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Recibido: 11 enero 2014. Aceptado: 21 febrero 2014

Photochemical and electrochemical studies on lanthanide complexes of 6-(hydroxymethyl)pyridine-2-carboxaldehyde[2-methyl-pyrimidine-4,6-diyl] bis-hydrazone

Abstract

Herein we report the synthesis of the 6-(hydroxymethyl)pyridine-2-carboxaldehyde[2-methyl-pyrimidine-4,6-diyl]bis-hydrazone by a condensation reaction between 6-(hydroxymethyl) picolinaldehyde with 4,6-(bis-hydrazino)-2-methylpyrimidine. This bis-hydrazone can be visualized as a two-arm system which exhibits photochemical induced [*E,E*]/[*E,Z*]/[*Z,Z'*] isomerizations and double coordination to metal centers. Configurational changes, upon UV light irradiation, were followed over time by ^{1}H NMR, establishing that isomerization, in both arms, is a consecutive reaction that follows first-order kinetics (k_1= 4.06 x 10^{-4} s^{-1} and k_2= 2.80 x 10^{-4} s^{-1}). Furthermore, the synthesis of bis-hydrazone metal complexes with La (III) and Sm (III) ions was achieved; subsequently, the absorption and emission properties of these complexes were studied, determining the fluorescence quantum yields, $\boldsymbol{\phi}_{La}$= 0.2024 and $\boldsymbol{\phi}_{Sm}$= 0.1413. Electrochemical studies of the complexes were conducted by square wave voltammetry, demonstrating that the bis-hydrazone and its complexes are electroactive species between +1.5 and -2.5 V.

Keywords: Lanthanide complexes, photochemistry, bis-hidrazones, isomerization, UV-Vis/Fluorescence, electrochemistry.

Estudios fotoquímicos y electroquímicos de complejos lantánidos de 6-(hidroximetil)piridin-2-carboxaldehído[2-metilpirimidina-4,6-diil] bishidrazona

Resumen

Se reporta la síntesis de la 6-(hidroximetil) piridin-2-carboxaldehído[2-metilpirimidina-4,6-diil]bishidrazona mediante la reacción de condensación entre el 6-(hidroximetil) piconaldehído con la 4,6-(bishidracino)-2-metilpirimidina. Esta bishidrazona puede ser visualizada como un sistema de dos brazos los cuales exhiben isomerizaciones [*E,E*]/[*E,Z*]/[*Z,Z'*] fotoquímicamente inducidas y coordinación a centros metálicos. Los cambios configuracionales, después de irradiación UV, fueron seguidos en el tiempo mediante RMN ^{1}H estableciendo que la isomerización, en ambos brazos del sistema, corresponde a una reacción consecutiva que sigue una cinética de primer orden (k_1= 4,06 x 10^{-4} s^{-1} y k_2= 2,80 x 10^{-4} s^{-1}). Además se prepararon complejos metálicos de La (III) y Sm(III), seguidamente, las propiedades de absorción y emisión de dichos complejos fueron estudiadas calculando rendimientos cuánticos de fluorescencia de $\boldsymbol{\phi}_{La}$ =0,2024 y $\boldsymbol{\phi}_{Sm}$= 0,1413. Estudios electroquímicos de los complejos se llevaron a cabo a través de voltametría de onda cuadrada indicando que los compuestos preparados poseen potenciales redox dentro del rango de trabajo del solvente.

Palabras clave: Complejos lantánidos, fotoquímica, bis-hidrazonas, isomerización UV-Vis/fluorescencia, electroquímica.

Estuduios fotoquímicos e eletroquímicos do complexos lantanídeos do 6-(hidroximetil) piridin-2-carboxaldeído[2-metilpirimidina-4,6-diil] bis-hidrazona

Resumo

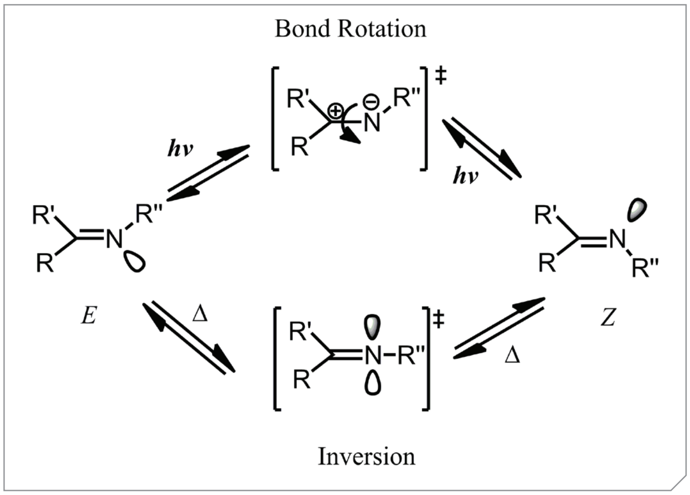
Reporta-se a síntese da 6-(hidroximetil) piridin-2-carboxaldeído[2-metilpirimidina-4,6-diil]bis-hidrazona mediante a reação de condensação entre o 6-(hidroximetil) piconaldeído e a 4,6-(bis-hidrazino)-2-metilpirimidina. Esta bis-hidrazona pode ser visualizada como um sistema de dois braços os quais exibem isomerizações [*E,E*]/[*E,Z*]/[*Z,Z'*] fotoquimicamente induzidas e coordenação com íons metálicos (dupla coordenação a íons metálicos). Após a irradiação UV, as mudanças configuracionais foram monitoradas com o tempo por RMN ^{1}H. Essas medidas estabeleceram que a isomerização em ambos braços do sistema corresponde a uma reação consecutiva apresentando uma cinética de primeira ordem (k_1= 4.06 x 10^{-4} s^{-1} e k_2= 2.80 x 10^{-4} s^{-1}). Além disso, os complexos metálicos de La (III) e Sm(III) foram preparados e suas propriedades de absorção e de emissão foram estudadas, calculando os rendimentos quânticos de fluorescência de $\boldsymbol{\phi}_{La}$= 0.2024 e de $\boldsymbol{\phi}_{Sm}$= 0.1413. Estudos eletroquímicos dos complexos foram feitos através de voltametria de onda quadrada indicando que os compostos preparados possuem potenciais redox dentro da faixa de trabalho do solvente.

Palavras-Chave: complexos lantanídeos, fotoquímica, bis-hidrazonas, isomerização UV-Vis/fluorescência, eletroquímica.

Introduction

Hydrazones are a family of organic compounds that contain the =R-C(R_1)=N-NH-R_2 group, which is formed by the condensation of hydrazine derivatives with aldehydes or ketones (1). Hydrazones have been of great interest due to three main characteristics: a) the possibility of attach different substituents R, R_1 and R_2 in their structure; b) the photochemically induced *E/Z* isomerization undergone by the double bond of the imine group; and c) the capacity to chelate metal ions according to the nature of their R groups. These characteristics allow hydrazones to present diverse applications in the industry as plasticizers, polymer stabilizers, antioxidants and polymerization initiators, or in the biomedicine field in the development of new compounds with anticonvulsant, antidepressant, analgesic, anti-inflammatory, antimalarial, antibiotic, antitubercular, vasodilatory, antitumor and antiviral properties, among others (2-5 and therein).

The hydrazones represent dynamic systems capable of acting as multiple state molecular devices in which, depending on the appropriated substituents, the presence of coordination sites allows the controlled blocking and unblocking by metal ions and the interconversion of different configurational states (6, 7). In addition, some of these compounds exhibit photoinduced *E/Z* isomerization which can be reversed under light or heat conditions to restore the initial configuration (7, 8). This property is one of the reasons that hydrazones have been of great importance, as they present high biological activity and a wide range of applications in molecular machines and for information storage devices (7). The photochemically and thermally induced isomerization process in hydrazones is illustrated in Scheme 1. When irradiated with ultraviolet light, these imino-type compounds undergo isomerization of the *E* state, which is the thermodynamically most stable state, to the least stable *Z* state.



Scheme 1. The photochemically and thermally activated isomerization process of hydrazones.

The capacity of these compounds to chelate metal ions has allowed the characterization of various structures including lanthanide elements (9-11). The great attraction of lanthanide metal complexes is mainly based on their low toxicity, their luminescent and paramagnetic properties, their relatively high natural abundance and their accessible price (except for Sc^{3+}) (12). In addition, the trivalent lanthanide ions (Ln^{3+}) potentially have high and diverse coordination numbers with flexible coordination environments, where they behave as Pearson hard acids, showing a strong affinity for strong bases with neutral or negatively charged oxygen or nitrogen atoms (13). However, the photoluminescence of trivalent lanthanide ions can be inefficient because they exhibit low molar absorption coefficients (ε), the majority of the transitions in the absorption spectra of the lanthanide ions are lower than 10 L mol^{-1} cm^{-1}. Consequently, only a very limited amount of radiation is absorbed by direct excitation of the 4*f* levels. However, this problem can be overcome by the so-called antenna effect (14), in which a chromophore compound promotes the sensitization of light emission in the lanthanides. The antenna is, in general, a highly π-conjugated aromatic or heteroaromatic system characterized by a high extinction coefficient that improves the crossing efficiency between systems, and therefore improves the energy transfer processes (see Figure 1) (15).

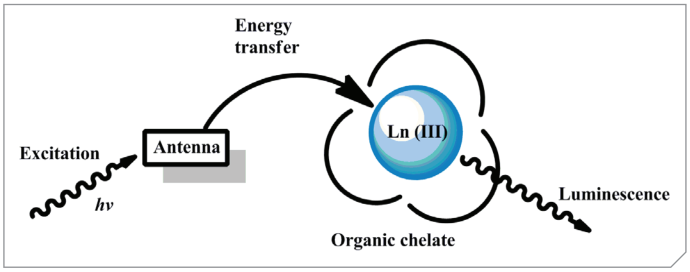
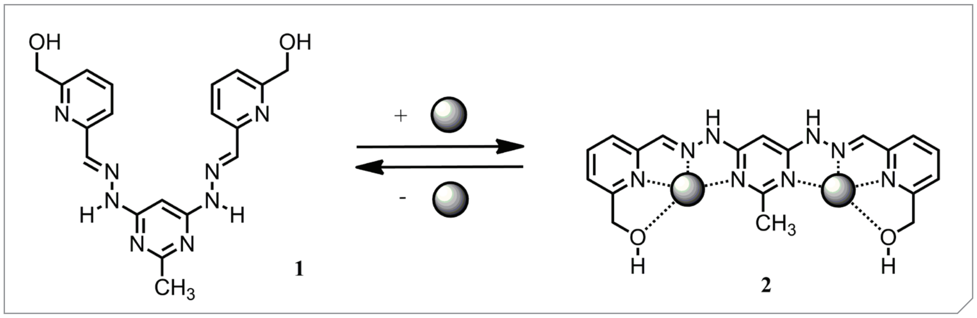


Figure 1. Sensitization mechanism in a lanthanide-antenna system.

Special interest is devoted to the design and development of dynamic multifunctional systems, within this aim, bis-hydrazone **1** (Scheme 2) was synthesized remarking that its structure can be visualized as a two-arm system, capable of coordinate two metal centers and it is able to undergo photochemical *E/Z* isomerization. Once compound **1** was prepared, light driven isomerization was studied over time; in addition, its effect as an antenna in the luminescence of La and Sm(III) complexes was investigated as well as their electrochemical properties in solution.

Materials and methods

The FT-IR, NMR (uni- and bidimensional), fluorescence and UV-vis spectra, melting point, refraction index, elemental analysis and elec-



Scheme 2. Structure of the complex formed with the 6-(hydroxymethyl)pyridine-2-carboxaldehyde[2-methyl-pyrimidine-4,6-diyl]bis-hydrazone.

trochemical studies were performed in a Shimadzu FTIR-8400 spectrophotometer, a 400 MHz Bruker Ultra Shield NMR spectrometer, a FP-8500 Jasco spectrofluorometer, a UV-Vis UV-1700 PharmaSpec Shimadzu spectrophotometer, a Stuart SMP3 melting point apparatus, an Atago NAR-2T refractometer, a Thermo Flash EA 1112 series elemental analyzer and a CHI760B CH instruments potentiostat, respectively. All reactants and solvents were purchased from Sigma-Aldrich and used without further purification.

Synthesis of [E,E′]- 6-(Hydroxymethyl)pyridine-2-carboxaldehyde[2-methyl-pyrimidine-4,6-diyl]bis-hydrazone (E,E′) (1)

Compound **1** was synthesized by dissolving 1 eq. of 6-(hydroxymethyl) picolinaldehyde and 2 eq. of 4,6-(bis-hydrazino)-2-methylpyrimidine in dry ethanol; this mixture was refluxed under argon atmosphere for 24 h. The bis-hydrazonic compound was characterized as a light yellow solid with m.p.: 305 °C in a 84 % yield; ^{1}H NMR (400 MHz, DMSO-d_6), δ/ppm: 11.33 (s, 2H), 8.08 (s, 2H), 7.91-7.81 (m, 4H), 7.43 (d, J = 7.03 Hz, 2H), 6.77 (s, 1H), 5.47 (t, J = 5.90 Hz, 2H), 4.58 (d, J = 6.02 Hz, 4H), 2.32 (s, 3H). ^{13}C RMN (101 MHz, DMSO-d_6); δ/ppm: 166.27, 161.98, 161.83, 152.61, 142.00, 137.24, 119.83, 117.45, 79.25, 64.12, 25.06. Elemental analysis calculated for $C_{19}H_{20}N_8O_2$ (%): C, 57.10; H, 5.32; N, 27.72; and found (%): C 57.15, H 5.24, N 27.65.

Photoisomerization of 1

Compound **1** was subjected to *E/Z* photoisomerization by UV light using a Mercury Vapor Lamp of 250 W. This process was monitored by ^{1}H NMR, for which samples of **1** were subjected to irradiation with UV light in a quartz NMR tube. The studies were performed in DMSO-d_6.

Synthesis of the metal complexes of La and Sm (III)

The formation of the metal complexes was conducted using $LaCl_3{\cdot}6H_2O$ and compound **1** in a 2:1 ratio, 2 equivalents of sodium hydroxide (NaOH) were added, and the mixture was subjected to reflux under argon for 24 h. The complex with Sm (III) was synthesized from **1** and $SmCl_3{\cdot}6H_2O$, in a similar procedure.

Spectroscopic analysis (UV-Vis/Fluorescence)

Eight solutions of known concentration of the metal complexes in ethanol were prepared adding buffer solutions at different pH values between 1 and 8 units. The study was monitored by fluorescence and UV-vis spectroscopy.

Determination of the fluorescence quantum yield (ϕ)

To perform this measurement, the comparative method of Williams *et al*. (16) was used, which involved the use of a standard sample (tryptophan) with known Φ (17). The emission spectra were collected in a wavelength range from 200 to 750 nm.

Electrochemical analysis of the ligand and the metal complexes

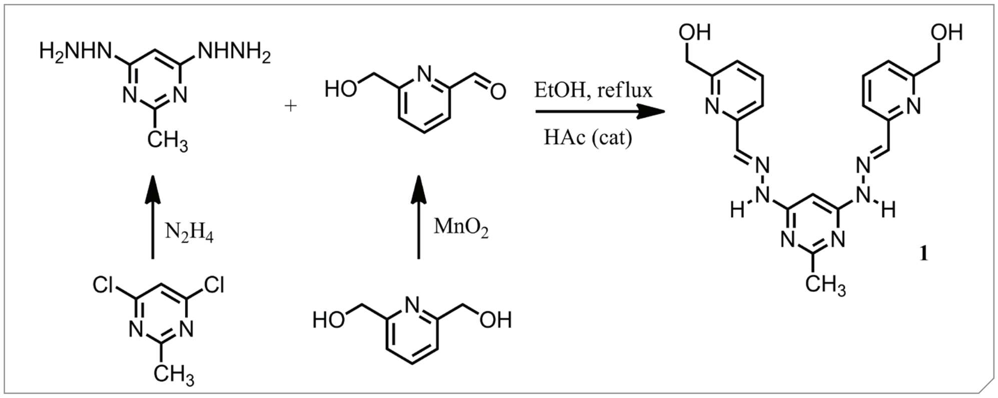
Osteryoung Square Wave Voltammetry was performed in THF containing 0.1 mol L^{-1} of $N(n\text{-}Bu)_4PF_6$ as the supporting electrolyte. The concentration in analyte was about 5.0x10^{-4} mol L^{-1}. A 2 mm diameter glassy carbon disk was used as the working electrode and a platinum wire as the counter electrode. A silver wire served as a pseudo reference electrode. A small amount of ferrocene was added at the end of each experiment and used as a reference for measuring the potentials.

Results and discussion

Synthesis of bis-hydrazone 1

Compound **1** was synthetized by the condensation reaction of 6-(hydroxymethyl)picolinaldehyde with 4,6-(bis-hydrazino)-2-methylpyrimidine in reflux of ethanol, with the addition of catalytic amounts of glacial acetic acid (Scheme 3). A yellow solid was obtained with a yield of 84% and a melting point of 305 °C; this solid was spectroscopically characterized by NMR (^{1}H, ^{13}C, DEPT-135 and COSY). Bidimiensional NMR studies confirmed the *transoid* structure of **1** and the *E,E* configuration.

Compound **1** contains two imine groups that can undergo *E* --> *Z* isomerization induced by UV light, this feature might allow the photochemical control of the movement of both arms and therefore this type of compounds exhibit configurational dynamics of potential use in molecular machines and information storage devices. The pyridine-imine-pyrimidine-imine-pyrimidine framework allows the formation of bimetallic complexes (3, 7) and, under special reaction conditions, is able of forming grids and other supramolecular architectures (3). On the other hand, the acidic N-H proton can be removed by the addition of a base, resulting in stronger metal complexes with different electronic properties.



Scheme 3. Synthesis of bis-hydrazone 1.

Photochemical studies of bis-hydrazone 1

Compound **1** was subjected to controlled *E*/*Z* isomerization with UV light. In order to investigate the occurrence of isomers in their *Z* and *E* configurations, solutions of 1-[*E,E'*] 30.58 mM in DMSO-d_6 were prepared in quartz NMR tubes and irradiated with a mercury vapor lamp of 250 W for different times varying between 0–90 min; the photoisomerization was monitored by ^{1}H NMR spectroscopy. To quantify the amounts of the *E,Z'* and *Z,Z'* isomers formed, the signal of proton 5 of the pyrimidine ring was taken as a reference (see Figure 2). When examining the ^{1}H NMR spectrum, the singlet at 6.83 ppm, corresponding to the *N-H* proton, splits as the *E,Z* and *Z,Z* isomers are formed, indicating the formation of intramolecular hydrogen bonds.

Photoisomerization was monitored over time and the relative amounts of each isomer were calculated (see Figure 3) and used to determine a first order consecutive reaction (of type *E,E' E,Z Z,Z'*) with kinetic constants k_1= 4.06 x 10^{-4} s^{-1} and k_2= 2.80 x 10^{-4} s^{-1}, the formation percentages of the *Z,Z'* and *E,Z* isomers were 43 and 46% respectively, after irradiating the sample during 90 min (when equilibrium was reached).

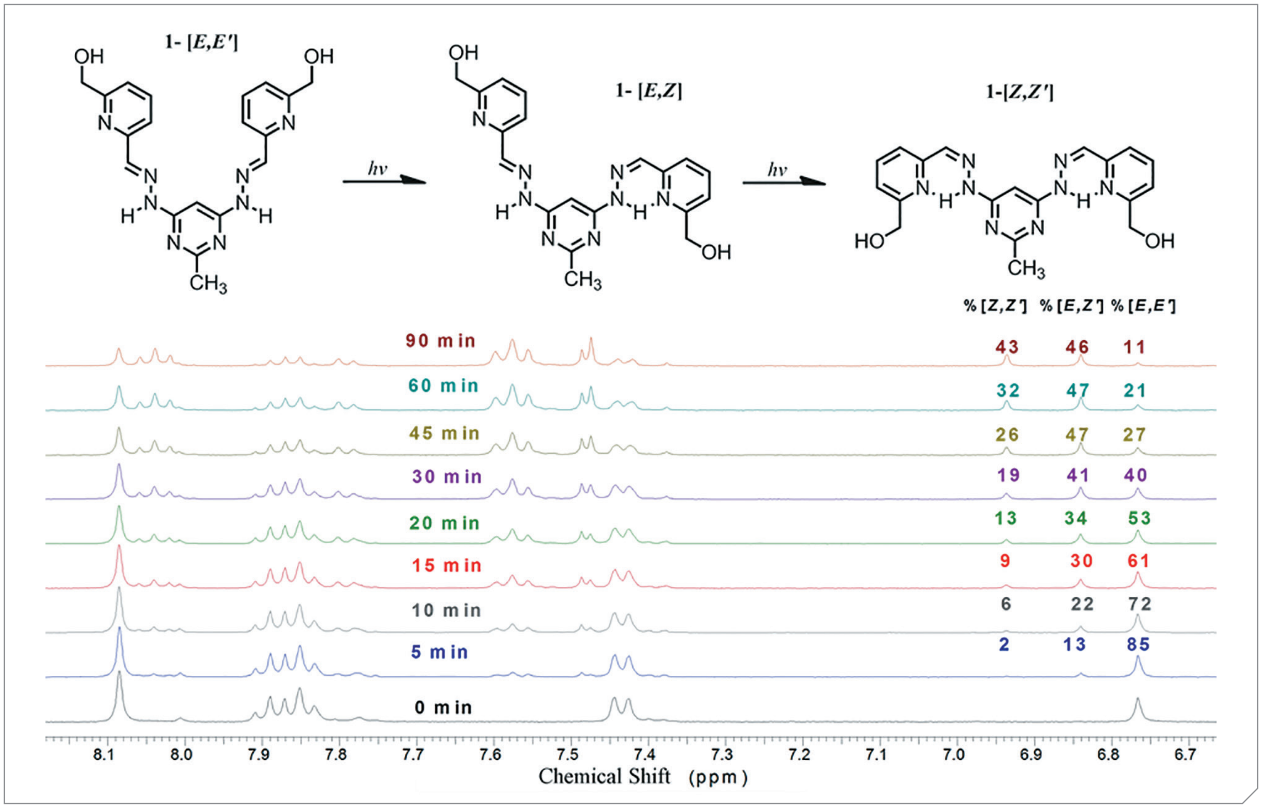


Figure 2. Photoisomerization of 1. Top: Scheme of photochemically activated isomerization. Bottom: ^{1}H NMR (400 MHz) spectra of bis-hydrazone **1** in DMSO-d_6 at different irradiation times in a quartz tube (for clarity, only the aromatic region of the spectra is shown).

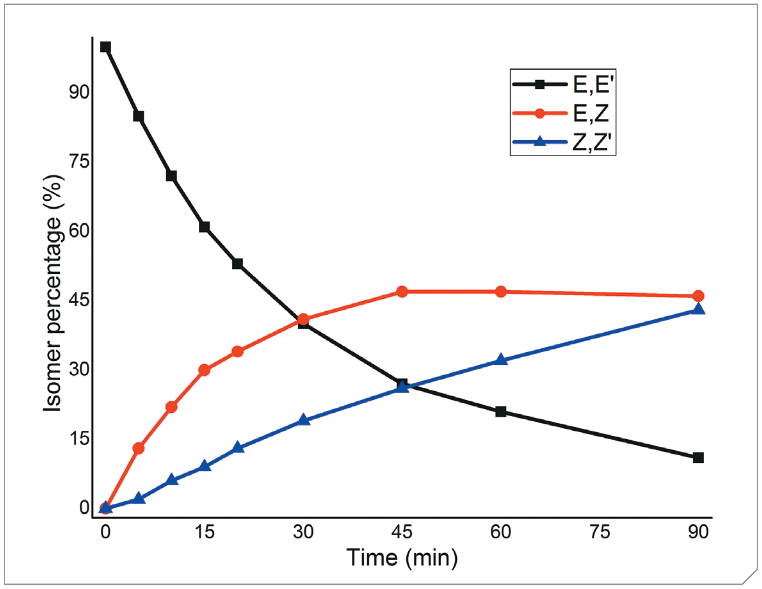


Figure 3. Isomer percentages *vs.* irradiation time.

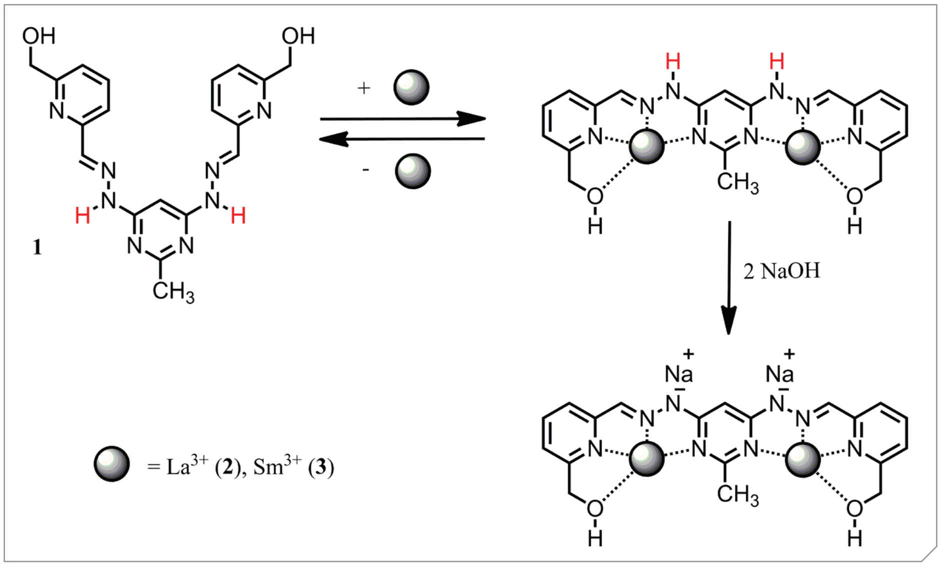
These results allowed quantification of the irradiation times at which separation would produce a greater yield of isomers [*E,Z*] and [*Z,Z'*]. In addition, the formation of metastable compounds such as [*E,Z*] and [*Z,Z'*] that exhibit different absorption and emission properties and that can also be thermally driven to [*E,E'*] makes it possible to obtain multiple dynamics systems.

Reaction of 6-(hydroxymethyl)pyridine-2-carboxaldehyde[2-methylpyrimidine-4,6-diyl]bis-hydrazone with lanthanide chlorides

The reaction of **1** in refluxing ethanol with trivalent metal salts ($LaCl_3 \cdot 6H_2O$ and $SmCl_3 \cdot 6H_2O$) in the presence of two equivalents of sodium hydroxide led to the formation of the neutral complexes **2** and **3** (Scheme 4). These compounds were obtained as solids with moderated yields (50–76%), (see Table 1).

Spectroscopic analysis (UV-Vis/Fluorescence)

Fluorescence and UV/Vis spectra were carried out in buffer solutions of pH between 1 and 8. The emission spectra of complex **3** in the pH interval of 6-8 exhibited a marked fluorescence improvement, while at pH between 4 and 5 the fluorescence intensity was sharply reduced. Consistently, the optical behavior shown by the complex at different pH values can be attributed to a sensitization of the hydrazine (antenna); this ligand can be protonated and deprotonated under acidic and alkaline conditions, and therefore, the coordination strength can be tunneled, as a consequence a greater efficiency is observed in the energy transmission (see Figure 4). The electronic spectrum of complex **3** has a band of significant absorption at a $\lambda_{máx}$ of ~ 311 nm in the pH interval of 3–5; this result indicates the protonation of the hydrazone. Consequently, it is demonstrated that the ligand, in this pH range, is a good organic chelator that absorbs energy and transfers it to the Sm (III) ion.



Scheme 4. Formation reaction of the metal complexes 2 and 3 with 1.

Table 1. Characteristics of the complexes 2 and 3.

Compound	Yield (%)	Color	Decomposition temperature (°C)
2	76	Violet	312
3	50	Dark yellow	298

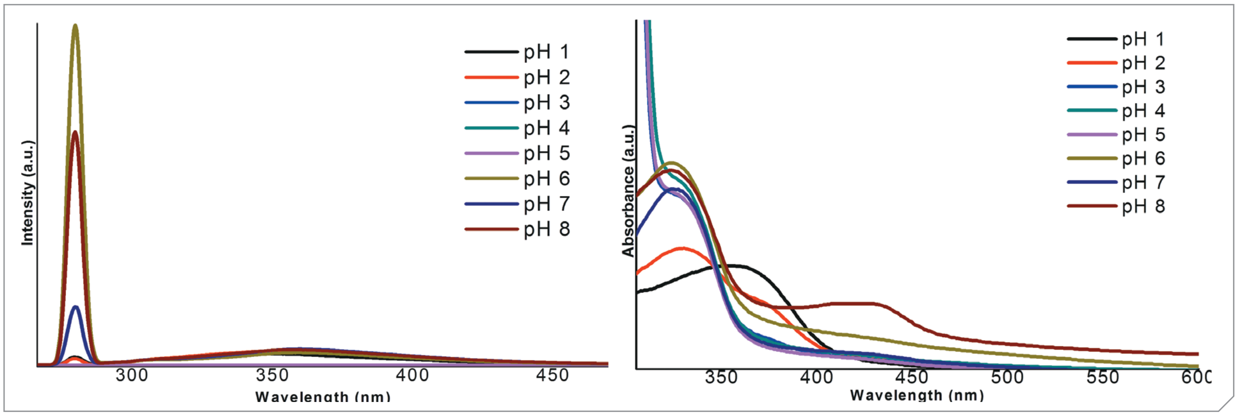


Figure 4. Spectra of 3 at different pH values. Left: Fluorescence at λ_{exc} = 280.5 nm. Right: UV-Vis.

This absorption maximum occurs due to the π-π* and n-π* transitions of the fluorophore.

Determination of the fluorescence quantum yield ($\boldsymbol{\phi}$)

The fluorescence quantum yields were determined by comparison to the emission intensity of a tryptophan sample in water as standard (16, 17). Compound **1** barely showed fluorescence in ethanol (see Table 2); however, its complexes with lanthanide ions exhibited a relatively strong fluorescence with an increase in $\boldsymbol{\phi}$ of ~74 times for complex **2** and ~52 times for complex **3**.

The greater $\boldsymbol{\phi}$ values result from the suppression of the non-radiant relaxation of the excited state through increased structure rigidity and the sensitization of the metal *f-f* transitions. A slight decrease in the $\boldsymbol{\phi}$ value of the complex with La(III) was observed with respect to the complex formed with Sm(III), caused by a decrease in the ionic radius. The acidity of the metal centers plays a fundamental role in the improvement of $\boldsymbol{\phi}$ due to an increase in the size of the different metal centers with the same oxidation state. According to Pearson´s acid-base concept, the trivalent lanthanide ions behave as hard acids, with low polarizability and high oxidation number (18). Because hard acids interact strongly with hard bases, the lanthanide ions preferentially form very stable complexes with ligands that contain donating atoms such as oxygen or nitrogen (13), so that La(III) will have a greater affinity towards the ligand; the greater ionic radius will decrease the distance between the sensitizer and the cation, consequently improving the $\boldsymbol{\phi}$ (19).

Electrochemical analysis of bis-hydrazone and metal complexes

The electrochemical properties of **1** and the complexes **2** and **3** were studied in solutions of $(n\text{-Bu})_4NPF_6$ mol L$_{-1}$ in THF at a scanning speed of 100 mV s^{-1}. They were measured using a glassy carbon electrode as the working electrode, a wire of silver as a pseudo-reference electrode and a wire of platinum as a counter electrode. After the measurements, ferrocene was added as an internal standard. The voltammogram of **1** shows two peaks at -2.23 and +0.59 V (*versus* Fc/Fc$^+$) corresponding to the reductive and oxidative processes on the hydrazone framework (see Figure 5); both processes are irreversible (by cyclic voltammetry) and characterized by a ΔE_{gap} of -2.82 V. The first oxidation potential of the hydrazone **1** is anodically shifted to +0.67 V in the complex **2** and to +1.21 V in the complex **3**. This anodic shift is due to the inherent inductive effect of a coordination between an aromatic ligand and a metal center and the difference (+0.67 vs +1.21 V) between the two complex probably is due to the electronegativity difference of both metals (see Table 3) although further studies are needed in order to corroborate this trend. Compound **3** does not exhibit a well-defined electrochemistry, at least in the solvent window.

The study of the hydrazonic structure demonstrated that both the hydrazone and its complexes have luminescent properties and are electrochemically active species in THF. It is noted that both **1** and its respective complexes have a maximum excitation wavelength between 380 and 400 nm, which facilitates the use of low cost excitation sources, avoids the use of quartz optics and makes them potential compounds for investigations in biological systems, as a light source in the visible range.

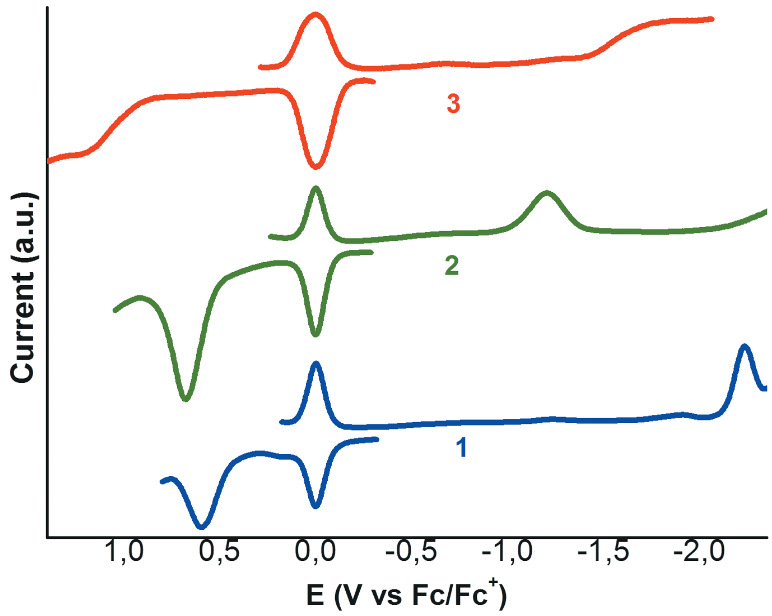


Figure 5. Osteryoung square wave voltammetry of the ligand (**1**) and its complexes (**2,3**), scanning speed: 100 mV s^{-1}.

Table 2. Fluorescence quantum yield for bis-hydrazone and the complexes.

Compound	Solvent	Quantum yield
Standard	Water	0.13 (theoretical)
1	Ethanol	0.0027
2		0.2024
3		0.1413

Table 3. Electrochemical peak potentials of the ligands and complexes.

Compound	$E_{red\ (1)}$ (V)	$E_{oxi\ (1)}$ (V)	ΔE_{gap} (V)
1	-2.23	0.59	-2.82
2	-1,20	0.67	-1.87
3	-1.36	1.21	-2.57

Conclusions

The 6-(hydroxymethyl)pyridine-2-carboxaldehyde[2-methyl-pyrimidine-4,6-diyl]bis-hydrazone ligand was successfully synthesized and obtained as a yellow solid with a yield of 84 %. This bis-hydrazone was effectively photoisomerized when irradiating the sample with a mercury vapor lamp of 250 W. After 90 min, it was possible to obtain the isomers *Z,Z'*, *E,Z* and *E,E'* with percentages of 43, 46 and 11%, respectively.

Reaction conditions were successfully established, and metal complexes of La (III) and Sm (III) with bis-hydrazone as ligand could be synthetized with yield percentages between 50–76%. Their photophysics was investigated by fluorescence and UV-vis spectroscopy at different pH values establishing that the pH ranges in which there is greater absorption and where improvement of the fluorescence intensity occurs are 3–5 and 6-8, respectively. The luminescence properties of the complexes were determined by the study of the fluorescence quantum yield, where it is observed that for the complexes **2** (0.2024) and **3** (0.1413), the luminescence increases significantly with respect to the ligand **1** (0.0027). This result is attributed to the suppression of the non-radiant relaxation of the excited state by the increased structural rigidity and the sensitization of the 4*f*–4*f* transitions of the lanthanide ions.

Acknowledgements

The authors are grateful to Colciencias (code grant 110656934339), to the "Fundación para la Promoción de la Investigación y la Tecnología (Banco de la República-3238)" the Vicerrectoría de Investigaciones (convocatoria interna) and the CENM from Universidad del Valle for their generous financial support.

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Article citation:
Fernández, M. A.; Barona, J.C.; Polo-Cerón, D.; Chaur, M.N. Photochemical and electrochemical studies on lanthanide complexes of 6-(hydroxymethyl)pyridine-2-carboxaldehyde[2-methyl-pyrimidine-4,6-diyl]bis-hydrazone. *Rev Colomb Quim*. 2014. **43**(1): 5-11. • DOI: http://dx.doi.org/10.15446/rev.colomb.quim.v43n1.50540