

Synthesis, Structure and Luminescent Properties of New Ce(III), Dy(III), Ho(III) and Tm(III) Complexes with 2-(1H-1,2,4-Triazol-3-yl)pyridine

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In this work, four new complexes of Ce³⁺, Dy³⁺, Ho³⁺ and Tm³⁺ with 2-(1H-1,2,4-triazol-3-yl)pyridine (Htzp) were synthesized and further studied. The complexes were prepared at 1/3 metal to ligand ratio and elemental analysis, mass spectrometry, thermal analysis, FT-IR and powder-XRD methods were used to investigate their structural configuration. Data obtained through analysis revealed the formation of the complexes with the general formula [Ln(tzp)₃(H₂O)₃] where Ln = Ce³⁺, Dy³⁺, Ho³⁺, Tm³⁺. Fluorescence spectroscopy revealed in case of Dy³⁺ complex specific metal centered narrow band emissions from the *f-f* transitions within 4*f* orbitals, while in case of Ce³⁺ complex a wide band emission was recorded most probable due to the heavy atom effect over the excited intra ligand states.

Keywords: Lanthanide complexes, Triazol-pyridine, Metal centered luminescence.

INTRODUCTION

The search for new suitable ligands capable of complexing the lanthanides is attracting much interest both in terms of expanding the knowledge over lanthanide chemistry and due to the unique features of the lanthanides which could be valued through complexation. Thus, lanthanide complexes are highly regarded in applications ranging from catalysis^{1,2}, optoelectronics^{3,4}, sensors to biomedical investigation techniques^{5,6}. Through the use of selected ligands, highly luminescent lanthanide complexes could be easily prepared. Their characteristic narrow emission bands are due to the radiative transitions occurring within 4*f* orbitals which are partially shielded by the 5*s* and 5*p* orbitals⁷. Owing to the small absorption coefficients of Ln³⁺ cations due to the shielded inner *f* orbitals, efficient radiative transitions can be achieved through efficient energy transfer from the ligand to the emissive lanthanide center. The sensitization of the lanthanide cation may be achieved through coordination of a chromophore containing ligand capable of energy absorption which could be efficiently transferred to the emitting state of the lanthanide cation.

A wide variety of lanthanide complexes have been studied so far as luminescent probes in biomedical investigations using various classes of ligands, among the most notable being carboxylates⁸, polyaminocarboxylates⁹, phosphonates¹⁰,

phosphinates¹¹, β-diketonates¹². Zhang and co-workers¹³ have successfully obtained dysprosium and thulium complexes using 4,4,4-trifluoro-1-phenyl-1,3-butanedione (Hbfa) and 1,10-phenanthroline (phen) ligands which are of interest for optical communications. Dy(bfa)₃phen complexes and Tm(bfa)₃phen complex are potential candidates for developing new materials suitable for broad band optical communications. Lanthanides have a larger radius and a higher affinity for hard donor centers and ligands with nitrogen atoms, especially azamacrocyclic (tri-, tetra-, penta-, hexa azamacrocyclic) ligands that are in favour of building complexes of lanthanides¹⁴. The triazole derivatives due to the position of the donor atoms within the five membered ring are potentially suitable candidates for preparation of lanthanide complexes. The triazole ligands may constitute a bridge between the metal ions. Depending on the donor atoms of the ligand, the bridge could have several different geometries, leading to various configurations of the prepared complexes. Caballero *et al.*¹⁵ describe the synthesis and physical properties of a new Dy³⁺ complex [Dy(mtpO)₃(H₂O)₆].9H₂O using the anionic form of the bioactive 5-methyl-1,2,4-triazolo[1,5-*a*]pyrimidin-7(4H)-one (HmtpO) as ligand. Ce³⁺ complexes were prepared with various ligands, among the most notable being pyridoxine, amoxicillin trihydrate¹⁶, pyridine-carboxamide¹⁷.

In this study Ce³⁺, Dy³⁺, Ho³⁺ and Tm³⁺ complexes with 2-(1H-1,2,4-triazol-3-yl)pyridine (Htzp) as ligand were synthe-

sized and investigated through elemental analysis, FT-IR, P-XRD, thermal analysis (TG/DTA) and mass spectrometry. Beside their structural investigation, a particular attention was given to their photoluminescent properties. The fluorescence spectroscopy revealed interesting details regarding their luminescence and the subsequent processes involved in achieving them. While for the Dy³⁺ complex the luminescence is achieved due to a “classic” ligand to metal energy transfer mechanism responsible for the specific narrow emission bands, in case of Ce³⁺ the recorded wide band emission is most probable a result of the heavy atom effect over the excited states of the surrounding ligands. From the practical point of view, the prepared complexes may be potential interesting for applications in optical devices or through embedding in suitable polymer matrices as luminescent probes for bioimaging.

