



Structure and luminescent investigation of the Ln(III)– β -diketonate complexes containing tertiary amides

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ABSTRACT

The synthesis and photoluminescent properties of Ln(III)–thenoyltrifluoroacetate and dibenzoylmethanate complexes (Ln = Eu(III) and Gd(III) ions) containing tertiary amides such as dimethylacetamide (DMA), dimethylformamide (DMF), and dimethylbenzamide (DMB) as neutral ligands are reported. The Ln complexes were characterized by elemental analysis, complexometric titration with EDTA, and infrared spectroscopy. Single-crystal X-ray structure data of the [Eu(DBM)₃·(DMA)] compound indicates that this complex crystallizes in the triclinic system, space group *P*1̄ with the following cell parameters: *a* = 10.2580(3) Å, *b* = 10.3843(2) Å, *c* = 22.3517(5) Å, α = 78.906(2)°, β = 78.049(2)°, λ = 63.239(2)°, *V* = 2066.41(9) Å³, and *Z* = 2. The coordination polyhedron for the Eu(III) complex may be described as an approximate C_{2v} distorted monocapped trigonal prism. The optical properties of the Eu(III) complexes were studied based on the intensity parameters and luminescence quantum yield (*q*). The values of the Ω_2 parameter of the Eu–DBM complexes are larger than those for the Eu–TTA complexes, indicating that the Eu(III) ion is in a more polarizable chemical environment in the former case. The geometries of the complexes have been optimized by using the Sparkle Model, and the results have been used to perform theoretical predictions of the ligand-to-metal energy transfer via direct and exchange Coulomb mechanisms.

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1. Introduction

Since a long time, trivalent lanthanides ions, Ln(III), are attractive in coordination chemistry. This interest is not only due their chemical properties that differ from those presented by the transition metal ions, but also because of their unique magnetic and spectroscopy properties [1–3]. When a lanthanide ion is in a compound, many of their properties are preserved owing to the shielding of 4f orbitals from the environment by outer 5s and 5p orbitals, causing the minimal perturbation by the external field generated by the ligands [4,5]. For example, lanthanide compounds are characterized as exhibiting narrow emitting and absorption bands.

Another important characteristic of the Ln(III) ions is that their emitting levels generally exhibit exceptionally long excited state

lifetime with a magnitude around microseconds, making them useful for biological applications. In this case, it is not surprising that these compounds are currently applied in different fields, ranging from fluoroimmunoassay reagents to light-emitting diodes to enable low-cost, full-color, and flat-panel displays [6–8].

Special attention has been devoted to the Eu(III) compounds, as their chelates generally exhibit red emission with higher intensity. Besides, the luminescent properties of the Eu(III) ion present some peculiarities, which reflect the internal structure of the energy levels for this metal ion perturbed by the ligand field. The emission bands arising from emitting non-degenerate level ⁵D₀ give information about the degenerescence loss of the ⁷F_j states in different chemical environments. In addition, the emission intensity rate of the ⁵D₀ → ⁷F₁ transition is allowed by magnetic-dipole mechanism and almost insensitive to the changes in the chemical environment around the europium ion [1]. Based on these characteristics, more detailed theoretical and experimental studies can be performed on the Eu(III) complexes than on other lanthanide ions. In this case, it

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is possible to obtain information about the coordination number, symmetry site around the metal ion, and intensity parameters up to the number of water molecules in the first coordination sphere of the Eu(III) ion [4,5].

One of the most important kinds of lanthanide compounds is that based on β -diketonate ligands as luminescent sensitizers (such as TTA, DBM, ACAC, and DPM) [1,9–12]. According to the “antenna effect”, the most important sensitization pathway of the europium excitation in the coordination compound has an excitation of the organic ligand as the first process. This sensitization occurs via its singlet state (S), intersystem crossing from singlet to triplet state, and energy transfer from the ligand triplet state (T) to the 4f excited levels belonging to Ln(III) ions. The ligand-to-metal energy transfer is dependent on the energy gap between the donor state and the receptor one. The highest energy transfer rates to the Eu(III) ion have been found when the organic ligands (antennas) have the T state position around 23000 cm^{-1} [1]. In this case, the TTA and DBM ligands, presenting their triplet energy around 20300 and 20600 cm^{-1} , respectively, are considered excellent luminescent sensitizers for the europium ion. Several works have reported the structural, photo, and electroluminescent properties of the TTA [1,13] and DBM [14–16] complexes. When these complexes present water molecules in the first coordination sphere of the Eu(III) ion, the luminescence intensity is significantly quenched by the multiphonon decay process involving O–H oscillators. On the other hand, when a second kind of ligands such as heterocyclic, sulfoxide, phosphine oxide, and amide replace the water molecules in the first coordination sphere of the metal, the emission quantum efficiency (η) increases, as well as the volatility, thermal stability, and carrier transport to electroluminescence devices [17,18].

Tertiary amides such as DMA and DMF are generally used as solvents; however, their high donor ability makes it possible for them to coordinate with metal ions in many complexes. For example, several works in literature report the coordination of these molecules to Ln(III) ions, acting as primary and secondary ligands [19–22]. Although a great number of studies have been concerned with ternary β -diketonate complexes, up to now, to the best of our knowledge, no work has reported the structural or spectroscopic properties of lanthanide diketonate complexes containing tertiary amides.

Our goal in this work is to describe the synthesis, characterization, and luminescent properties of Eu(III) and Gd(III) complexes with TTA and DBM, along with tertiary amides such as DMA, DMF, and DMB as secondary ligands. The photoluminescent investigations of the complexes were discussed in terms of the experimental intensity parameters Ω_2 and Ω_4 , Einstein's emission coefficient (A), quantum emission efficiency (η), and quantum yield (q). Based on the single crystal X-ray data, the structure of the [Eu(DBM)₃DMA] complex has also been discussed. Theoretical structures of the complexes were also calculated and optimized using semiempirical *Sparkle Model for the Calculation of Lanthanide Complexes* (SMC). With the help of these data, a theoretical investigation of the ligand-to-metal energy transfer mechanism has been performed.

2. Experimental

2.1. Reagents and syntheses

Lanthanide oxides (Eu₂O₃ and Gd₂O₃), thenoyltrifluoroacetone (HTTA), and dibenzoylmethane (HDBM) ligands were purchased from Aldrich Co. and used as they had been received. The Ln₂O₃ were converted to their chlorides by treatment with concentrated hydrochloric acid as described by Teotonio et al. [9]. The amides

DMA, DMF, and DMBZ were purchased from Merck and used without any previous treatment.

2.2. Syntheses of Ln(III) complexes

[Ln(TTA)₃(H₂O)₂] and [Ln(DBM)₃(H₂O)] precursor complexes (Ln(III) = Eu and Gd) were synthesized according to the literature [9,23]. Considering that Eu and Gd complexes containing amide ligands were prepared in the same general way, the preparations of the [Eu(TTA)₃(DMA)₂] and [Eu(DBM)₃(DMA)] compounds are given as representative.

2.2.1. [Eu(TTA)₃(DMA)₂]

DMA (0.26 g, 2.94 mmol) was added drop wise to a stirred solution of [Eu(TTA)₃(H₂O)₂] (1.00 g, 1.17 mmol) in acetone (30 mL). The reaction mixture was kept as a standby at room temperature overnight, yielding a solid product that was washed with water to remove the excess of dimethylacetamide ligand, filtered, and then vacuum dried. Yield: 1.10 g (94.8%). *Anal. Calc.* for C₃₂H₃₀EuF₉N₂O₈S₃: C, 38.83; H, 3.03; N, 2.83; Eu, 15.35. Found: C, 38.90; H, 3.12; N, 2.73; Eu, 15.25%. IR (cm⁻¹, Nujol): $\bar{\nu}$ = 1643 (m), 1610 (s), 1535 (s), 1502 (s), 1434 (s), 1412 (s), 1354 (m), 1307 (s), 1232 (m), 1180 (s), 1130 (s), 1059 (w), 933 (w), 854 (w), 781 (m), 717 (m), 679 (m), 640 (m), 579 (m), 480 (w).

2.2.2. [Eu(TTA)₃(DMF)(H₂O)]

Yield: 1.03 g (96.74%). *Anal. Calc.* for C₂₇H₂₁EuF₉NO₈S₃: C, 35.77; H, 2.11; N, 1.55; Eu, 16.76. Found: C, 36.25; H, 2.36; N, 1.97; Eu, 16.68%. IR (cm⁻¹, Nujol): $\bar{\nu}$ = 3626 (w), 1674 (m), 1649 (s), 1599 (s), 1537 (s), 1506 (s), 1462 (s), 1412 (s), 1379 (m), 1356 (m), 1305 (s), 1250 (m), 1229 (m), 1180 (s), 1140 (s), 1063 (m), 932 (m), 858 (m), 787 (m), 720 (m), 679 (m), 640 (m), 580 (m), 492 (m), 461 (w).

2.2.3. [Eu(TTA)₃(DMBZ)₂]

Yield: 1.25 g (95.56%). *Anal. Calc.* for C₄₂H₃₄EuF₉N₂O₈S₃: C, 45.29; H, 3.08; N, 2.51; Eu, 13.64. