

SYNTHESIS, CHARACTERIZATION AND PHOTOPHYSICAL STUDY OF 4,4'-DIAMINO-2,2'-STILBENEDISULFONATE WITH LANTHANIDE IONS COMPLEXES

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Abstract. Complex of 4,4'-diamino-2,2'-stilbenedisulfonic acid (DSD) with trivalent lanthanide ions Eu^{3+} and Tb^{3+} were prepared at the ratio of 3:1 (DSD:Ln). The complexes with ions present in the form of powder show black (Eu^{3+}) and brown (Tb^{3+}) colors. The complexometric titration and CHN elemental analysis suggest that these complexes have the general formula $\text{Eu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_3 \cdot 3\text{H}_2\text{O}$ and $\text{Tb}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_2(\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$. The shift of the 330 nm band for DSD to a longer wavelength in the infrared spectra of the complexes and the disappearance of the bands at 2921 and 2623 cm^{-1} are indicative of the formation of complexes with ions Eu^{3+} and Tb^{3+} . Thermal analysis shows that DSD is thermally stable up to 573 K and the decomposition process of the complexes shows two and three mass losses for ions Eu^{3+} and Tb^{3+} , respectively. The analysis of luminescence indicates that the complexes do not present the emission from the lanthanide moiety in the visible region. This may be related to the ligand triplet states, which are probably at lower energy than the emission state of the Eu^{3+} ($^5\text{D}_0$) and Tb^{3+} ($^5\text{D}_4$) ions.¹

Keywords: complex, 4,4'-diamino-2,2'-stilbenedisulfonic acid, lanthanides, luminescence.

1. Introduction

Some compounds of trivalent lanthanide ions possess appropriate properties to be used as informational and structural probes in living systems and analytical chemistry, because they have intense luminescence in the visible region when excited in the ultraviolet region, giving rise to narrow bands corresponding to atomic transitions in the 4f-4f central ion.¹ The f-f transitions in the lanthanide ions are forbidden electric dipole because there is no change in parity (Laporte rule), but the influence of the ligand field is strong enough to promote a mix of parity in the states, relaxing the rule of Laporte and thus allowing the f-f transitions to occur by the forced electric dipole mechanism.²

The ultraviolet (UV) radiation from sunlight can cause various problems such as photodegradation of organic compounds and damage to human health, for example, causing sunburns, accelerated aging, provoking skin cancer, among others.^{3,4} Organic materials such as 4,4'-diamino-2,2'-stilbenedisulfonic acid (DSD), 4-hydroxy-3-methoxybenzoic acid, 2-hydroxy-4-methoxybenzophenon-5-sulfonic, *p*-aminobenzoic acid and urocanic acid have a strong absorption of UV radiation⁵ and have been used as blocking sunlight agents. However, some organic compounds that absorb UV radiation can pose a safety problem when used in high concentration, since they can be absorbed by the *stratum corneum*. In recent years, several studies focused on the formulation of UV filters in micro and nanocarriers, encapsulation and intercalation to protect them from photo-degradation and to prevent skin permeation.⁴⁻⁹ That is why incorporating organic materials into inorganic materials nanospecies (intercalation) is a good alternative to direct contact of skin with organic molecules.⁶⁻⁹

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4,4'-Diamino-2,2'-stilbenedisulfonic acid (DSD) is also widely used as fluorescent whitening agent in the textile, paper, plastics, and household detergents, due to its property of transforming part of solar radiation in a fluorescent blue light, giving the sense of brilliant whiteness.^{3,10} Stilbene derivatives are widely used as fluorescent brighteners and the main raw material for obtaining these is DSD. The sodium salt of DSD absorbs UV radiation at 340 nm and has emission in the visible region (blue).

This work aims to synthesize luminescent complexes with trivalent lanthanide ions (Eu^{3+} and Tb^{3+}) and the 4,4'-diamino-2,2'-stilbenedisulfonic acid. The choice of ligand is due to the DSD being capable of absorbing ultraviolet radiation and able to form complex with lanthanide ions by your donor atoms.

2. Experimental

2.1. Materials

The chemical substances used as reagents in the synthesis of lanthanide complexes were: 4,4'-diamino-2,2'-stilbenedisulfonic acid (DSD) – Acros Organics (95%); sodium hydroxide – Vetec Fine Chemicals Ltd (98.00%); europium oxide – Spectrum Chemical Corp. (99.99%); terbium oxide – Spectrum Chemical Corp. (99.99%).