EXPERIMENTAL

2-(1H-1,2,4-Triazol-3-yl)pyridine (97 %) was purchased from Sigma-Aldrich while cerium chloride (CeCl₃·H₂O, 99.99 %), dysprosium chloride (DyCl₃·H₂O, 99.99 %), holmium chloride (HmCl₃·H₂O, 99.99 %) and thulium chloride (TmCl₃·H₂O, 99.99 %) were purchased from Alfa-Aesar. Absolute ethanol and high purity Milli-Q water were used for preparation and washing operations.

Preparation of 2-(1H-1,2,4-triazol-3-yl)pyridine complexes: All the investigated complexes were prepared at 1:3 molar ratio (central cation/ligand). Aqueous solution of Ce, Dy, Ho and Tm chlorides are prepared by dissolving 1 mmol of each in 2 mL high purity MiliQ water, in separate glass beakers provided with magnetic stirrers. Four solutions of 2-(1H-1,2,4-triazol-3-yl)pyridine (Htzp) are prepared by dissolving 3 mmol of ligand in a mixture of a 3 mL MiliQ water and 1 mL ethanol. The complexes were obtained by mixing each prepared ligand solution with the corresponding Ce, Dy, Ho and Tm chloride solutions. The complexation reactions were carried out under mild heating (40-50 °C) and stirring for about 3 h. After drying in ambient conditions, each resulted complex was washed with MiliQ water and further re-dried in ambient conditions followed by drying at 65-70 °C, under vacuum, till constant weight. The reaction involved in the process and also the generic structure of the prepared complexes are presented in Fig. 1.

Elemental chemical analysis was performed on thermo Fisher Scientific Flash EA-1112CHNS/O equipment provided with Eager 300 software. FT-IR spectra were recorded in a

KBr matrix using an Digilab Scimitar FTS-2000 FT-IR spectrometer in 4000-400 cm⁻¹ range. Thermal analysis was performed on a Mettler Toledo TGA-SDTA851e, under an air flow rate of 20 mL/min at a heating rate was adjusted at 10 °C/min in the 50-900 °C range. All the samples were additionally dried under vacuum at 50 °C for about 6 h, prior to investigation. Powder-XRD diffractograms were recorded in the range 5-70° 2θ range on a Panalytical X ‘Pert Pro diffractometer equipped with a Cu-K_α radiation source (λ = 0.154060 nm). Unit cell parameters of the investigated complexes were further refined using Panalytical X ‘Pert High Score Plus software. High-resolution MS and MS/MS spectra were acquired on an AGILENT 6520 QTOF mass spectrometer (Agilent Technologies, Santa Clara, CA) equipped with a dual ESI source. The source parameters optimized for the analyzed complexes were set as follows: Vcap = 4000 V, fragmentor voltage = 175 V, drying gas temperature = 325 °C, drying gas flow = 5 L/min and nebulizer pressure = 35 psig. The same direct infusion ESI MS analysis protocol was applied for all analyzed samples. The samples, 0.1 mM complex solutions in ethanol, were injected using a syringe pump at a flow rate of 0.5 mL/min. Nitrogen was used as spraying gas. MS/MS experiments were conducted using nitrogen as collision gas at a pressure of 18 psig inside the collision cell.

Fluorescence spectroscopy was performed on a Horiba Fluoromax 4P provided with the solid sample analysis adapter. Visual testing of photoluminescent properties was performed using a Philips UVA TL4WBLB lamp with the emission maximum located in the 370-390 nm range.

RESULTS AND DISCUSSION

Chemical analysis: Lanthanide, carbon, hydrogen and nitrogen contents of the complexes shown in Table-1 are in good agreement with those required by the proposed formula. Also, the experimental results obtained are in good concordance and with data obtained from thermal analysis and mass spectroscopy.

FT-IR analysis: FT-IR spectra for the prepared complexes and also for the free ligand were recorded in the 4000-400 cm⁻¹ range. Investigation of the recorded IR spectra revealed the interactions occurred between the 2-(1H-1,2,4-triazol-3-yl)pyridine ligand (HL) and the selected trivalent lanthanide cations. Fig. 2 presents the recorded spectra for the free ligand and prepared complexes, for each case the significant absorption peaks were also included. The IR spectra of the lanthanides

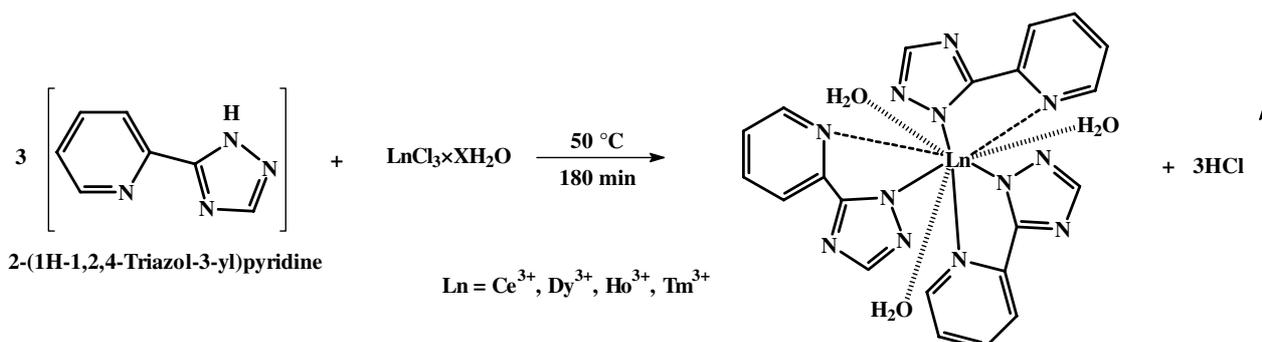


Fig. 1. Reaction and generic structure of the prepared complexes

TABLE-1
ELEMENTAL ANALYSIS OF THE Ln³⁺ COMPLEXES

Prepared complex	Experimental values (%): Found (calcd.)					Formula of complexes	m.f.
	Ln	C	H	N	O		
1	22.2 (22.1)	39.7 (39.9)	3.7 (3.8)	26.5 (26.6)	7.7 (7.6)	[Ce(tzp) ₃ (H ₂ O) ₃]	CeC ₂₁ H ₁₆ N ₁₂
2	23.9 (24.8)	38.7 (38.5)	3.8 (3.7)	26.1 (25.6)	7.4 (7.3)	[Dy(tzp) ₃ (H ₂ O) ₃]	DyC ₂₁ H ₁₆ N ₁₂
3	25.2 (25.0)	38.2 (38.3)	3.7 (3.6)	25.5 (25.6)	7.2 (7.3)	[Ho(tzp) ₃ (H ₂ O) ₃]	HoC ₂₁ H ₁₆ N ₁₂
4	25.7 (25.5)	37.9 (38.1)	3.5 (3.6)	25.4 (25.4)	7.1 (7.2)	[Tm(tzp) ₃ (H ₂ O) ₃]	TmC ₂₁ H ₁₆ N ₁₂

TABLE-2
SIGNIFICANT CHANGES IN FT-IR (cm⁻¹) SPECTRA OCCURRING THROUGH COMPLEXATION PROCESS

Compound	v(OH) (H ₂ O)	δ ^p HNC	v(C=N) pyridine	δ(CH)	Non-planar pyridine ring def.	δ(N-H)	γ(N-H)	v(Ln-N)
Htzp	-	1798	1601	1003	463	505	667	-
[CeL ₃ (H ₂ O) ₃]	3086	-	1605	987	474	-	-	413
[DyL ₃ (H ₂ O) ₃]	3086	-	1601	991	474	-	-	413
[HoL ₃ (H ₂ O) ₃]	3090	-	1605	995	482	-	-	417
[TmL ₃ (H ₂ O) ₃]	3086	-	1605	995	482	-	-	417

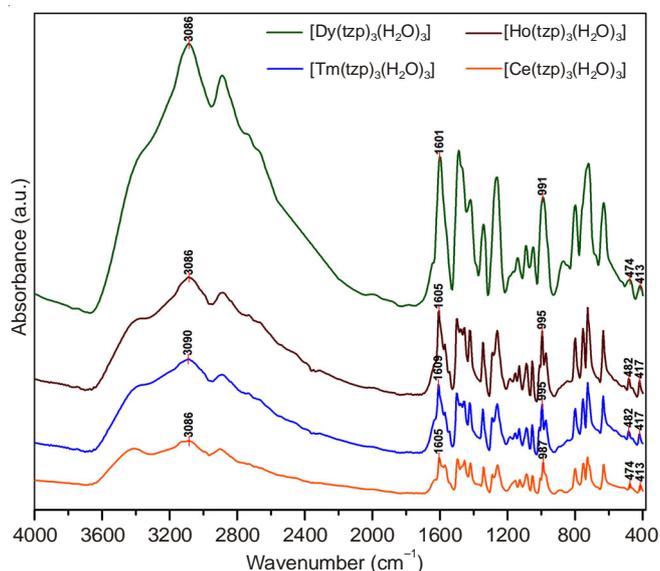


Fig. 2. FT-IR spectra of [Ce(tzp)₃(H₂O)₃], [Dy(tzp)₃(H₂O)₃], [Ho(tzp)₃(H₂O)₃] and [Tm(tzp)₃(H₂O)₃]

complexes are very similar between them, but significantly different from the free ligand. FT-IR spectra of the complexes present modification of the ligand bands due to the emergence of new covalent and coordinative bonds occurring between the central cation and ligands. It showed that lanthanides ions were bonded with the ligands. Besides displacements of various peaks due to the occurring rearrange-ments of various groups, through complexation a series of peaks as -NH specific stretching or deformation vibrations are no more present in recorded spectra of all prepared complexes while new peaks become present (417-413 cm⁻¹) due to the new established covalent bonds between the central cation and nitrogen atom from the former -NH group located in the triazole ring. Also, the stretching vibration bond of v(C-N) triazole from 1477 cm⁻¹, which appears as a strong peak in the free ligand splits and moved to higher wave numbers in the case of complexes as a result of coordination between triazole ring with trivalent cations.

The 1601 cm⁻¹ peak characteristic to the v(C=N) group in the pyridine ring appears displaced at higher wavenumbers in

the spectra of complexes, suggesting the coordinative bond established between central cation and the nitrogen atom in the pyridine ring. The coordination of the nitrogen atom to Ce³⁺, Dy³⁺, Ho³⁺ and Tm³⁺ ions is further sustained by the characteristic vibration frequency displacement of the v(CH), γ(CH) in the pyridine ring. Table-2 presented the most significant changes occurring through complexation process.

In the upper region (3100-3000 cm⁻¹) all the complexes presents a medium intensity broad band peak which is attributed to the stretching vibrations of the OH groups suggesting the presence of water in all prepared complexes. The bands corresponding to region 750-650 cm⁻¹, can be assigned to relatively intense deformation vibration of the group (OH). By cumulating this information it is concluded the ligand is anionic bidentate and the water is present in coordination sphere^{18,19} from the structure of complexes.

ESI MS and MS/MS characterization: The prepared lanthanide complexes were structurally identified by mass spectrometry experiments. First, the mass of the complexes was measured by electrospray mass spectrometry *via* direct injection of the samples from ethanol solutions. The obtained masses and the theoretical values are listed for comparison in Table-3. All the observed ion species corresponded to proton charged lanthanides complexes (formed in the ESI process) with general formula [Ln(tzp)₃+H]⁺.

TABLE-3
MASS SPECTROMETRY RESULTS FOR
THE LANTHANIDES COMPLEXES

Sample	Measured monoisotopical mass	Theoretical monoisotopical mass
[Ce(tzp) ₃ +H] ⁺	576.0032	576.0675
[Dy(tzp) ₃ +H] ⁺	600.0230	600.0912
[Ho(tzp) ₃ +H] ⁺	601.0255	601.0923
[Tm(tzp) ₃ +H] ⁺	605.0278	605.0962

Furthermore, the ionic species assigned as proton charged lanthanides complexes [Ln(tzp)₃+H]⁺ were analyzed at molecular level by fragmentation in the collision cell of the QTOF mass spectrometer. The [Ln(tzp)₃+H]⁺ parent ions yielded fragments at around 20 eV (E_{lab}).

In every MS/MS spectrum of the analyzed samples (the fragmentation spectrum of Ho complexes is given as an example in Fig. 3) there were remarked two main daughter ions resulted from neutral loss of 146 Da and 104 Da, respectively. The loss of 146 Da is consistent with the cleavage of one ligand moiety and the formation $[\text{Ln}(\text{tzp})_2]^+$ daughter ions while the loss of 104 Da is corresponding to the cross-ring cleavage of the smaller ring belonging to the ligand. Thus, the observed peaks are corresponding to the hypothesized structures for the observed gas phase ionic species.

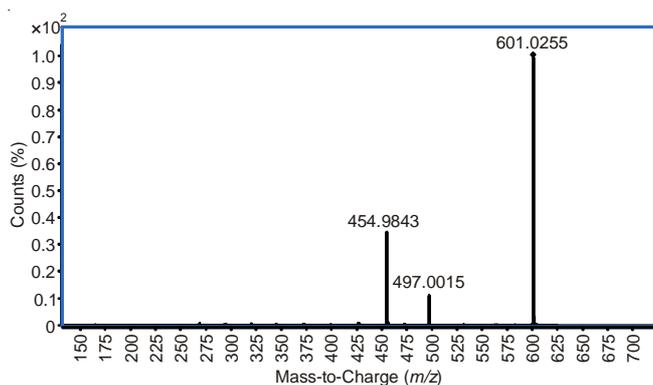
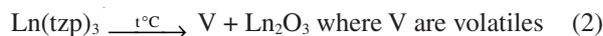


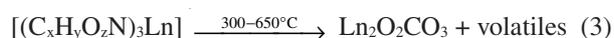
Fig. 3. Fragmentation spectrum of $[\text{Ho}(\text{tzp})_3 + \text{H}]^+$ ion species

Thermal analysis: Based on registered derivatograms, the results of thermal decomposition including the kinetic parameters of the free ligand and prepared complexes are presented in Table-4. For the free 2-(1H-1,2,4-triazol-3-yl)-pyridine ligand the decomposition take place in 2 stages while in case of the prepared complexes 4-5 stages were recorded.

The decomposition of the complexes is summarized by the following processes:



In the first stage, the small amounts of physical bonded water and also the coordinated water is lost (1). In the second stage, the percent of mass losses suggests the breaking of the covalent C-C bond between the two constituent rings of the ligand (Fig. 1) and the elimination of the pyridine ring. The process is sustained by the electromer effects occurring in the presence of the central cation and its coordinative bond established with the nitrogen atom in the pyridine ring. In the upper stages the decomposition processes evolves with further deconstruction of the complexes accompanied by volatile exhaustions (2).



Besides the volatile products, a series of intermediate products like lanthanide oxocarbonates may occur (3) which further decomposes to stable Ln_2O_3 (4)^{20,21} which is suggested by the recorded values of final residue which may also contain small amounts of products resulted from decomposition of the ligand.

Powder X-ray diffraction: The unit cell parameters parameters are given in Table-5. The crystallization system is triclinic for all prepared complexes while in case of free ligand a monoclinic configuration was found.

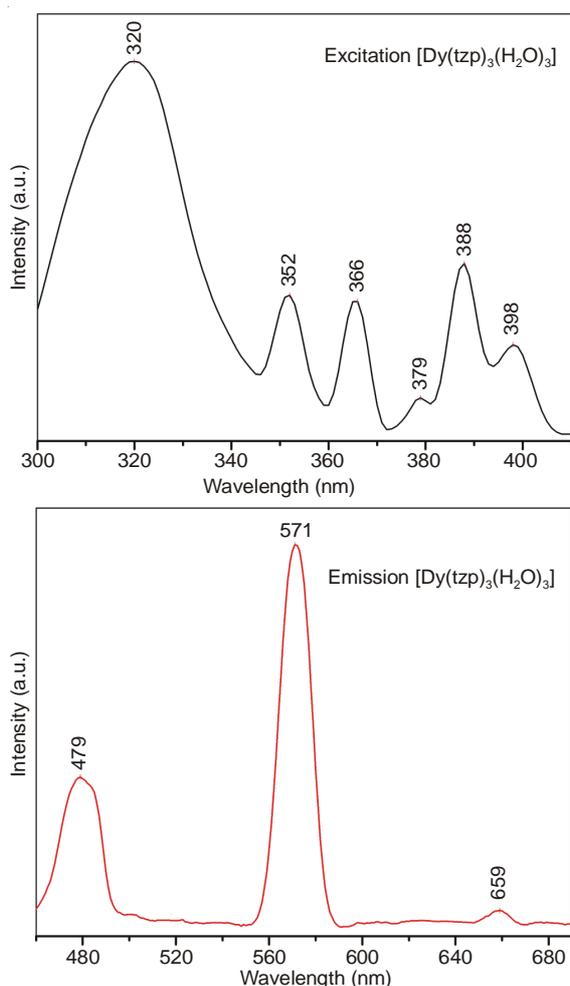
TABLE-4
KINETIC PARAMETERS IN THERMAL DECOMPOSITION OF THE FREE LIGAND AND ITS Ln^{3+} COMPLEXES

Stage	Parameter	Ligand	$[\text{Ce}(\text{tzp})_3(\text{H}_2\text{O})]$	$[\text{Dy}(\text{tzp})_3(\text{H}_2\text{O})]$	$[\text{Ho}(\text{tzp})_3(\text{H}_2\text{O})]$	$[\text{Tm}(\text{tzp})_3(\text{H}_2\text{O})_3]$
1	A	1.62×10^{18}	2.77	5.97×10^5	1.47	1.76
	E_a (kJ/mol)	74.05	21.12	60.08	20.67	19.25
	N	0.33	0.63	0.99	0.30	0.54
	Temp. interval	203-272	73-151	77-141	80-170	90-171
	Loss (%)	88.1	12.04	14.65	5.22	10.63
2	A	20.1×10^{18}	-	-	1.29×10^{15}	4.67×10^3
	E_a (kJ/mol)	45.3	-	-	166.29	64.57
	N	0.55	-	-	0.36	0.38
	Temp. interval	365-516	255-286	237-310	221-318	220-316
	Loss (%)	10.67	34.68	12.02	5.60	14.89
3	A	-	1.33×10^{20}	5.12×10^2	-	8.71×10^2
	E_a (kJ/mol)	-	-	-	-	67.45
	N	-	-	64.09	-	0.76
	Temp. interval	-	313-456	351-476	355-460	355-456
	Loss (%)	-	3.22	26.62	26.19	21.38
4	A	-	0.11×10^2	3.42	5.72×10^2	2.25×10^2
	E_a (kJ/mol)	-	54.83	48.11	56.36	77.13
	N	-	0.14	0.34	0.61	0.81
	Temp. interval	-	499-590	520-603	524-691	543-585
	Loss (%)	-	23.69	17.1	21.68	16.81
5	A	-	-	9.29×10^{31}	2.25×10^{15}	-
	E_a (kJ/mol)	-	-	-	280.69	-
	N	-	-	725-842	0.81	-
	Temp. interval	-	-	-	786-826	786-826
	Loss (%)	-	-	11.31	11.13	13.59
Residue %		1.32	26.37	18.25	31.18	22.70

