

The paramagnetic metal effect on the luminescence of rare-earth-metal complexes with pyridine-based nitrogen ligands



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ABSTRACT

The synthesis and the characterization in the solid state are presented of La(III), Gd(III) and Lu(III) nitrate complexes with the pyridine-based ligands **L1** (N,N'-bis(2-pyridylmethylidene)-1,2-(R,R+S,S)-cyclohexanediamine) and **L2** (N,N'-bis(2-pyridylmethyl)-1,2-(R,R+S,S)-cyclohexanediamine). The crucial role of the nature of both the lanthanide ion and the ligand in the luminescence spectroscopy of the metal complexes, in the solid state at room temperature, is demonstrated and discussed. In particular, the "paramagnetic effect" of the Gd(III) ion inducing an increased phosphorescence emission is observed in the complex with **L1** ligand and, in a lesser extent, in the complex with **L2** ligand. At variance with this observation, only fluorescence emission of the La(III) and Lu(III) diamagnetic metal complexes is detected.

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1. Introduction

Lanthanide compounds have attracted much attention in the field of luminescence spectroscopy. The excited state behavior of trivalent lanthanide ions have been studied extensively [1–9]. The electronic spectra of Ln³⁺ with fⁿ (n = 2–13) electron configuration are dominated by intra-configurational f–f electronic transitions, that are in principle strictly parity-forbidden. In addition, many f–f transitions are also spin-forbidden although this selection rule is partially relaxed by the spin–orbit coupling which facilitates a mixing with spin-allowed transitions. The f–f transitions have small absorption coefficients and the radiative lifetimes of f excited states are in the μs (for Er³⁺, Yb³⁺ and Nd³⁺) or in the ms (for Eu³⁺, Tb³⁺ and Sm³⁺) ranges.

In order to bypass the parity-forbidden nature of the f–f transitions, enhancing the light absorption by Ln³⁺ complexes, an efficient intramolecular energy transfer from the triplet state of a coordinated organic ligand (antenna) to the excited state of Ln³⁺ ion can be exploited. The antenna effect has been extensively used in Lanthanide complexes with potential applications in several fields, such as medical diagnostics and optical cell imaging [7,10,11], where high values of the brightness ($\epsilon \cdot \phi$) are required in order to detect traces of analytes. We note that the f–f transitions of Gd³⁺ are located at high energies due to the extreme stability of its half-filled f-shell (f⁷). The lowest-energy f–f transition appears as an emission line around 310 nm and, for this

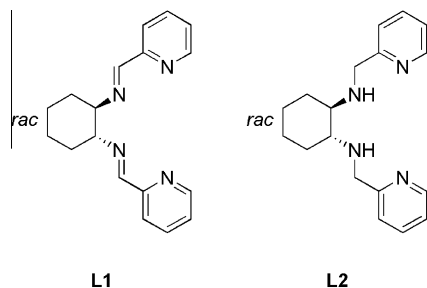
reason, in the Gd(III)-based complexes no antenna effect is usually detected. Accordingly, Gd(III) complexes are frequently characterized by emissive intraligand (IL) states at lower energies. Lanthanide ions produce a heavy-atom effect to ligands by inducing increased spin–orbit coupling. Gd(III) in particular, due to its heavy-atom effect and paramagnetism (the so called paramagnetic metal effect), can induce a strong singlet/triplet mixing in the ligands [12]. As a consequence, the fluorescence of the ligand is quenched since intersystem crossing becomes faster. For the same reason, the radiative lifetime of the triplet decreases and the phosphorescence quantum yield grows [13–16]. Intra-ligand phosphorescence of several Gd(III) complexes appears also at room temperature [17,18] revealing the importance of this phenomenon for potential technological applications.

