

Synthesis, Characterization and Photo-Physical Properties of Europium(III) and Terbium(III) Complexes with Thiosemicarbazones

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Europium(III) and Terbium(III) complexes of type $[\text{Eu}(\text{L})\text{Cl}(\text{H}_2\text{O})_2]$ and $[\text{Tb}(\text{L})\text{OAc}(\text{H}_2\text{O})_2]$ (H_2L = thiosemicarbazone ligands derived from substituted thiosemicarbazide and benzil/diacetyl) were synthesized. The ligands and synthesized complexes were characterized on the basis of elemental analysis, FT-IR and ^1H NMR and X-ray diffraction studies. Photo-physical properties such as excitation spectra, emission spectra and luminescence curves of complexes were investigated. The most intense peak of Eu^{3+} ion found at 618 nm attributed to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition and peak of Tb^{3+} ion at 549 nm attributed to $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition.

Keywords: Thiosemicarbazone, Benzil, Diacetyl, IR, ^1H NMR, Luminescence spectra.

INTRODUCTION

Schiff bases are considered as an important class of organic compounds because of their ability to form complexes with transition and lanthanide metal ions [1-6] and for their photo-physical properties. Thiosemicarbazones have much interest for their variable N, S donor properties [7]. They have several physiological and biological properties such as antitumour, antibacterial, antiamoebic, antiviral, antimalarial properties [8,9]. Other useful applications are telecommunications, optical computing, optical storage, and optical information processing [10]. The derivative of thiosemicarbazones and their metal complexes have been broadly inspected [11-15]. Lanthanide complexes with organic Schiff base ligands have gained much attention from decades for their photo-physical properties such as catalysis, magnetism, luminescence, etc. [16-18]. The Schiff base lanthanide complexes doped by CdTe quantum dots have significantly improved their cytotoxic effect and indicate great potential of lanthanide doped quantum dots as cytocompatible and fluorophores for several bio-labelling applications [19]. The luminescent properties of lanthanides have been studied due to their wide applications in liquid crystal, biophysics, laser technology, optical telecommunication system and light emitting diodes (OLEDs) [20,21]. The fluorescence of some lanthanide ions (Eu^{3+} and Tb^{3+}) can be increased after their

coordination with appropriate organic ligands [22]. The decrease in fluorescence properties of Tb^{3+} showed sensitivity towards Cu^{2+} ions at low concentrations [23]. Lanthanide coordination compounds can be used as active centers of luminescent materials [24-26]. Rare earth complexes have much interest due to their biomedical diagnostic to photonic devices and solar energy conversion. The terbium complexes can possibly auxiliary analyze a few diseases in clinical practice through pH recognition of routine urine test [27]. Lanthanide complexes show luminescent properties with organic Schiff base ligands which are broadly studied in recent years [28-32]. This encouraged us to study the synthesis, structure and luminescent properties of new complexes of europium(III) and terbium(III) derived from substituted thiosemicarbazides and benzil/diacetyl.

EXPERIMENTAL

The reagents and solvents used were of analytical grade; europium(III) chloride were purchased from Sigma Aldrich (product of USA) and terbium(III) acetate were purchased from Alfa Aesar "A Johnson Matthey company" (product of Russia). Elemental analyses were analyzed by Elementar Vario EL III Carlo Erba 1108 models. FT-IR spectra were recorded on a Matson 1000 model FT-IR spectrophotometer as KBr disks. ^1H NMR spectra were recorded on a Perkin-Elmer R32 spectro-

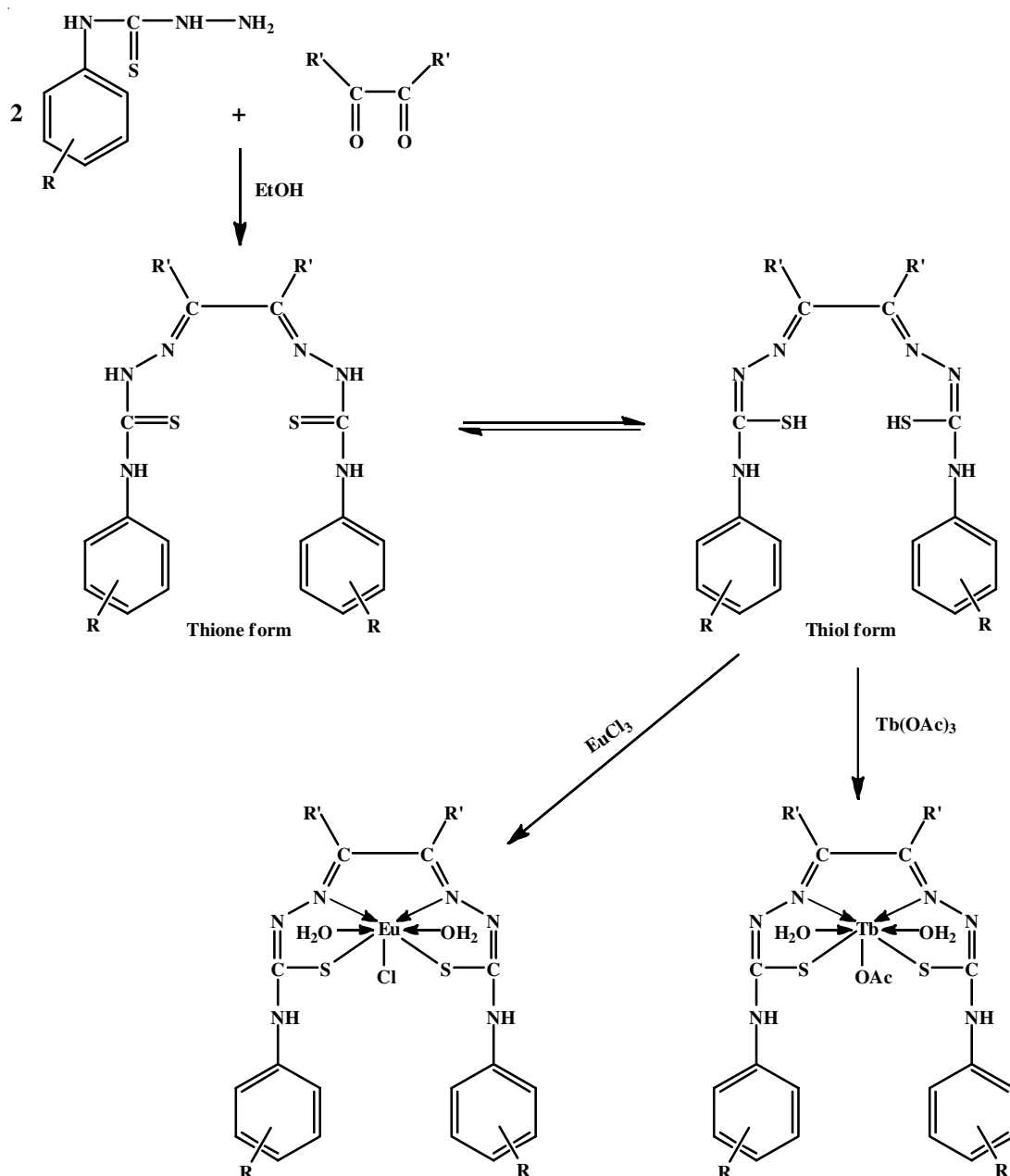
photometer using DMSO- d_6 as solvent. Chemical shifts (δ) are reported in ppm (parts per million) relative to an internal standard of tetramethylsilane. Scanning electron microscopy was recorded on JEOL model JSM-6390LV. Powdered XRD was scanned by Rigaku Geigerflex X-ray diffractometer with $\text{CuK}\alpha$ (1.54060) radiation. Luminescence spectra were recorded on a Shimadzu RF-5301 PC spectrofluorimeter with a 150 W xenon lamp.

Synthesis of Schiff base ligands: The ligands were prepared as reported in literature [33,34]. The required substituted aryl thiosemicarbazides have been prepared by the method of Kazakov *et al.* [35]. A mixture of appropriate amine (0.2 mol), liquid ammonia (33 cm^3) and carbon disulphide (19 cm^3) in methanol was treated with sodium salt of chloroacetic acid and then refluxed for 5-6 h with excess of hydrazine hydrate (11 cm^3). The reaction mixture was then poured into ice-cold

water. The product was filtered off and recrystallized. Then the obtained thiosemicarbazide and benzil/diacetyl in molar ratio of 2:1, respectively in ethanol (30 cm^3) containing few drops of concentrated hydrochloric acid was refluxed for 6-8 h and further recrystallized.

Synthesis of Eu(III) and Tb(III) complexes: An ethanolic solution (20 cm^3) of the appropriate europium chloride/ terbium acetate was added drop-wise to an ethanolic solution (20 cm^3) of Schiff base (0.02 mol) and sodium hydroxide (0.01 mol) and the reaction mixture was refluxed for 15-18 h. Colored precipitate were separated which were filtered, washed with ether and finally dried in *vacuo*.

The details of reactions along with the analytical data of the complexes are given in Table-1. The synthetic route is shown in **Scheme-I**.



[R = H, R' = Ph (L_1H_2); 4- NO_2 , R' = Ph (L_2H_2); 4-Br, R' = Ph (L_3H_2); H, R' = CH_3 (L_4H_2); 4- NO_2 , R' = CH_3 (L_5H_2); 4-Br, R' = CH_3 (L_6H_2)]

Scheme-I: Reaction scheme for the synthesis of ligands and their Eu(III) and Tb(III) complexes

TABLE-1
 SYNTHETIC AND ANALYTICAL DATA OF Eu(III) AND Tb(III) COMPLEXES

Reactants	Refluxing time (h)	Product	Yield (%)	Colour	Elemental analysis (%): Found (calcd.)			
					C	H	N	Ln
EuCl ₃ + L ₁ H ₂	16	[Eu(L ₁)Cl(H ₂ O) ₂]	65	Brown	46.01 (46.15)	3.55 (3.64)	11.51 (11.74)	20.89 (21.05)
EuCl ₃ + L ₂ H ₂	16	[Eu(L ₂)Cl(H ₂ O) ₂]	68	Yellow	41.09 (41.25)	2.74 (2.94)	13.65 (13.80)	18.51 (18.65)
EuCl ₃ + L ₃ H ₂	18	[Eu(L ₃)Cl(H ₂ O) ₂]	67	Brown	36.51 (36.75)	2.64 (2.84)	12.46 (12.66)	16.46 (16.74)
EuCl ₃ + L ₄ H ₂	16	[Eu(L ₄)Cl(H ₂ O) ₂]	60	Brown	35.23 (35.65)	3.25 (3.55)	13.54 (13.72)	25.09 (25.22)
EuCl ₃ + L ₅ H ₂	16	[Eu(L ₅)Cl(H ₂ O) ₂]	66	Yellow	31.12 (31.36)	2.59 (2.84)	16.23 (16.55)	21.37 (21.61)
EuCl ₃ + L ₆ H ₂	18	[Eu(L ₆)Cl(H ₂ O) ₂]	65	Brown	27.24 (27.45)	2.49 (2.76)	14.39 (14.64)	19.23 (19.48)
Tb(OAc) ₃ + L ₁ H ₂	17	[Tb(L ₁)OAc(H ₂ O) ₂]	70	Yellow	47.34 (47.41)	3.82 (3.95)	11.25 (11.47)	20.58 (20.76)
Tb(OAc) ₃ + L ₂ H ₂	15	[Tb(L ₂)OAc(H ₂ O) ₂]	60	Brown	42.36 (42.54)	3.19 (3.40)	13.22 (13.54)	18.71 (18.97)
Tb(OAc) ₃ + L ₃ H ₂	17	[Tb(L ₃)OAc(H ₂ O) ₂]	68	Yellow	38.21 (38.45)	2.75 (2.91)	11.68 (11.84)	16.74 (16.96)
Tb(OAc) ₃ + L ₄ H ₂	18	[Tb(L ₄)OAc(H ₂ O) ₂]	63	Brown	37.48 (37.76)	3.52 (3.82)	13.15 (13.44)	25.20 (25.45)
Tb(OAc) ₃ + L ₅ H ₂	16	[Tb(L ₅)OAc(H ₂ O) ₂]	65	Brown	33.04 (33.28)	3.26 (3.56)	15.42 (15.72)	21.74 (21.97)
Tb(OAc) ₃ + L ₆ H ₂	16	[Tb(L ₆)OAc(H ₂ O) ₂]	70	Brown	29.05 (29.28)	2.60 (2.95)	13.56 (13.88)	19.38 (19.69)

RESULTS AND DISCUSSION

The complexes are partially soluble in common organic solvents. However these complexes are soluble in DMF and DMSO. Magnetic susceptibility measurement showed that the complexes are paramagnetic in nature. The presence of coordinated water molecule is inferred from thermogravimetric analysis, which indicates loss of two water molecules at 150–170 °C. The electrical conductivity measurements show that the complexes are non-electrolytes.

IR spectra: The IR spectra provide valuable information regarding the nature of functional group attached to the metal ion given in the Table-2. The characteristic absorption of all complexes shows bands at 3440–3400 cm⁻¹ which corresponded to the ν(O-H) [36]. Schiff base shows the medium intensity band about 3250–3180 cm⁻¹ due to ν(N-H) which remains almost at the same position in the complexes indicating the non-involvement of the (N-H) group in the bond formation [37]. The absorption due to C=N group of the free ligand present around 1610–1600 cm⁻¹ region undergoes a negative shift by 51–18 cm⁻¹ (1559–1582 cm⁻¹) in the spectra of the complexes indicating the coordination of azomethine nitrogen to the metal. The ν(N-N) bands of the ligands are present around ~1060 cm⁻¹. The increase in frequency of this band 1082–1062 cm⁻¹ in the spectra of the complexes provides evidence for the coordination *via* the azomethine nitrogen [38]. A strong band in the 3020–2988 cm⁻¹ region attributed to ν(N-H) group of –NH–N=C–. The band present around 856–810 cm⁻¹ in the spectra of thiosemicarbazone ligands is assigned to –HN–C=S

group. This band is not present in the spectra of the complexes. But new bands are present at 1540–1525 and 758–740 cm⁻¹ which are assigned to the new azomethine group –C=N–N and –C–S, respectively. These observation indicate the enolization of the –NH–C=S group and subsequent deprotonation before coordination to the metal. On the other hand spectra of Ln(III) complexes exhibit new bands of ν(Ln–N), ν(Ln–O) and ν(Ln–S) at (594–552), (527–510) and (480–440) cm⁻¹, respectively which indicates that the Ln(III) ion is coordinated through the azomethine N, thio S and phenolic oxygen on loss of the OH proton (Fig. 1).

¹H NMR: The proton magnetic resonance spectra of terbium(III) complexes have been measured in DMSO-*d*₆. Chemical shifts for proton in different atmosphere have been

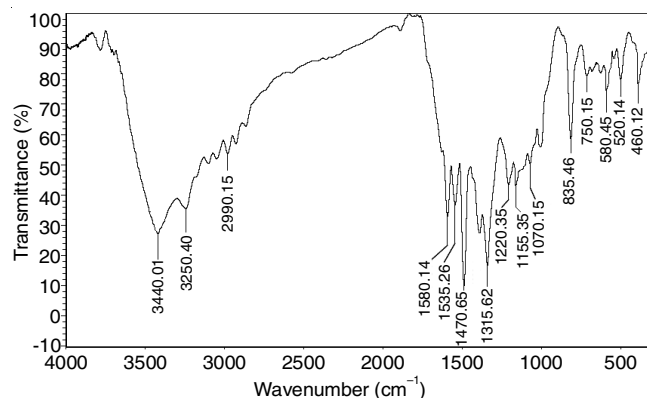


Fig. 1. Infrared spectrum of one of the representative [Eu(L₂)Cl(H₂O)₂] complex

 TABLE-2
 IMPORTANT INFRARED FREQUENCIES (cm⁻¹) OF Eu(III) AND Tb(III) COMPLEXES

Complexes	ν(O–H)	ν(C=N)	ν(N–N)	ν(N–H)	ν(Ln–N)	ν(Ln–S)	ν(Ln–O)
[Eu(L ₁)Cl(H ₂ O) ₂]	3440	1580	1070	2990	580	520	460
[Eu(L ₂)Cl(H ₂ O) ₂]	3435	1565	1070	2988	552	510	440
[Eu(L ₃)Cl(H ₂ O) ₂]	3425	1580	1070	3000	580	520	445
[Eu(L ₄)Cl(H ₂ O) ₂]	3420	1580	1075	3000	570	525	455
[Eu(L ₅)Cl(H ₂ O) ₂]	3425	1580	1082	2995	575	525	445
[Eu(L ₆)Cl(H ₂ O) ₂]	3410	1580	1072	2990	570	520	460
[Tb(L ₁)OAc(H ₂ O) ₂]	3435	1580	1075	2995	594	525	470
[Tb(L ₂)OAc(H ₂ O) ₂]	3440	1559	1075	2995	575	520	450
[Tb(L ₃)OAc(H ₂ O) ₂]	3420	1582	1062	3005	590	527	460
[Tb(L ₄)OAc(H ₂ O) ₂]	3425	1580	1070	3015	580	520	440
[Tb(L ₅)OAc(H ₂ O) ₂]	3435	1570	1075	3020	575	525	460
[Tb(L ₆)OAc(H ₂ O) ₂]	3400	1570	1078	3015	580	515	480

given in Table-3. Schiff bases ligands show signal at about δ 3.75 ppm due to $-\text{SH}$ proton indicates the existence of the ligands in thiol form. In complexes, $-\text{SH}$ signal disappears due to formation of sulfur and metal bond. Schiff bases and their Ln(III) complexes indicate signals at δ 1.80-1.86 ppm due to methyl proton. The chemical shift about δ 7.10-8.19 ppm appears as multiplet due to aromatic rings in the spectra of Schiff bases and their complexes. Ln(III) complexes show new signals at δ 5.52-5.58 ppm due to water proton. The chemical shift at about δ 12.35 ppm appears as singlet for $-\text{NH}$ proton in Schiff bases and their complexes.

SEM analysis: The morphology of the samples was studied using a scanning electron microscope (SEM). The sample shows cuboid like morphology for europium(III) complexes.

On the other hand terbium complexes shows granular irregular like morphology. The obtained morphology is shown in Fig. 2.

X-ray powder diffraction pattern: Our efforts to prepare single crystals of these complexes were unsuccessful due to high molecular mass of the metal ions involved. Therefore, powder diffraction patterns were recorded. Powder diffraction is a rapid analytical technique based on constructive interference of monochromatic X-ray and a crystalline sample [39,40]. The X-ray techniques are generated by a cathode ray tube, filtered to produce monochromatic radiation to concentrate and directed towards the sample.

X-ray powder diffraction pattern of one of the representative complex $[\text{Eu}(\text{L}_2)\text{Cl}(\text{H}_2\text{O})_2]$ is shown in Fig. 3. The peak

TABLE-3
 ^1H NMR DATA (δ , ppm) OF Tb(III) COMPLEXES

Complexes	Aromatic ring	$-\text{CH}_3$	$-\text{NH}$	$-\text{OAc}$	H_2O
$[\text{Tb}(\text{L}_1)\text{OAc}(\text{H}_2\text{O})_2]$	7.10-7.79(m)	—	12.35(s)	2.21(s)	5.52(s)
$[\text{Tb}(\text{L}_2)\text{OAc}(\text{H}_2\text{O})_2]$	7.42-8.19(m)	—	12.30(s)	2.19(s)	5.54(s)
$[\text{Tb}(\text{L}_3)\text{OAc}(\text{H}_2\text{O})_2]$	7.19-7.47(m)	—	12.25(s)	2.25(s)	5.58(s)
$[\text{Tb}(\text{L}_4)\text{OAc}(\text{H}_2\text{O})_2]$	7.10-7.85(m)	1.80(s)	12.26(s)	2.22(s)	5.51(s)
$[\text{Tb}(\text{L}_5)\text{OAc}(\text{H}_2\text{O})_2]$	7.50(d), 8.19(d)	1.83(s)	12.15(s)	2.20(s)	5.54(s)
$[\text{Tb}(\text{L}_6)\text{OAc}(\text{H}_2\text{O})_2]$	7.19(d), 7.45(d)	1.86(s)	12.22(s)	2.26(s)	5.57(s)

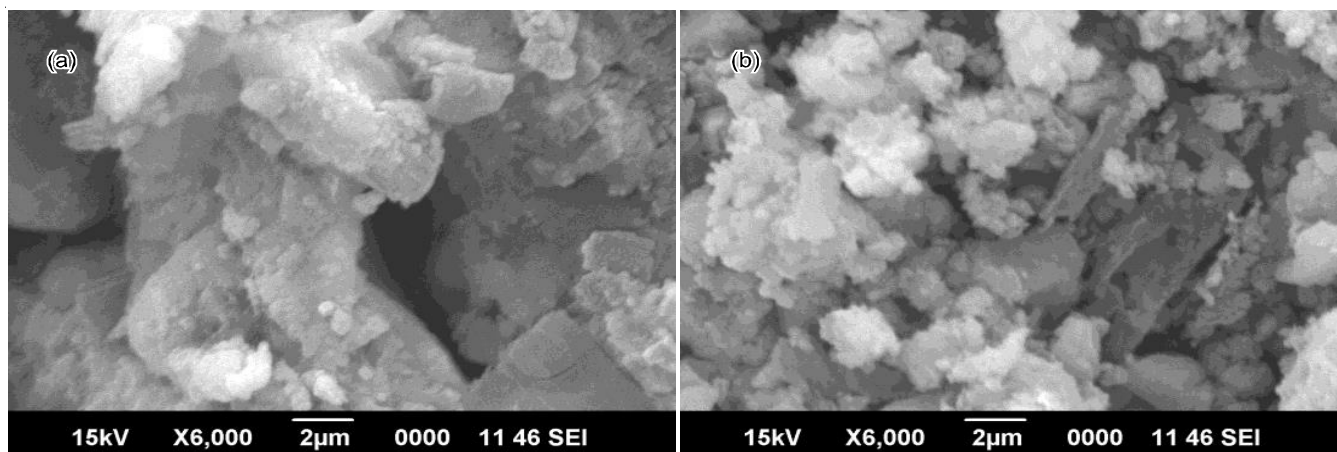


Fig. 2. SEM images of (a) $[\text{Eu}(\text{L}_2)\text{Cl}(\text{H}_2\text{O})_2]$ and (b) $[\text{Tb}(\text{L}_2)\text{OAc}(\text{H}_2\text{O})_2]$ complexes

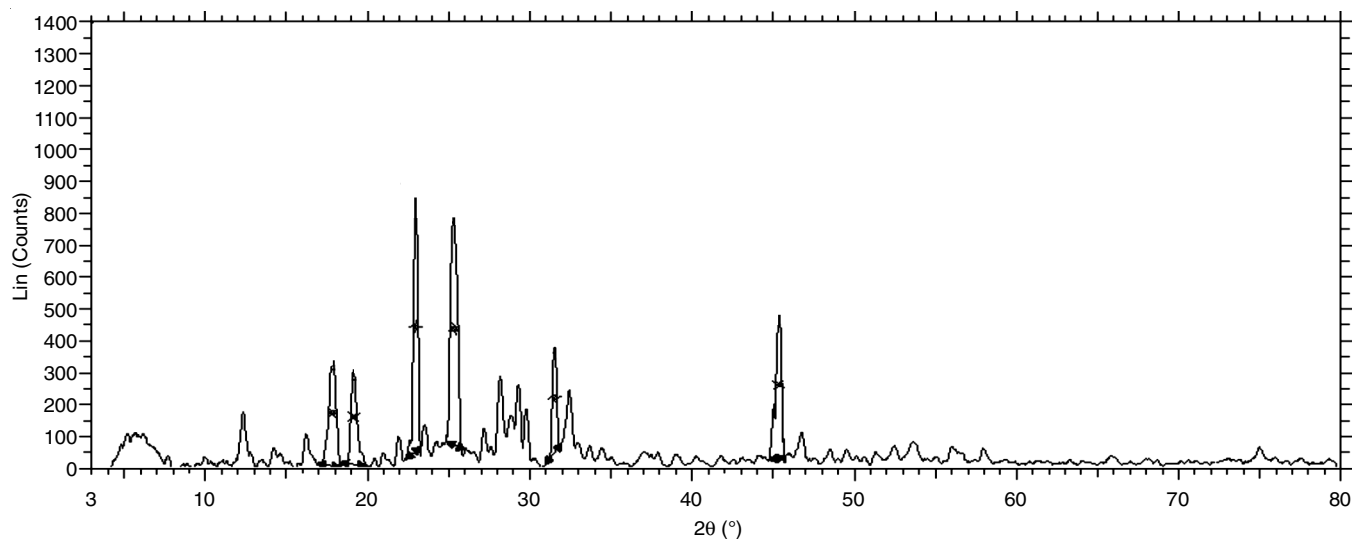


Fig. 3. X-ray powder diffraction pattern of one representative complex $[\text{Eu}(\text{L}_2)\text{Cl}(\text{H}_2\text{O})_2]$

broadening at lower angle is significant for the calculation of particle size and therefore the size of the particle has been calculated using the Debye-Scherrer formula [41-44]:

$$D = \frac{0.94\lambda}{\beta \cos \theta}$$

where D is the size of the particle; λ is the wavelength of X-rays; β (in rad) is the full width at half maximum after correcting the instrument peak broadening; and θ is the Bragg angle. The size of the particles is found to be in the range of 15-30 nm.

The indexing of h k l for complex was carried out using the N-TREOR program. The Miller indices (h k l) relate the peak positions or *d*-spacings to the lattice parameters by an equation specific to the crystal system. The trial and error method was used to determine the initial unit cell parameters. These unit cell parameters were refined from the regression analysis and the best crystal system and space group were assigned using CHEKCELL program. It was found that the complex [Eu(L₂)Cl(H₂O)₂] reveal monoclinic crystal system with the most probable space group P2₁/c. The lattice parameters observed and calculated X-ray diffraction data for the complexes have been shown in Table-4.

Photo-physical properties: The photoluminescence behaviour of europium(III) and terbium(III) compounds were measured in DMF at room temperature. Excitation and emission spectra of luminescent complexes of [Eu(L₃)Cl(H₂O)₂] and [Tb(L₃)OAc(H₂O)₂] are presented in Figs. 4 and 5. The embedded pictures of these complexes were taken under excitation with a 4 W UV-A Philips TL4WBLB fluorescent lamp.

[Eu(L₃)Cl(H₂O)₂] exhibits the most intense excitation peak of Eu³⁺ centered at 393 nm which corresponds to the ⁷F₀ → ⁵L₇ excited level transition. The emission spectrum of Eu(III) complex consists of five emission bands at 460, 580, 618, 638 and 685 nm corresponding to the ⁵D₃ → ⁷F₃, ⁵D₀ → ⁷F₀, ⁵D₀ → ⁷F₂, ⁵D₀ → ⁷F₃ and ⁵D₀ → ⁷F₄ electronic transitions, respectively (Fig. 4a-b). The less intense emission peak at 580 nm is attributed to ⁵D₀ → ⁷F₀ partially allowed magnetic dipole transition which is known to be unaffected by the surrounding symmetry. Among the ⁵D₀ → ⁷F₂ electrical-dipole allowed transition is most intense and exhibits the strong red emission which is known to be highly affected by the symmetry of the crystal field surrounding the Eu³⁺ cation, being relatively stronger in case of lower surrounding symmetry.

TABLE-4
UNIT CELL PARAMETERS AND OBSERVED & CALCULATED X-RAY DIFFRACTION DATA OF [Eu(L₂)Cl(H₂O)₂]

d (obs.)	d (calc.)	Δ (d)	I/I _m × 100	2θ (obs)	2θ (calc.)	Δ (2θ)	h k l
4.98841	5.41537	-0.42696	37.81	17.7660	16.355	1.411	2 0 1
4.65087	4.31396	0.33691	37.09	19.067	20.572	-1.505	-2 0 2
3.87716	4.31396	-0.43679	100.00	22.919	20.572	2.347	2 0 2
3.52468	3.44107	0.08361	97.11	25.247	25.871	-0.624	-3 1 1
3.16921	3.19860	-0.02939	34.09	28.134	27.870	0.264	-2 2 1
2.83825	2.80036	0.03788	46.81	31.495	31.932	-0.437	-1 1 4
1.99707	1.98211	0.01496	58.82	45.376	45.738	-0.362	-6 0 1

a = 11.9958 Å; b = 7.6258 Å; c = 12.2642 Å; β = 100.29°; V = 1103.855 Å³

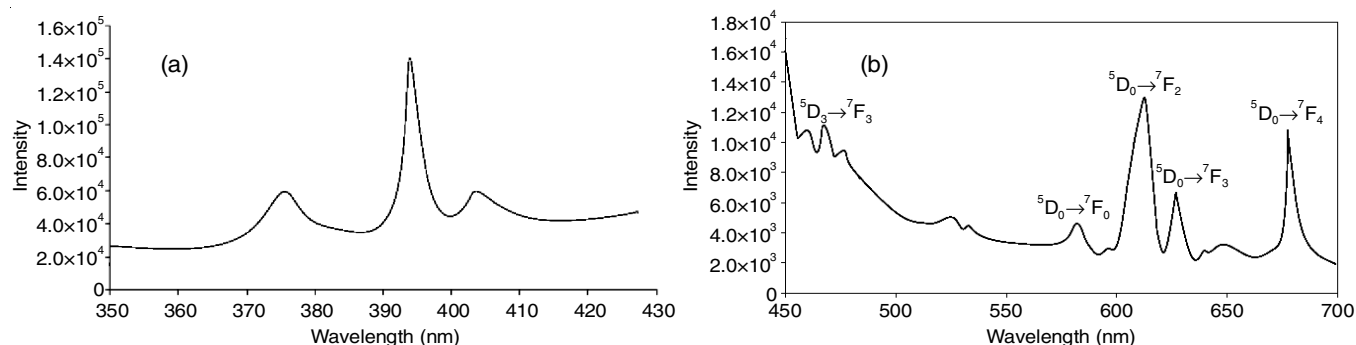


Fig. 4. (a) Excitation and (b) emission spectra of the [Eu(L₃)Cl(H₂O)₂]

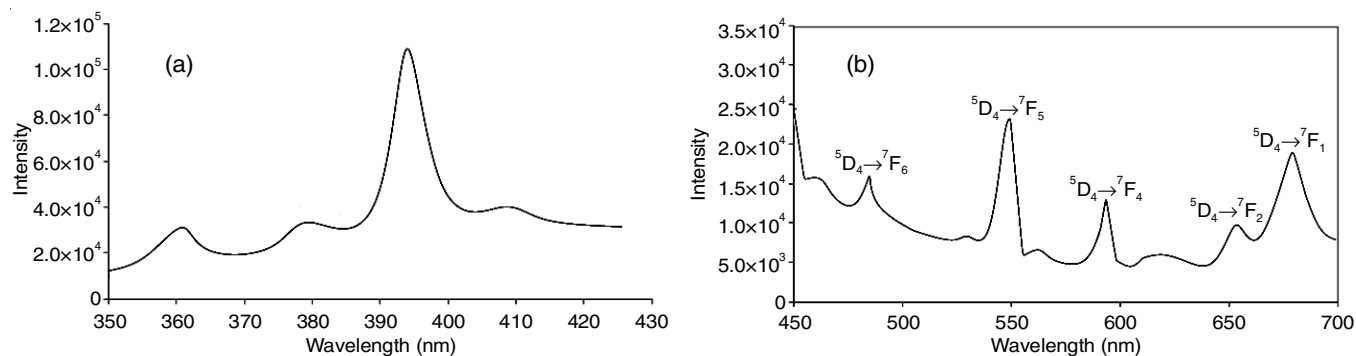


Fig. 5. (a) Excitation and (b) emission spectra of the [Tb(L₃)OAc(H₂O)₂]

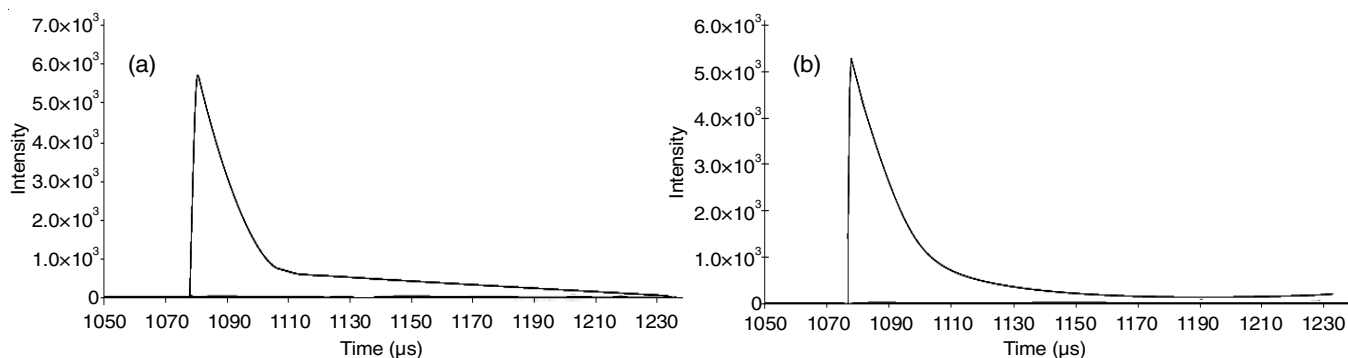


Fig. 6. Luminescence decay curve of (a) $[\text{Eu}(\text{L}_3)\text{Cl}(\text{H}_2\text{O})_2]$ (b) $[\text{Tb}(\text{L}_3)\text{OAc}(\text{H}_2\text{O})_2]$

On the other hand, the excitation spectra of terbium(III) complex $[\text{Tb}(\text{L}_3)\text{OAc}(\text{H}_2\text{O})_2]$ exhibits the most intense excitation peak at 395 nm which corresponds to the $^7\text{F}_6 \rightarrow ^5\text{L}_{10}$ excited level transition of Tb^{3+} . The emission spectrum of the Tb(III) complex exhibits five emission bands at 485, 549, 592, 656 and 678 nm corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, $^5\text{D}_4 \rightarrow ^7\text{F}_2$ and $^5\text{D}_4 \rightarrow ^7\text{F}_1$ electronic transitions, respectively (Fig. 5a-b). $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition is most intense and practically unaffected by the symmetry of the crystalline field surrounding the emissive centre exhibits the strong green emission. The less intense emission peak centered at 656 nm is attributed to $^5\text{D}_4 \rightarrow ^7\text{F}_2$ which is known to be moderately sensitive to the surrounding site. Furthermore, this emission spectra of the europium and terbium complexes shows a high background which can be ascribed as the characteristic fluorescence for the ligand L. It is shown that the energy of H_2L ligand transfers to Eu^{3+} and Tb^{3+} totally. This property of emission spectrum is similar to that of the reported complexes [45]. The appearance of weak characteristics emission of Eu(III) and Tb(III) ions and the fluorescence of the ligand L may be due to the competition between the ligand fluorescence process and the energy transfer process from the lowest triplet state level of the ligand to the excited state level of the ligand to the excited state of Eu(III) and Tb(III). Through intersystem crossing, the efficient energy transfer from the triplet state of the ligands crossed to reach the emissive level of the central lanthanides cation is achieved only when the prepared complexes are in crystalline or solid form. The two water molecule presented in the coordination sphere seem to play less important role in quenching the luminescent emission of the lanthanide cation since they are equally present in the luminescent prepared complexes.

The quantum yield and luminescence life times of both europium(III) and terbium(III) complexes were investigated. The quantum yields of $[\text{Eu}(\text{L}_3)\text{Cl}(\text{H}_2\text{O})_2]$ and $[\text{Tb}(\text{L}_3)\text{OAc}(\text{H}_2\text{O})_2]$ complexes were found to be 0.49 and 0.53, respectively. Luminescence decay curves obtained at room temperature by monitoring the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions (618 nm) for europium(III) complexes and $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (549 nm) for terbium(III) complexes. Decay curves for the both complexes can be good fitted by single exponential function and the lifetime values were found to be 16 and 11 μs for $[\text{Eu}(\text{L}_3)\text{Cl}(\text{H}_2\text{O})_2]$ and $[\text{Tb}(\text{L}_3)\text{OAc}(\text{H}_2\text{O})_2]$ complexes, respectively (Fig. 6a-b).

Conclusion

In this work, new Eu(III) and Tb(III) complexes of thiosemicarbazones are synthesized and characterized. The analy-

tical and spectral data reveal that the Schiff base coordinates to the central Ln(III) by its two azomethine nitrogen atoms and two oxygen atoms of water molecule. Europium(III) and terbium(III) complexes exhibit characteristic luminescence in red and green regions, respectively.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- N.F. Choudhary, N.G. Connelly, P.B. Hitchcock and G.J. Leigh, *J. Chem. Soc., Dalton Trans.*, 4437 (1999); <https://doi.org/10.1039/a908337e>
- Z.L. You, L.L. Tang and H.L. Zhu, *Acta Crystallogr. Sect. E Struct. Rep. Online*, **61**, m36 (2005); <https://doi.org/10.1107/S1600536804031368>
- S.A. Abdallah, G. Mohamed, M. Zayed and M. El-Ela, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **73**, 833 (2009); <https://doi.org/10.1016/j.saa.2009.04.005>
- P.A. Vigato and S. Tamburini, *Coord. Chem. Rev.*, **248**, 1717 (2004); <https://doi.org/10.1016/j.cct.2003.09.003>
- S.L. Barnholtz, J.D. Lydon, G. Huang, M. Venkatesh, C.L. Barnes, A.R. Ketring and S.S. Jurisson, *Inorg. Chem.*, **40**, 972 (2001); <https://doi.org/10.1021/ic001073m>
- S. Chattopadhyay, M.G.B. Drew and A. Ghosh, *Eur. J. Inorg. Chem.*, 1693 (2008); <https://doi.org/10.1002/ejic.200701025>
- B. Gingras, R. Somorjai and C. Bayley, *Can. J. Chem.*, **39**, 973 (1961); <https://doi.org/10.1139/v61-122>
- J. Perez, A. Matesanz, A. Martinambite, P. Navarro, C. Alonso and P. Souza, *J. Inorg. Biochem.*, **75**, 255 (1999); [https://doi.org/10.1016/S0162-0134\(99\)00096-3](https://doi.org/10.1016/S0162-0134(99)00096-3)
- P.F. Kelly, A.M.Z. Slawin and A. Soriano-Rama, *J. Chem. Soc., Dalton Trans.*, 53 (1996); <https://doi.org/10.1039/dt9960000053>
- Y.P. Tian, C.Y. Duan, C.Y. Zhao, X.Z. You, T.C.W. Mak and Z.Y. Zhang, *Inorg. Chem.*, **36**, 1247 (1997); <https://doi.org/10.1021/ic9603870>
- M.J. Campbell, *Coord. Chem. Rev.*, **15**, 279 (1975); [https://doi.org/10.1016/S0010-8545\(00\)80276-3](https://doi.org/10.1016/S0010-8545(00)80276-3)
- S. Padhye and G.B. Kauffman, *Coord. Chem. Rev.*, **63**, 127 (1985); [https://doi.org/10.1016/0010-8545\(85\)80022-9](https://doi.org/10.1016/0010-8545(85)80022-9)
- D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, P.B. Sonawane, A.S. Kumbhar and R.G. Yerande, *Coord. Chem. Rev.*, **123**, 49 (1993); [https://doi.org/10.1016/0010-8545\(93\)85052-6](https://doi.org/10.1016/0010-8545(93)85052-6)

14. N. Farrell, *Coord. Chem. Rev.*, **232**, 1 (2002); [https://doi.org/10.1016/S0010-8545\(02\)00100-5](https://doi.org/10.1016/S0010-8545(02)00100-5)
15. T.S. Lobana, R. Sharma, G. Bawa and S. Khanna, *Coord. Chem. Rev.*, **253**, 977 (2009); <https://doi.org/10.1016/j.ccr.2008.07.004>
16. J.C.G. Bunzli and C. Piguet, *Chem. Soc. Rev.*, **34**, 1048 (2005); <https://doi.org/10.1039/b406082m>
17. J.C.G. Bunzli, S. Comby, A.S. Chauvin and C.D.B. Vandevyver, *J. Rare Earths*, **25**, 257 (2007); [https://doi.org/10.1016/S1002-0721\(07\)60420-7](https://doi.org/10.1016/S1002-0721(07)60420-7)
18. J. Kido and Y. Okamoto, *Chem. Rev.*, **102**, 2357 (2002); <https://doi.org/10.1021/cr010448y>
19. H. Buchtelova, V. Strmiska, Z. Skubalova, S. Dostalova, P. Michalek, S. Krizkova, D. Hynek, L. Kalina, L. Richtera, A. Moulick, V. Adam and Z. Heger, *J. Nanobiotechnology*, **16**, 43 (2018); <https://doi.org/10.1186/s12951-018-0369-7>
20. L.M. Hayden, W.-K. Kim, A.P. Chafin and G.A. Lindsay, *Macromolecules*, **34**, 1493 (2001); <https://doi.org/10.1021/ma001796p>
21. J.-C.G. Bunzli and G.R. Choppin, *Chemical and Earth Sciences: Theory and Practice*, Elsevier: Amsterdam, p. 432 (1989).
22. L.Z. Guo, S.Z. Wu, F. Zeng and J.Q. Zhao, *Eur. J. Polym.*, **42**, 1670 (2006); <https://doi.org/10.1016/j.eurpolymj.2006.01.025>
23. R. Chan-Navarro, P. Elizondo, M.C. García-López, R.M. Jiménez-Barrera, N. Pérez, M. Guadalupe-Sánchez and L.A. Garza, *Polyhedron*, **149**, 66 (2018); <https://doi.org/10.1016/j.poly.2018.04.026>
24. P.N. Remya, S. Biju, M.L.P. Reddy, A.H. Cowley and M. Findlater, *Inorg. Chem.*, **47**, 7396 (2008); <https://doi.org/10.1021/ic800615y>
25. C.M.G. dos Santos, A.J. Harte, S.J. Quinn and T. Gunnlaugsson, *Coord. Chem. Rev.*, **252**, 2512 (2008); <https://doi.org/10.1016/j.ccr.2008.07.018>
26. F.T. Edelmann, *Coord. Chem. Rev.*, **253**, 343 (2009); <https://doi.org/10.1016/j.ccr.2008.03.003>
27. A.-M. Luo, Y. Shao, K.-J. Zhang, Y.-W. Wang and Y. Peng, *Chin. Chem. Lett.*, **28**, 2009 (2017); <https://doi.org/10.1016/j.ccllet.2017.08.037>
28. N.P. Kuz'mina and S.V. Eliseeva, *Russ. J. Inorg. Chem.*, **51**, 73 (2006); <https://doi.org/10.1134/S0036023606010141>
29. H.J. Kim, J.E. Lee, Y.S. Kim and N.G. Park, *Opt. Mater.*, **21**, 181 (2003); [https://doi.org/10.1016/S0925-3467\(02\)00133-7](https://doi.org/10.1016/S0925-3467(02)00133-7)
30. G. Vicentini, L.B. Zinner, J. Zukerman-Schpector and K. Zinner, *Coord. Chem. Rev.*, **196**, 353 (2000); [https://doi.org/10.1016/S0010-8545\(99\)00220-9](https://doi.org/10.1016/S0010-8545(99)00220-9)
31. J.C.G. Bunzli and C. Piguet, *Chem. Rev.*, **102**, 1897 (2002); <https://doi.org/10.1021/cr010299j>
32. K. Binnemans, *Chem. Rev.*, **109**, 4283 (2009); <https://doi.org/10.1021/cr8003983>
33. M. Christlieb and J.R. Dilworth, *Eur. J. Chem.*, **12**, 6194 (2006); <https://doi.org/10.1002/chem.200501069>
34. H.D. Yin and S.W. Chen, *Inorg. Chim. Acta*, **359**, 3330 (2006); <https://doi.org/10.1016/j.ica.2006.03.024>
35. V.Y. Kazakov and I.Y. Postouskii, *Dokl. Akad. Nauk SSSR*, **134**, 824 (1960).
36. K. Singh, M.S. Barwa and B.P. Tyagi, *Eur. J. Med. Chem.*, **42**, 394 (2007); <https://doi.org/10.1016/j.ejmech.2006.10.016>
37. C. Jayabalakrishnan, R. Karvembu and K. Natarajan, *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 1099 (2002); <https://doi.org/10.1081/SIM-120013023>
38. A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press: New York (1968).
39. C.J. Athira, Y. Sindhu, M.S. Sujamol and K. Mohanan, *J. Serb. Chem. Soc.*, **76**, 249 (2011); <https://doi.org/10.2298/JSC100414025A>
40. U. Holzwarth and N. Gibson, *Nat. Nanotechnol.*, **6**, 534 (2011); <https://doi.org/10.1038/nnano.2011.145>
41. K.S. Rathore, D. Patidar, Y. Janu, N.S. Saxena, K. Sharma and T.P. Sharma, *Chalcogenide Lett.*, **5**, 105 (2008).
42. A. Altomare, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, R. Rizzi and P.-E. Werner, *J. Appl. Cryst.*, **33**, 1180 (2000); <https://doi.org/10.1107/S0021889800006427>
43. J. Laugier and B. Bochu, LMGP-Suite of Programs for the Interpretation of X-Ray Experiments, ENSP, Saint Martin d'Hères, France (2002).
44. D. Armentano, G. De Munno, F. Lloret, A.V. Palli and M. Julve, *Inorg. Chem.*, **41**, 2007 (2002); <https://doi.org/10.1021/ic011100o>
45. Z.H. Zhang, T. Okamura, Y. Hasegawa, H. Kawaguchi, L.Y. Kong, W.Y. Sun and N. Ueyama, *Inorg. Chem.*, **44**, 6219 (2005); <https://doi.org/10.1021/ic050453a>