h. The products obtained were separated out by evaporation of ethanol and further recrystallized from ethanol-ether mixture (1:1) (Figure 1).



Where, R= H, R'=Ph (L₁), R=4-NO₂, R'=Ph (L₂), R=2-Cl, R'=Ph (L₃), R= H, R'=CH₃ (L₄), R= 4-NO₂, R'=CH₃ (L₅), R=2-Cl, R'=CH₃ (L₆)

Figure 1. Synthesis of ligands.

Preparation of complexes: A solution of Eu(III) chloride/Tb(III) acetate (0.01 mol) in ethyl alcohol (25 cm³) was added to a refluxing solution of Schiff base (0.01 mol) in ethyl alcohol (30 cm³) having saturated alcoholic solution of sodium hydroxide (10 cm³). The whole mixture was refluxed for about 15-18 h. Colored precipitate was separated out which was filtered, washed with ethanol and ether and dried in *vacuo*. The synthetic data are given in table 1.

Table 1. Synthetic data of Eu(III) and Tb(III) complexes

S.No	Reactants (molar ratio)	Refluxing Time	Product Yield (%)	Empirical formula*	Color
1	EuCl ₃ + L ₁ (1:1)	15	[Eu(L ₁)Cl ₃ (H ₂ O) ₃] (69%)	C ₃₀ H ₂₈ N ₈ S ₂ O ₃ Cl ₃ Eu	Yellow
2	EuCl ₃ + L ₂ (1:1)	16	[Eu(L ₂)Cl ₃ (H ₂ O) ₃] (70%)	C ₃₀ H ₂₆ N ₁₀ S ₂ O ₇ Cl ₃ Eu	Brick red
3	EuCl ₃ + L ₃ (1:1)	18	[Eu(L ₃)Cl ₃ (H ₂ O) ₃] (63%)	C ₃₀ H ₂₆ N ₈ S ₂ O ₃ Cl ₅ Eu	Yellow
4	EuCl ₃ + L ₄ (1:1)	16	[Eu(L ₄)Cl ₃ (H ₂ O) ₃] (68%)	C ₂₀ H ₂₄ N ₈ S ₂ O ₃ Cl ₃ Eu	Brown
5	EuCl ₃ + L ₅ (1:1)	16	[Eu(L ₅)Cl ₃ (H ₂ O) ₃] (65%)	C ₂₀ H ₂₂ N ₁₀ S ₂ O ₇ Cl ₃ Eu	Brick red
6	EuCl ₃ + L ₆ (1:1)	18	[Eu(L ₆)Cl ₃ (H ₂ O) ₃] (61%)	C ₂₀ H ₂₂ N ₈ S ₂ O ₃ Cl ₅ Eu	Brown
7	Tb(OAc) ₃ + L ₁ (1:1)	17	[Tb(L ₁)(OAc) ₃ (H ₂ O) ₃] (65%)	C ₃₆ H ₃₇ N ₈ S ₂ O ₉ Tb	Orange
8	Tb(OAc) ₃ + L ₂ (1:1)	18	[Tb(L ₂)(OAc) ₃ (H ₂ O) ₃] (68%)	C ₃₆ H ₃₅ N ₁₀ S ₂ O ₁₃ Tb	Orange
9	Tb(OAc) ₃ + L ₃ (1:1)	16	[Tb(L ₃)(OAc) ₃ (H ₂ O) ₃] (62%)	C ₃₆ H ₃₅ N ₈ S ₂ O ₉ Cl ₂ Tb	Orange
10	Tb(OAc) ₃ + L ₄ (1:1)	15	[Tb(L ₄)(OAc) ₃ (H ₂ O) ₃] (67%)	C ₂₆ H ₃₃ N ₈ S ₂ O ₉ Tb	Orange
11	Tb(OAc) ₃ + L ₅ (1:1)	17	[Tb(L ₅)(OAc) ₃ (H ₂ O) ₃] (69%)	C ₂₆ H ₃₁ N ₁₀ S ₂ O ₁₃ Tb	Red
12	Tb(OAc) ₃ + L ₆ (1:1)	18	[Tb(L ₆)(OAc) ₃ (H ₂ O) ₃] (63%)	C ₂₆ H ₃₁ N ₈ S ₂ O ₉ Cl ₂ Tb	Yellow

* Satisfactory carbon, hydrogen and nitrogen analyses were obtained.

RESULTS AND DISCUSSION

The complexes of europium(III) and terbium(III) are soluble in organic solvents like DMF, DMSO, chloroform and all the complexes are stable at room temperature. The molar conductance values (DMF) in the range of 10-13 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating that the complexes are non-electrolytic in nature.

Magnetic behavior and electronic spectra: The magnetic moment values of europium(III) and terbium(III) complexes lie in the range of 3.30-3.48 BM and 9.45-9.63 BM, respectively. These values show little deviation from actual values of free trivalent Eu(III) and Tb(III) ions [41].

The absorption bands europium(III) and terbium(III) complexes in the UV and visible regions appear due to transitions from the ground levels 7F_0 and 7F_6 , respectively to the excited J levels of 4f configuration. For europium(III) complexes, bands observed in the region of 17,150-18, 200, 23, 000-23,700, 26, 200-27, 500 and 30,050-31, 200 cm^{-1} correspond to the transition from 7F_0 level to 5D_1 , 5D_6 , $^5L_{10}$ and 5H_4 excited energy level, respectively. Terbium(III) complexes show bands in the region of 22,700-23,300, 27,000-27, 900 and 31, 300-32, 200 cm^{-1} correspond to the transition from 7F_6 level to 5D_4 , 5D_3 and 5D_0 , excited energy level, respectively. The slight shifts in the bands have been ascribed by Jorgensen to the impact of crystal fields upon the inter-electronic repulsion between the 4f electrons. Further, a checked improvement in the intensity of the bands, upon complexation is moreover examined. The values of β , δ and $b_{1/2}$ calculated from the spectral data are given in table 2.

Table 2. Electronic spectral parameters of europium(III) and terbium(III) complexes with Schiff bases derived from 5-(phenyl/substituted phenyl)-2-hydrazino-1,3,4-thiadiazole and benzil/ diacetyl

S.No.	Complex	β	δ	$b^{1/2}$
1	[Eu(BPHT)Cl ₃ (H ₂ O) ₃]	0.9929	0.7150	0.0595
2	[Tb(BPHT)(OAc) ₃ (H ₂ O) ₃]	0.9886	1.1531	0.0754
3	[Eu(BPNHT)Cl ₃ (H ₂ O) ₃]	0.9936	0.6441	0.0565
4	[Tb(BPNHT)(OAc) ₃ (H ₂ O) ₃]	0.9875	1.2658	0.0790
5	[Eu(BOCHT)Cl ₃ (H ₂ O) ₃]	0.9928	0.7252	0.0600
6	[Tb(BOCHT)(OAc) ₃ (H ₂ O) ₃]	0.9881	1.2043	0.0771
7	[Eu(DPHT)Cl ₃ (H ₂ O) ₃]	0.9910	0.9081	0.0670
8	[Tb(DPHT)(OAc) ₃ (H ₂ O) ₃]	0.9858	1.4404	0.0842
9	[Eu(DPNHT)Cl ₃ (H ₂ O) ₃]	0.9915	0.8572	0.0651
10	[Tb(DPNHT)(OAc) ₃ (H ₂ O) ₃]	0.9859	1.4301	0.8396
11	[Eu(DOCHT)Cl ₃ (H ₂ O) ₃]	0.9925	0.7556	0.0612
12	[Tb(DOCHT)(OAc) ₃ (H ₂ O) ₃]	0.9867	1.3479	0.0815

Infrared spectra: The characteristic IR spectral bands of Eu(III) and Tb(III) complexes are given in table 3. The IR spectra provide valuable information regarding the coordination behavior of the Schiff bases. The bands in IR spectra of complexes 1, 4, 7 and 10 at *ca.* 3120-3040 cm^{-1} assigned for the $\nu(\text{Ar-H})$. The bands in complexes 2, 5, 8 and 11 at *ca.* 1540-1530 cm^{-1} can be assigned to the presence of NO_2 group [44]. The IR spectra of complexes 3, 6, 9 and 12 shows at *ca.* 785-765 cm^{-1} assigned for the C-Cl stretching modes [45]. The spectra of the Schiff bases having (N-H) group show a band at 3200-3170 cm^{-1} which remains at the same position in complexes indicating the non-involvement of N-H group in bond formation. The ligands shows one medium intensity band at *ca.* 1635 cm^{-1} assignable [44, 46] to $\nu(\text{C}=\text{N})$ which shifts to lower the value of 20-40 cm^{-1} *i.e.* 1615-1595 cm^{-1} in the complexes. This shifting indicates the coordination of azomethine nitrogen to metal ion [47-50]. The $\nu(\text{Ln-N})$ appears at *ca.* 415-395 cm^{-1} . The $\nu(\text{C-S-C})$ vibration appears as a strong band at *ca.* 1130 cm^{-1} in free ligand which remains at the same position in complex indicating the non-coordination of thiadiazole ring sulfur to metal ion [51]. In complexes 7-12, Ln-O band appears at 425-415 cm^{-1} which indicates that acetate molecules are bonded to metal. The broad band appears at 3445-3425 cm^{-1} indicating the presence of coordinated water molecule.

Table 3. Significant IR spectral bands of Europium(III) and Terbium(III) complexes

S.No	Compounds	$\nu(\text{O-H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N-H})$	$\nu(-\text{NO}_2)$	$\nu(\text{Ln-N})$	$\nu(\text{Ln-O})$	$\nu(\text{Ln-Cl})$
1	$\text{C}_{30}\text{H}_{28}\text{N}_8\text{S}_2\text{O}_3\text{Cl}_3\text{Eu}$	3425s	1605s	3175m	-	395m	-	315m
2	$\text{C}_{30}\text{H}_{26}\text{N}_{10}\text{S}_2\text{O}_7\text{Cl}_3\text{Eu}$	3440s	1610s	3170m	1530m	398 m	-	320m
3	$\text{C}_{30}\text{H}_{26}\text{N}_8\text{S}_2\text{O}_3\text{Cl}_5\text{Eu}$	3445s	1595s	3175m	-	405m	-	315m
4	$\text{C}_{20}\text{H}_{24}\text{N}_8\text{S}_2\text{O}_3\text{Cl}_3\text{Eu}$	3430s	1602s	3180m	-	415m	-	315m
5	$\text{C}_{20}\text{H}_{22}\text{N}_{10}\text{S}_2\text{O}_7\text{Cl}_3\text{Eu}$	3425s	1605s	3185m	1535m	395m	-	320m
6	$\text{C}_{20}\text{H}_{22}\text{N}_8\text{S}_2\text{O}_3\text{Cl}_5\text{Eu}$	3445s	1598s	3180m	-	405m	-	325m
7	$\text{C}_{36}\text{H}_{37}\text{N}_8\text{S}_2\text{O}_9\text{Tb}$	3440s	1605s	3190m	-	410m	420m	-
8	$\text{C}_{36}\text{H}_{35}\text{N}_{10}\text{S}_2\text{O}_{13}\text{Tb}$	3435s	1590s	3185m	1540m	415m	415m	-
9	$\text{C}_{36}\text{H}_{35}\text{N}_8\text{S}_2\text{O}_9\text{Cl}_2\text{Tb}$	3420s	1595s	3195m	-	405m	420m	-
10	$\text{C}_{26}\text{H}_{33}\text{N}_8\text{S}_2\text{O}_9\text{Tb}$	3440s	1615s	3198m	-	402m	415m	-
11	$\text{C}_{26}\text{H}_{31}\text{N}_{10}\text{S}_2\text{O}_{13}\text{Tb}$	3445s	1605s	3195m	1535m	405m	425m	-
12	$\text{C}_{26}\text{H}_{31}\text{N}_8\text{S}_2\text{O}_9\text{Cl}_2\text{Tb}$	3440s	1615s	3185m	-	410m	420m	-

Scanning electron microscope (SEM): The morphology of the complexes was examined utilizing filtering electron magnifying instrument. The sample of europium(III) demonstrates cuboid like morphology and terbium(III) indicates granular morphology at 5 μm determination (Figure 2).

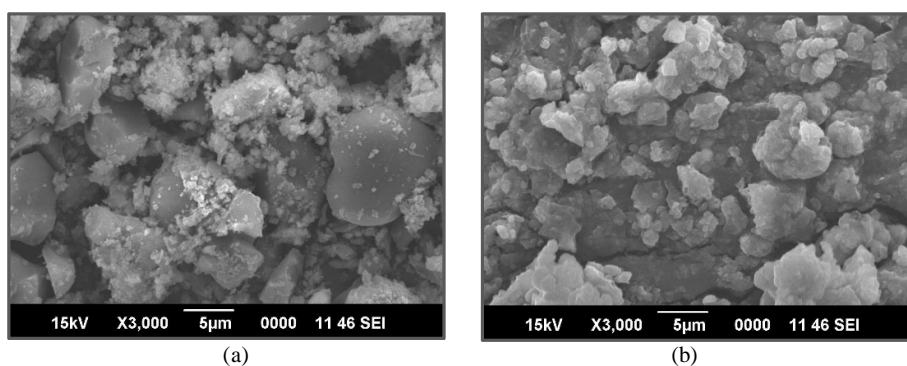


Figure 2. SEM images of (a) $[\text{Eu}(\text{L}_2)\text{Cl}_3(\text{H}_2\text{O})_3]$ and (b) $[\text{Tb}(\text{L}_3)(\text{OAc})_3(\text{H}_2\text{O})_3]$.

X-ray powder diffraction pattern: XRD is a systematic procedure utilizing electron diffraction on powder or microcrystalline samples for structural characterization and was completed utilizing an X-beam powder diffractometer (Figure 3). The X-beam powder diffraction of one of the denoted complex $[\text{C}_{36}\text{H}_{35}\text{N}_8\text{S}_2\text{O}_9\text{Cl}_2\text{Tb}]$ is appeared in figure 3. The size of the particle have been ascertained by utilizing Debye Scherrer formula [52-55] given as

$$D = 0.94\lambda / \beta \cos \theta$$

Where, D = size of the particle, λ = wavelength of X-rays, β = full width at half maximum (FWHM) and θ is the Bragg's angle diffraction. The particles size lies in the range of 09-20 nm.

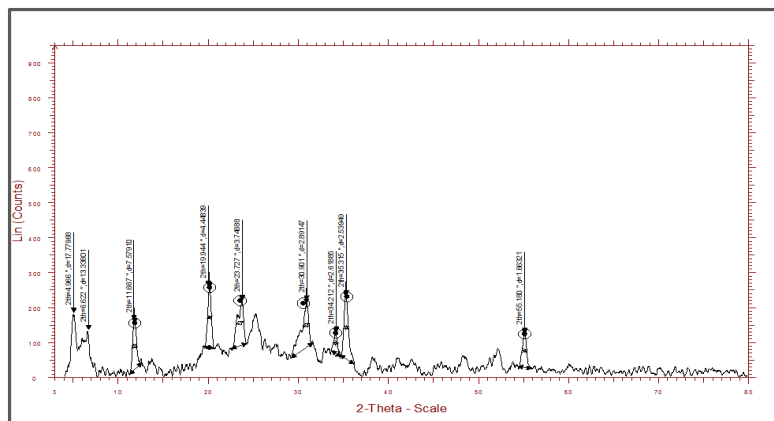


Figure 3. X-ray powder diffraction pattern of $[C_{36}H_{35}N_8S_2O_9Cl_2Tb]$.

Photoluminescence properties: The significance of the energy transfer from the excited organic ligand of the complex molecule is well known for lanthanide(III) ion [56]. The emission spectra of newly synthesized Eu(III) and Tb(III) complexes were measured in dichloromethane at room temperature (Fig. 4). There are five emission peak found at 390 nm excitation wavelength for Eu(III) complex and six emission peak found at 360 nm excitation wavelength for Tb(III) complex. Five emission peaks of Eu(III) complexes are at 374 nm, 419 nm, 448 nm, 575 nm, and 618 nm exhibits $^5D_3 \rightarrow ^7F_6$, $^5D_3 \rightarrow ^7F_1$, $^5D_3 \rightarrow ^7F_3$, $^5D_0 \rightarrow ^7F_0$, and $^5D_0 \rightarrow ^7F_2$ transitions, respectively. Six emission peaks of Tb(III) complexes are at 376 nm, 415 nm, 445 nm, 550 nm, 600 nm, 620 nm assignable to $^5D_3 \rightarrow ^7F_6$, $^5D_3 \rightarrow ^7F_5$, $^5D_3 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_3$ transitions, respectively. Difference in the position of the peak is due to environmental difference around the metals. The characteristic peaks of Eu(III) and Tb(III) exhibit the strong red and green emission found at 618 and 550 nm corresponding to $^5D_0 \rightarrow ^7F_2$ and $^5D_4 \rightarrow ^7F_5$ transitions, respectively which are electrical dipole allowed transitions. The peak at 618 nm is strongest for the Eu(III) complex and the peak at 550 nm is strongest for the Tb(III) complex. Nonetheless, the peak at 374 nm of Eu(III) complex and peak at 376 nm of Tb(III) complex are slightly stronger, which imitates the modification of the transition prospect and effect of diverse coordination spheres.

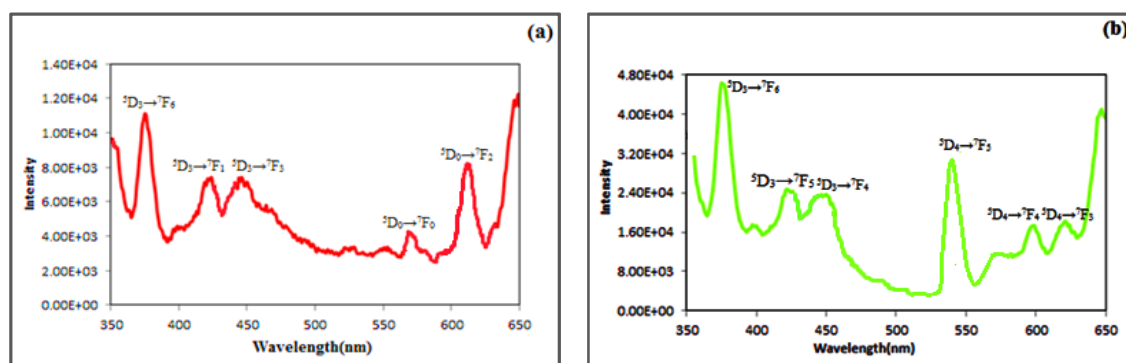
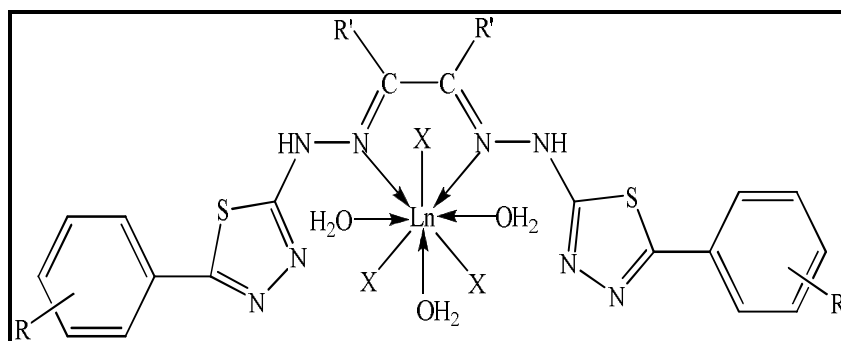


Figure 4. Emission spectra of (a) complex 3 and (b) complex 11

Thus, on the basis of elemental analyses and spectral data, the following structure is tentatively proposed for the complexes (Fig. 5).



(Where, Ln= Eu, Tb; X= Cl in case of Eu and OAc in case of Tb)

Figure 5. Proposed structure of complexes.

CONCLUSION

From the analytical and spectral information, it is concluded that the ligands act as bidentate chelating agents. The complexes with Eu(III) and Tb(III) demonstrated characteristic luminescence property which shows that the ligands have 'antenna effect' which absorbs and transfer energy to the lanthanide ion. The complexes of europium(III) and terbium(III) demonstrates solid characteristic outflow in red and green areas, individually.

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