In the present work, we have focused our attention on the La(III), Gd(III) and Lu(III) complexes of two racemic nitrogen-based ligands N,N'-bis(2-pyridylmethylidene)-1,2-(R,R+S,S)-cyclohexanediamine, **L1**; and N,N'-bis(2-pyridylmethyl)-1,2-(R,R+S,S)-cyclohexanediamine, **L2**. The nature of both the lanthanide ion and the ligand plays a significant role on the luminescence spectroscopy of the metal complex, in the solid state at room temperature.

2. Experimental

N,N'-bis(2-pyridylmethylidene)-1,2-(R,R+S,S)-cyclohexanediamine (**L1**) and N,N'-bis(2-pyridylmethyl)-1,2-(R,R+S,S)-cyclohexanediamine (**L2**) (scheme 1) were obtained as previously reported [19,20]. All the complexes have been synthesized by

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Scheme 1. Molecular structure of the ligands under investigation.

addition of the desired ligand (**L1** or **L2**) to an ethanolic solution of $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Gd}$ and Lu) added in a equimolar amount. All the complexes insoluble in ethanol have been collected by filtration after 3 h of stirring of the mixture.

2.1. La(III) complexes

L1La(NO₃)₃: Yield 77%. Elemental *Anal.* Calc. for $\text{C}_{18}\text{H}_{20}\text{LaN}_7\text{O}_9 \cdot 3\text{H}_2\text{O}$ (MW 671.34): C, 32.20; H, 3.90; N, 14.60. Found: C, 32.28; H, 3.98; N, 14.65%. ESI-MS (Scan ES+; m/z): 555 ($[\text{L1La}(\text{NO}_3)_2]^+$).

L2La(NO₃)₃: Yield 56%. As the XRPD (X-ray powder diffraction pattern) of **L2La(NO₃)₃** and **L2Eu(NO₃)₃** are superimposable, they possess the same molecular crystal structure (and formula). For more details see the results and discussion section. ESI-MS (Scan ES+; m/z): 559 ($[\text{L2La}(\text{NO}_3)_2]^+$).

2.2. Gd(III) complexes

L1Gd(NO₃)₃: Yield 76%. As the XRPD (X-ray powder diffraction pattern) of **L1Gd(NO₃)₃** and **L1Eu(NO₃)₃** are superimposable, they possess the same molecular crystal structure (and formula). For more details see the results and discussion section. ESI-MS (Scan ES+; m/z): 574 ($[\text{L1Gd}(\text{NO}_3)_2]^+$).

L2Gd(NO₃)₃: Yield 56%. As the XRPD (X-ray powder diffraction pattern) of **L2Gd(NO₃)₃** and **L2Eu(NO₃)₃** are superimposable, they possess the same molecular crystal structure (and formula). For more details see the results and discussion section. ESI-MS (Scan ES+; m/z): 578 ($[\text{L2Gd}(\text{NO}_3)_2]^+$).

2.3. Lu(III) complexes

L1Lu(NO₃)₃: Yield 71%. Elemental *Anal.* Calc. for $\text{C}_{18}\text{H}_{20}\text{LuN}_7\text{O}_9 \cdot 2\text{H}_2\text{O}$ (MW 689.39): C, 31.36; H, 3.51; N, 14.22. Found: C, 31.41; H, 3.44; N, 14.28%. ESI-MS (Scan ES+; m/z): 591 ($[\text{L1Lu}(\text{NO}_3)_2]^+$).

L2Lu(NO₃)₃: Yield 59%. As the XRPD (X-ray powder diffraction pattern) of **L2Lu(NO₃)₃** and **L2Eu(NO₃)₃** are superimposable, they possess the same molecular crystal structure (and formula). For more details see the results and discussion section. ESI-MS (Scan ES+; m/z): 595 ($[\text{L2Lu}(\text{NO}_3)_2]^+$).

2.4. Powder X-ray diffraction

X-ray powder diffraction (XRPD) patterns were measured with a Thermo ARL XTRA powder diffractometer, operating in the Bragg–Brentano geometry and equipped with a Cu-anode X-ray source ($K\alpha$, $\lambda = 1.5418 \text{ \AA}$), using a Peltier Si(Li) cooled solid state detector. The patterns were collected with a scan rate of $0.02^\circ/\text{s}$ in the 5° – 90° 2θ range. Polycrystalline samples were ground in a mortar and then put in a low-background sample holder for the data collection.

The ESI mass spectra have been collected by means of a Bruker ion trap mass spectrometer Esquire 6000, equipped with an electrospray ionization (ESI) source.

Elemental analyses were carried out by using a CHN Thermo Scientific “Flash Analyzer 2000”.

2.5. Luminescence

Room temperature emission and excitation spectra and emission decay curves were measured with a Fluorolog 3 (Horiba-Jobin Yvon) spectrofluorimeter, equipped with a Xe lamp, a double excitation monochromator, a single emission monochromator (mod. HR320) and a photomultiplier in photon counting mode for the detection of the emitted signal.

3. Results and discussion

All the synthesized complexes have been characterized by means of elemental analysis, ESI-MS and X-ray powder diffraction (XRPD).

The XRPD patterns of the Gd(III) and Eu(III) complexes with the ligand **L1** are superimposable. The pattern of the Eu(III) complex has been collected on a powdered sample obtained by grinding crystals of known structure [20]. From a close inspection of the Fig. 1, we can observe the close similarity between the XRPD patterns of all the investigated complexes with the ligand **L2** and the one of the **L2Eu(NO₃)₃**. Also in this case, the powder of the latter compound has been obtained by grinding crystals whose structure has been previously reported [20]. As the La(III), Gd(III), Lu(III) and Eu(III) complexes with **L2** are isostructural they must possess the same molecular crystal structures. The same argument can be used to claim that the Gd(III) and Eu(III) complexes with the ligand **L1** have the same molecular crystal structure.

As far as the structures of the **L1** complexes with Eu(III) and Gd(III) and of the **L2** complexes with Eu(III), La(III), Gd(III) and Lu(III) are concerned, in all cases the metal center is bound to three bidentate nitrate anion and one tetradentate ligand molecule and the crowded Ln(III) environments are characterized by a 10-fold coordination, as observed for the Eu(III) complex [20].

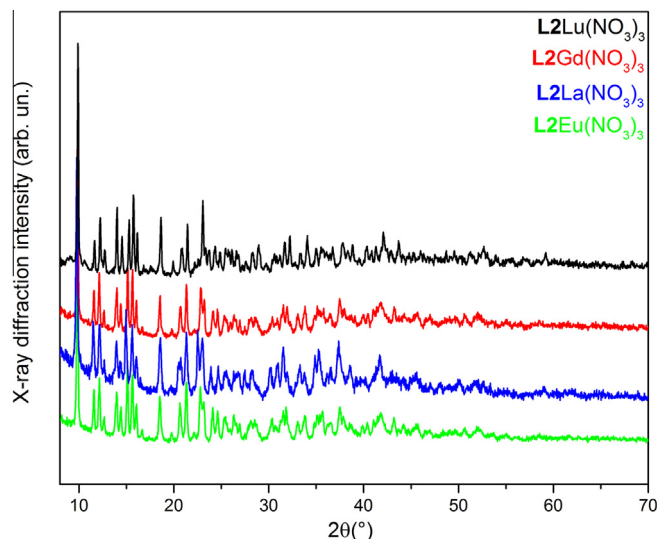


Fig. 1. XRPD of the complexes of Ln(III) ($\text{Ln} = \text{Eu}, \text{La}, \text{Gd}$ and Lu) ions with the ligand **L2**. The powder of **L2Eu(NO₃)₃** has been obtained by grinding crystals which the structure has been previously reported [20]. (The observed powder patterns of **L2Eu(NO₃)₃** and the one calculated from the single crystal structure are identical).

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