2.2. Synthesis of Complexes 4,4'-Diamino-2,2'-stilbenedisulfonic Acid with Lanthanide Ions (Eu^{3+} and Tb^{3+})

The complexes 4,4'-diamino-2,2'-stilbenedisulfonic acid (DSD) with Eu^{3+} ion were obtained by the reaction of lanthanide chloride with DSD, and the complex with Tb^{3+} ion was obtained using trifluoromethanesulfonate salt of terbium [$\text{Tb}(\text{CF}_3\text{SO}_3)_3 \cdot 3.8\text{H}_2\text{O}$]. The complexes were obtained in a 3:1 (DSD/chloride Ln) and 3:1 (DSD/ $\text{Tb}(\text{CF}_3\text{SO}_3)_3 \cdot 3.8\text{H}_2\text{O}$). The 4,4'-diamino-2,2'-stilbenedisulfonic acid was suspended in acetonitrile in the presence of a NaOH solution at 5 % until a pH range of 7-8 to its deprotonation and formation of sodium 4,4'-diamino-2,2'-stilbenedisulfonate. Next 1 mmol of Eu^{3+} chloride or Tb^{3+} trifluoromethanesulfonate were added, leaving the mixture under stirring and heating at 333 K for 8 h. After washing three times with acetonitrile and drying at 343 K, the complexes were obtained as black and brown powders for Eu^{3+} and Tb^{3+} , respectively.

2.3. Characterization

The complexes were characterized by complexometric titration with EDTA. 20 mg of the complexes 4,4'-diamino-2,2'-stilbenedisulfonic acid (DSD) with Eu^{3+} or Tb^{3+} , 10 ml of distilled water, 3 mL of acetic acid/sodium acetate buffer solution (pH = 5.8), 1 drop of pyridine and 5 drops of the orange xylenol indicator were added. The solution was titrated with the $0.01 \text{ mol} \cdot \text{L}^{-1}$ of EDTA solution until the color changed from violet-pink to pale yellow. The elemental analysis (CHN) was determined in the laboratory of the Central Analytical Department of Fundamental Chemistry, UFPE, using a Carlo Erba 1110 equipment. The absorption spectra in the UV-Vis region of the complexes were recorded in the range of 200 to 800 cm^{-1} , using a Shimadzu 1800 UV spectrophotometer. Measurements were performed in acetonitrile solution at the concentration of $10^{-3} \text{ mol} \cdot \text{L}^{-1}$. The coefficient of molar absorptivity was calculated using the Lambert-Beer expression. The absorption spectra in the infrared region were recorded in the range of 400 to 4000 cm^{-1} . The samples were dispersed in KBr, previously crushed and pressed into tablets. The data were collected on a spectrophotometer Fourier transform infrared (FTIR) Nexus 470 Thermo Licolet, with 32 number scanning and resolution of 4 cm^{-1} . The TGA/DTG curves were obtained using a Shimadzu TGA-50 equipment. The excitation and emission spectra were recorded on a Hitachi model F 4500 spectrometer, measurements were performed in the solid state in the region of 200 to 280 nm and 250–600 nm for excitation and emission, respectively.

3. Results and Discussion

3.1. Complexometric Titration with EDTA and Elemental Analysis (CHN)

Table 1 presents data on percentages of lanthanides (Ln), carbon, hydrogen, and nitrogen in the complexes. Data from the complexometric titration and elemental analysis (CHN) suggest that the complexes have the molecular formulae $\text{Eu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_3 \cdot 3\text{H}_2\text{O}$ and $\text{Tb}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_2(\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$. These results indicate that only one of the sulfonate groups of the DSD is deprotonated and the metal is coordinated by the oxygen of sulfonate group and the amine nitrogen in forming a total coordination number between 8 and 9.

Table 1. Percentages of lanthanides (Ln), carbon, hydrogen, and nitrogen in the complexes

Ln	% Ln		% C		% H		% N	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
Eu	11.56	11.39	38.35	38.15	3.42	3.46	6.39	5.96
Tb	8.89	9.53	31.61	31.07	2.90	3.12	5.08	5.10

3.2. Absorption Spectroscopy in the UV-Visible Region

Fig. 1 shows the spectra of UV-visible to the ligand and the complexes with Eu^{3+} and Tb^{3+} ions. The UV-visible spectrum for the 4,4'-diamino-2,2'-stilbenedisulfonic acid in aqueous medium at the concentration of $10^{-3} \text{ mol}\cdot\text{L}^{-1}$ shows two bands at 198 and 330 nm (Fig. 1a) corresponding to the transitions $n \rightarrow \text{p}^*$.³ The calculated value for the coefficient of molar absorptivity (ϵ) to the DSD is $1164 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

The spectrum of the complex 4,4'-diamino-2,2'-stilbenedisulfonate with the europium ion (Fig. 1c) was obtained in aqueous concentration of $10^{-3} \text{ mol}\cdot\text{L}^{-1}$, showing a similar number of bands in the spectrum of 4,4'-diamino-2,2'-stilbenedisulfonic acid, which band at 330 nm of DSD was shifted to a longer wavelength in the spectrum of the complex. This shift may be indicative of complex formation. The band at 200 nm is related to the transition $n \rightarrow \text{p}^*$ ligand.³ The calculated value for the coefficient of molar absorptivity (ϵ) for the complex with the europium ion is $923 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

The absorption spectrum of 4,4'-diamino-2,2'-stilbenedisulfonate with terbium ion shows an intense band with maximum absorption at 332 nm (Fig. 1b). The same as in the absorption spectrum for 4,4'-diamino-2,2'-stilbenedisulfonate with the europium ion, the band at

200 nm is related to the transition $n \rightarrow \text{p}^*$ ligand.³ This spectrum was also obtained in aqueous concentration of $10^{-3} \text{ mol}\cdot\text{L}^{-1}$ and the calculated value for the coefficient of molar absorptivity (ϵ) for the complex with terbium ion is $1043 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. Two bands are observed, one at 200 nm due to the transition $n \rightarrow \text{p}^*$ ligand³ and another – in the region of 330 nm, attributed to the coordination between 4,4'-diamino-2,2'-stilbenedisulfonate with lanthanide ions.

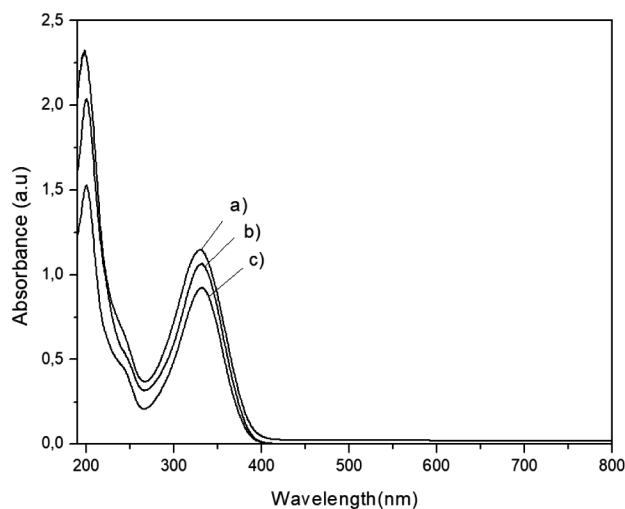
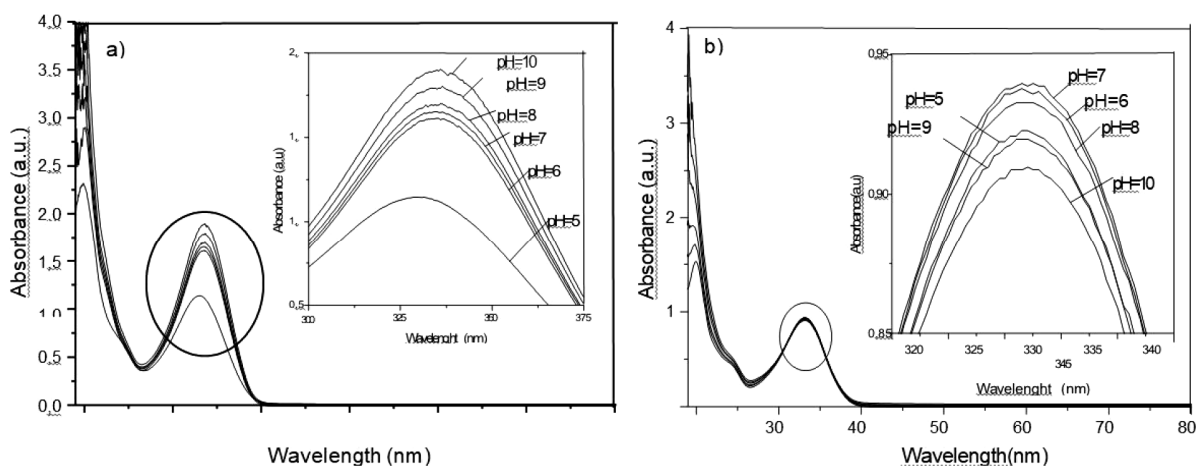

Fig. 1. Overlap of the UV-Vis spectra for 4,4'-diamino-2,2'-stilbenedisulfonate (a), 4,4'-diamino-2,2'-stilbenedisulfonate Tb^{3+} ion (b) and 4,4'-diamino-2,2'-stilbenedisulfonate Eu^{3+} ion (c)

Fig. 2. Overlap of UV-Vis spectra of 4,4'-diamino-2,2'-stilbenedisulfonic acid (a) and 4,4'-diamino-2,2'-stilbenedisulfonate Eu^{3+} ion (b) at different pH

Fig. 2 shows the overlap of the UV-visible spectra, obtained in the pH range between 5 and 10, for 4,4'-diamino-2,2'-stilbenedisulfonic acid (Fig. 2a) and 4,4'-diamino-2,2'-stilbenedisulfonate with Eu^{3+} ion (Fig. 2b), respectively. In the spectra of the ligand, there was observed an increase in the intensity of the absorption when changing pH, as well a band shift in the region of 330–336 nm, indicating that two sulfonate groups are deprotonated with the addition of NaOH ($0.5 \text{ mol}\cdot\text{L}^{-1}$). In the spectra of the complexes, a band shift in the region of 330 nm is observed, increasing the absorbance intensity with the change in pH, indicating that only one sulfonate group is deprotonated as expected, since the other group already is monodeprotonated, leaving the oxygen free to coordinate with lanthanide ions.

3.3. Absorption Spectroscopy in the Infrared Region

The absorption spectrum in the infrared region for 4,4'-diamino-2,2'-stilbenedisulfonic acid (DSD) (Fig. 3a) present bands at 3501 and 3412 cm^{-1} corresponding to the axial deformation modes of asymmetric and symmetric N–H free primary amine and also the O–H stretch.¹¹ The bands at 3141 and 3070 cm^{-1} are associated with the amine attached to aromatic rings. The vibrations at 2921 and 2623 cm^{-1} are assigned to the compounds that have SO_2 group in their structure.⁶ The bands at 1615, 1536 and 1496 cm^{-1} correspond to the angular deformation of N–H. The band at 1615 cm^{-1} is also attributed to C=C bonds. The asymmetric axial deformation of the group $\text{S}(\text{=O})_2$ has two bands –quite intense one at 1191 cm^{-1} and another one at 1128 cm^{-1} . Axial symmetric deformations, showed by the bands at 1031 and 1091 cm^{-1} , are characteristic of the sulfonic group.¹² The regions at 965, 826 and 706 cm^{-1} are related to the vibrations of the aromatic ring.¹¹

In the infrared spectrum of the complex of DSD with the Eu^{3+} ion (Fig. 3b), the shift of the bands at 2921 and 3372 cm^{-1} to 2623 and 3207 cm^{-1} , respectively, can be attributed to compounds that have SO_2 group in their structure, which may be an indication that the metal is coordinated by the oxygen of sulfonic group,⁶ considering that only one sulfonic group is deprotonated. The band at 3372 cm^{-1} corresponding to the O–H stretch is attributed to coordination of water. The band at 1615 cm^{-1} , which appears in the FTIR spectrum of the DSD on the C=C

absorption, is shifted to 1596 cm^{-1} in the compound with the Eu^{3+} ion, indicating a possible coordination of the Eu^{3+} ion with 4,4'-diamino-2,2'-stilbenedisulfonate. The band at 1191 cm^{-1} in DSD is shifted to a lower wavenumber, 1180 cm^{-1} in the complex with Eu^{3+} ion, being also an indicative of metal-oxygen of sulfonic group bonding.

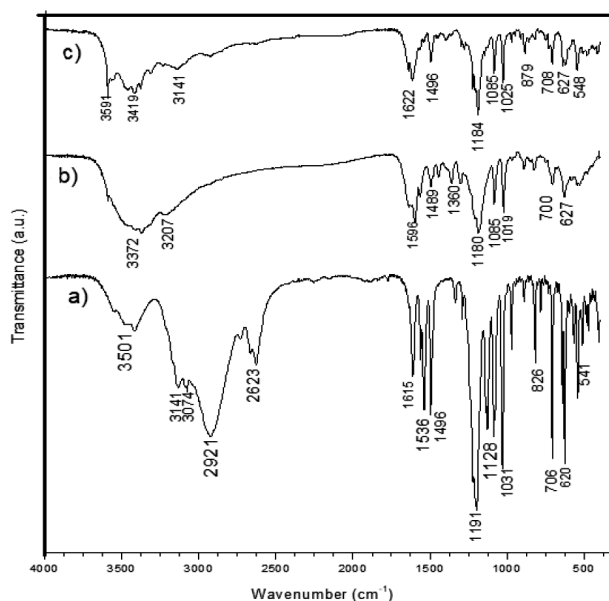


Fig. 3. FTIR spectra overlap for 4,4'-diamino-2,2'-stilbenedisulfonate (a), 4,4'-diamino-2,2'-stilbenedisulfonate Eu^{3+} ion (b) and 4,4'-diamino-2,2'-stilbenedisulfonate Tb^{3+} ion (c)

In the infrared spectrum of the DSD for the complex with Tb^{3+} ion (Fig. 3c), a shift of the band at 3501 cm^{-1} to higher wavenumber (3591 cm^{-1}) is observed for 4,4'-diamino-2,2'-stilbenedisulfonic acid. This shift corresponds to axial deformation modes of asymmetric and symmetric N–H primary amine-free and also is associated with the O–H stretch of coordinated water.¹¹ The shifts of the bands at 2921 and 2623 cm^{-1} to 3419 and 3313 cm^{-1} , respectively, are attributed to compounds that have SO_2 group in their structure. Again, the Eu^{3+} and Tb^{3+} complex FTIR spectra can indicate that the metal is coordinated to the oxygen of sulfonic group,⁶ taking also into account that only one sulfonic group is deprotonated. The band at 1615 cm^{-1} that appears in the DSD FTIR attributed to the absorption of C=C bonds is also shifted to a higher wavenumber (1622 cm^{-1}), in the compound with the ion Tb^{3+} , indicating a possible coordination of the ion Tb^{3+} with 4,4'-diamino-2,2'-

stilbenedisulfonate. The band at 1191 cm^{-1} in DSD is shifted to 1184 cm^{-1} in Tb^{3+} complex, more indicative of metal-oxygen of sulfonic group bonding.

3.4. Thermal Analysis

Fig. 4 shows the TGA curve of the ligand and the complexes with Eu^{3+} and Tb^{3+} ions. The TGA curve for 4,4'-diamino-2,2'-stilbenedisulfonic acid (Fig. 4a) is decomposed in a single step and is thermally stable in the range of $313\text{--}40\text{ }^\circ\text{C}$ to 648 K . The decomposition of DSD occurs gradually in the range of $648\text{--}1046\text{ K}$. The TGA curve for the complex of europium with DSD (Fig. 4b) shows two main mass losses. The first one between 300 and 409 K , corresponding to coordinated/physisorbed water, and is followed by a weight loss within $396\text{--}693\text{ K}$, corresponding to partial decomposition of 4,4'-diamino-2,2'-stilbenedisulfonic acid. The second significant weight loss occurs between 750 and 903 K , which is observed in the total loss of mass of DSD. The formation of residual lanthanide oxide occurs from 973 K . The TGA curve for the complex of terbium with DSD (Fig. 4c) has three mass losses. The first one at $300\text{--}433\text{ K}$ refers to the loss of coordinated/physisorbed water, the second one between 434 and 799 K refers to the decomposition trifluoromethanesulfonate and the third one at $800\text{--}900\text{ K}$ corresponds to the total decomposition of DSD. The final residue is TbF_3 .¹³

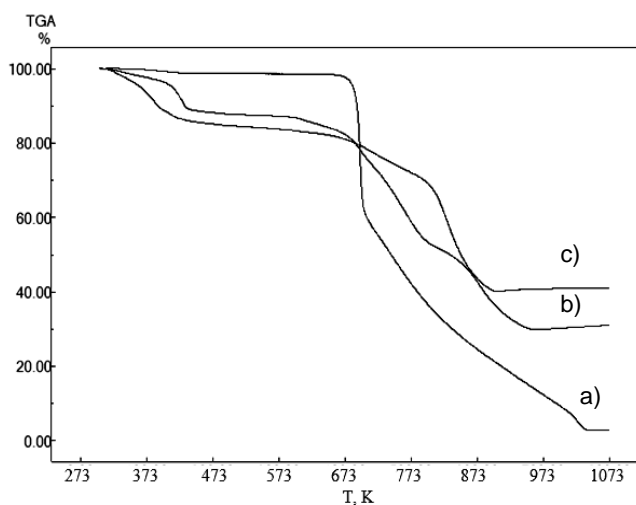


Fig. 4. Overlap of the TGA curves for 4,4'-diamino-2,2'-stilbenedisulfonate (a), 4,4'-diamino-2,2'-stilbenedisulfonate with Eu^{3+} ion (b) and 4,4'-diamino-2,2'-stilbenedisulfonate with Tb^{3+} ion (c) in N_2 at 283 K

3.5. Luminescence Spectroscopy

3.5.1. Luminescence spectroscopy of solid state

The excitation spectrum of 4,4'-diamino-2,2'-stilbenedisulfonic acid, obtained in solid state, fixing the wavelength of emission at 300 nm , shows two bands with high intensity centered at 218 nm and another one at about 266 nm . For the $\text{Eu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_3 \cdot 3\text{H}_2\text{O}$ and $\text{Tb}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_2(\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$ complexes, the excitation spectra show two excitation bands centered at $225\text{--}262\text{ nm}$ and $227\text{--}263\text{ nm}$, respectively. These two bands appear close to the regions of the excitation spectrum of 4,4'-diamino-2,2'-stilbenedisulfonic acid but with different intensities between them. These bands are related to the DSD transitions.¹⁰

The emission spectrum of 4,4'-diamino-2,2'-stilbenedisulfonic acid, obtained in solid form and setting the excitation wavelength ($\lambda_{\text{ex}} = 220\text{ nm}$), presents a broad band centered at 392 nm with several peaks at $308, 350, 392, 467, 482$ and 492 nm . These peaks are related to transitions $p\text{ } \textcircled{\text{R}} \text{ } p^*$ and $p^* \rightarrow n$ of 4,4'-diamino-2,2'-stilbenedisulfonic acid,^{3,10} showing that DSD has a wide band and a relatively high intensity in the visible region.

The emission spectra fixing the excitation wavelength at 265 nm and obtained with the samples in solid state are showed in Fig. 5.

These spectra have the same profile for all samples. An intense band in the region of 295 nm is observed; this transition is attributed to 4,4'-diamino-2,2'-stilbenedisulfonic acid or sodium salt, considering that this ligand does not transfer energy to the metal ions, when compared with other organic ligands. So, no bands were obtained regarding the f-f transitions of Eu^{3+} or Tb^{3+} ion.¹⁴

The lack of luminescence of these ions in the complexes may be related to the ligand triplet states, which are probably at lower energy than the emitter state of the Eu^{3+} ($^5\text{D}_0$) and Tb^{3+} ($^5\text{D}_4$).¹⁴ The phosphorescence spectra (Fig. 6), setting the excitation wavelength at 220 nm , confirm this speculation.¹⁵ A large band of weak intensity that is able to quench the emission level of Eu^{3+} ($^5\text{D}_0$: 17300 cm^{-1} and $^5\text{D}_1$: 19027 cm^{-1}) and Tb^{3+} ($^5\text{D}_4$: 20 and 566 cm^{-1}) is observed.

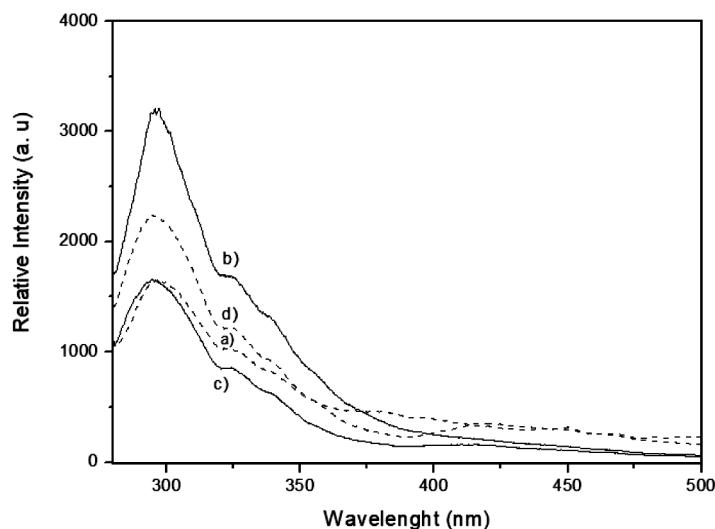


Fig. 5. Spectra of emission, fixing the excitation wavelength at 265 nm, in solid state of 4,4'-diamino-2,2'-stilbenedisulfonic acid (a); the complex $\text{Eu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_3 \cdot 3\text{H}_2\text{O}$ (b); the complex $\text{Tb}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_2(\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$ (c) and sodium 4,4'-diamino-2,2'-stilbenedisulfonate (d)

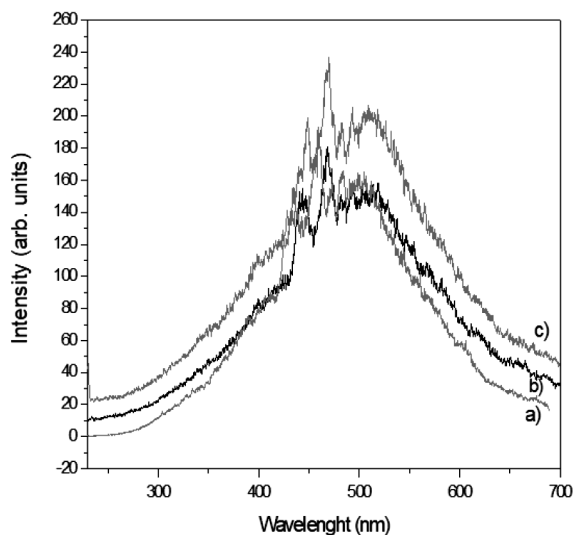


Fig. 6. Phosphorescence spectra, fixing the excitation wavelength at 220 nm, in solid state of 4,4'-diamino-2,2'-stilbenedisulfonic acid (a); the complex $\text{Eu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_3 \cdot 3\text{H}_2\text{O}$ (b); and the complex $\text{Tb}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_2(\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$ (c)

3.5.2. Luminescence spectroscopy in acetonitrile solution

The emission spectrum of 4,4'-diamino-2,2'-stilbenedisulfonic acid, obtained in acetonitrile solution and fixing the excitation wavelength at 265 nm, shows a large band in the region of 350–425 nm. Fixing $\lambda_{ex} = 220$ nm, the emission spectrum obtained presents the same profile but with low intensity.

In the emission spectra of sodium 4,4'-diamino-2,2'-stilbenedisulfonate it is possible to observe an intense band in the region of 412 nm. This band is also observed in the spectrum of the complex $\text{Tb}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_2(\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$, consequently, this transition can be attributed to the anion 4,4'-diamino-2,2'-stilbenedisulfonate, considering that this ligand does not transfer energy to the metals ions. The spectrum of $\text{Eu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_3 \cdot 3\text{H}_2\text{O}$ has the same profile, presenting a small shift with maximum intensity at 410 nm.

The overlapping emission spectra, obtained in solid state and in acetonitrile solution and fixing the excitation wavelength at 265 nm, are shown in Fig. 7.

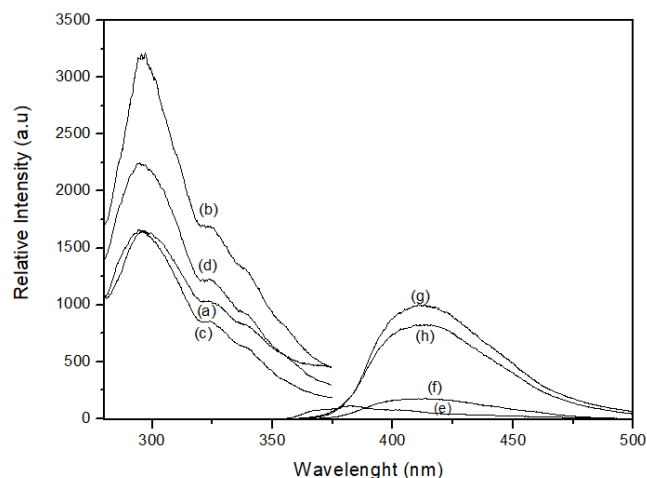
The stilbene acids and derivatives have their well-characterized photochemical reactivity. In solution phenomena like fluorescence and trans-cis isomerization are observed.¹⁶ The trans-cis isomerization is the main

quenching funnel of fluorescence. Another aspect of the stilbene chromophores is their potential ground- and excited-state reactivity with a variety of reagents. This reactivity can be modified strongly by the precise microenvironment experienced by the chromophore in different assemblies.^{15,16} Due to a possible effect of the solvent or greater freedom to rotate in solution, a shift to lower energy region in the spectra of the compounds in solution is observed. The excitation spectra obtained in acetonitrile solution (not shown), fixing the wavelength of emission in the wavelength of the most intense bands of emission spectra ($\gg 410$ nm), present different shape and intensity for all the analyzed compounds.

The excitation spectrum of 4,4'-diamino-2,2'-stilbenedisulfonic acid shows a large band comprising the region from 200 to 375 nm.