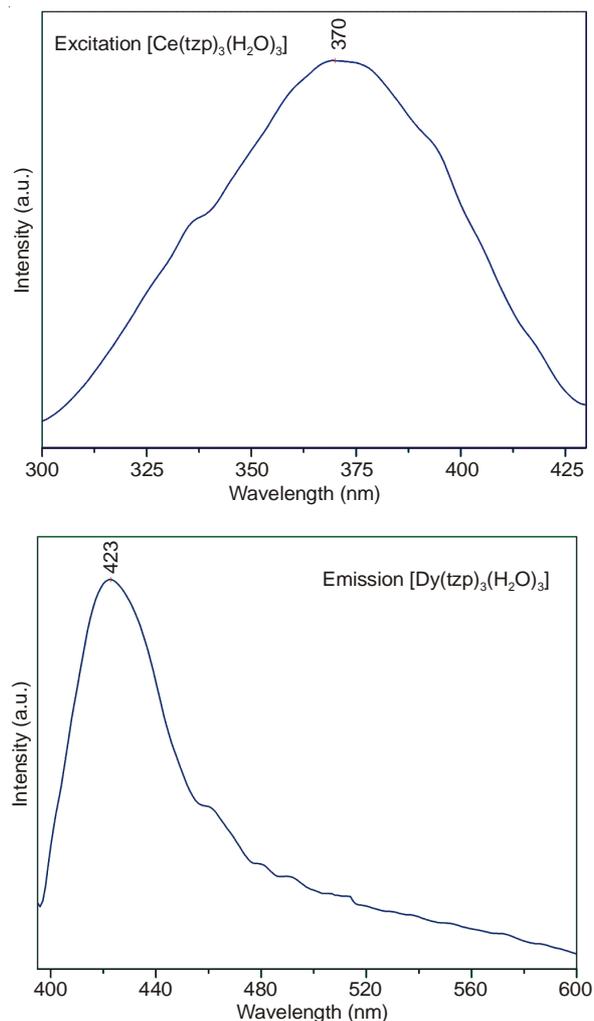
TABLE-5
 UNIT CELL PARAMETERS OF THE PREPARED COMPLEXES AND FREE LIGAND

Compound	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)	Crystallization system
Htzp	10.53	3.96	8.90	90	110.7	90	347	Monoclinic
[Ce(tzp) ₃ (H ₂ O) ₃]	8.86	7.5	10.9	83.0	92.5	102.5	702	Triclinic
[Dy(tzp) ₃ (H ₂ O) ₃]	10.22	10.4	9.68	86.2	117.5	71.4	837	Triclinic
[Ho(tzp) ₃ (H ₂ O) ₃]	11.33	11.2	8.89	89.3	136.3	85.3	944	Triclinic
[Tm(tzp) ₃ (H ₂ O) ₃]	11.24	12.7	10.11	91.0	128.8	87.5	924	Triclinic

Fluorescence analysis: In case of [Dy(tzp)₃(H₂O)₃] complex the recorded photoluminescence (PL) emission spectrum revealed metal centered specific narrow band emissions due to the *f-f* transitions within 4*f* orbitals due to a ligand to metal charge transfer (LMCT) mechanism²². The sensitization induced by the 2-(1H-1,2,4-triazol-3-yl)pyridine ligand and also the configuration achieved through complexation could explain the efficient sensitization of the Dy³⁺ cation. The process may rely on an indirect sensitization through the “antenna effect” of the pyridine ring coupled to the triazole ring coordination site which subsequently transfers its excited states to the covalently bonded trivalent cation. The efficient sensitization process may be further aided by the presence of the coordinative bond between the nitrogen in the pyridine ring with the trivalent lanthanide cation. Fig. 4 presented the excitation and emission spectra recorded for the prepared [Dy(tzp)₃(H₂O)₃] complex.


 Fig. 4. Excitation and photoluminescence emission spectra of the prepared [Dy(tzp)₃(H₂O)₃] complex

The most intense emission peak located at 571 nm is due to the ⁴F_{9/2} → ⁶H_{13/2} transition while the medium intensity peak recorded at 479 nm is due to the ⁴F_{9/2} → ⁶H_{15/2} transition. The barely observable peak located at 659 nm is attributed to ⁴F_{9/2} → ⁶H_{11/2} radiative transition^{23,24}. The recorded excitation spectra revealed an intense wider peak located at 320 nm and a series of less significant narrower peaks located in 350-400 nm range. In case of [Ce(tzp)₃(H₂O)₃] no specific metal centered radiative transitions were observed the moderate photoluminescent emission with the wide peak located at 423 nm (Fig. 5) is most probably due to the heavy ion influence²⁵ over the excited states of the ligand. While the photoluminescence emission is quite intense in case of the [Dy(tzp)₃(H₂O)₃] complex being easily observable with naked eye, in case of the [Ce(tzp)₃(H₂O)₃] complex the photoluminescence was only instrumentally recorded.


 Fig. 5. Excitation and photoluminescence emission spectra of the prepared [Ce(tzp)₃(H₂O)₃] complex

In case of the $[\text{Ho}(\text{tzp})_3(\text{H}_2\text{O})_3]$ and $[\text{Tm}(\text{tzp})_3(\text{H}_2\text{O})_3]$ no photoluminescence was recorded most probable due to the unfulfillment of the minimal required energy transfer to the excited states of the central cations.

Conclusion

The paper reports four new complexes of Ce^{3+} , Dy^{3+} , Ho^{3+} and Tm^{3+} with 2-(1H-1,2,4-triazol-3-yl)pyridine. In all prepared lanthanide complexes, the coordination number of the central cation was found to be 9 with three bidentate ligands and also three coordinated water molecules in the first coordination sphere. The suggested structure was confirmed by elemental analysis, thermal analysis, mass spectroscopy and FT-IR analysis being in accordance with other studies concerning trivalent lanthanide complexes. Fluorescence spectroscopy investigations revealed significant photoluminescent properties only in case of Dy^{3+} complex while in case of the other three complexes weak or no luminescence was observed. The luminescence properties of the Dy^{3+} prepared complex is achieved in its solid, crystalline form, which may recommend it for applications in optical materials or through embedding in a compatible media as tracing agents for biological and medical investigations.

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