The spectrum of sodium 4,4'-diamino-2,2'-stilbenedisulfonate shows three bands at 245, 280 and 366 nm. For the complex $\text{Eu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_3 \cdot 3\text{H}_2\text{O}$ the excitation spectrum shows two excitation bands at 235 and 347 nm with a shoulder at 315 nm. The excitation spectrum of the complex $\text{Tb}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_2(\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$ shows two excitation bands centered at 260 and 374 nm. These two bands appear close to regions of the excitation spectrum of the sodium 4,4'-diamino-2,2'-stilbenedisulfonate but with different intensities between them.

Fig. 7. Spectra of emission, fixing the excitation wavelength at 265 nm, in solid state of 4,4'-diamino-2,2'-stilbenedisulfonic acid (a); the complex $\text{Eu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_3 \cdot 3\text{H}_2\text{O}$ (b); the complex $\text{Tb}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_2(\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$ (c); and sodium 4,4'-diamino-2,2'-stilbenedisulfonate (d). Spectrum of emission, fixing the excitation wavelength at 265 nm, in acetonitrile solution of 4,4'-diamino-2,2'-stilbenedisulfonic acid (e); the complex $\text{Eu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_3 \cdot 3\text{H}_2\text{O}$ (f); the complex $\text{Tb}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_2(\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$ (g) and sodium 4,4'-diamino-2,2'-stilbenedisulfonate (h)



The spectra emission intensity in solution is increased when the maximum excitation wavelength observed in the excitation spectra of the compounds is used. However, as expected, this intensity is lower than the emission intensity of the spectra in the solid state, because vibrational mode of the molecules that may quench the luminescence, decreases in this physical state.

4. Conclusions

The complexes with Eu^{3+} and Tb^{3+} ions are presented in the form of powder with black and brown colors, respectively. Data from the complexometric titration with EDTA suggest that these complexes have the general formulae $\text{Eu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_3 \cdot 3\text{H}_2\text{O}$ and $\text{Tb}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_2(\text{CF}_3\text{SO}_3) \cdot 3\text{H}_2\text{O}$. The UV-visible spectra show that there was coordination in only one of the sulfonate groups, indicating that the ligand is monodeprotonated. The FTIR spectra show that there is a coordination of complex sulfonate group by oxygen (SO_2). Thermal analysis shows that the ligand is thermally stable up to 573 K. The analysis of luminescence indicates that the complexes do not present emission from the f-f transition of the trivalent lanthanides ions. This may be related to the ligand triplet states, which probably have lower energy than the emitter state of the Eu^{3+} and Tb^{3+} ($^5\text{D}_0$ and $^5\text{D}_4$) ions.

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СИНТЕЗ, ХАРАКТЕРИСТИКА ТА ФОТОФІЗИЧНЕ ДОСЛІДЖЕННЯ КОМПЛЕКСІВ 4,4'-ДІАМІНО-2,2'-СТИЛБЕНДІСУЛЬФОНАТУ З ЙОНАМИ ЛАНТАНІДУ

Анотація. Одержано комплекс 4,4'-діаміно-2,2'-стилбендісульфонової кислоти (DSD) з йонами тривалентного лантаніду Eu^{3+} і Tb^{3+} у співвідношенні 3:1 (DSD:Ln). Комплекси у вигляді порошку мають чорний (Eu^{3+}) і коричневий (Tb^{3+}) кольори. За допомогою комплексометричного титрування та елементного аналізу CHN визначено загальну формулу комплексів: $\text{Eu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_3 \cdot 3\text{H}_2\text{O}$ та $\text{Tb}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_3\text{SO}_3\text{H})_2(\text{CF}_3\text{SO}_3)_2 \cdot 3\text{H}_2\text{O}$. Зсув смуги DSD при 330 нм до більшої величини в інфрачервоних спектрах комплексів та зникнення смуг при 2921 та 2623 cm^{-1} свідчать про утворення комплексів з йонами Eu^{3+} і Tb^{3+} . За допомогою теплового аналізу визначено, що DSD є термостабільним до 573 К, а розклад комплексів вказує на другу та третю втрату маси для йонів Eu^{3+} і Tb^{3+} , відповідно. За результатами люмінесцентного аналізу визначено, що комплекси не забезпечують випромінювання з лантаноїдної частини у видимій області, що може бути пов'язано з триплетними станами ліганду, які, ймовірно, мають меншу енергію, ніж емісійний стан йонів Eu^{3+} ($^5\text{D}_0$) and Tb^{3+} ($^5\text{D}_4$).

Ключові слова: комплекс, 4,4'-діаміно-2,2'-стилбендісульфонова кислота, лантаніди, люмінесценція.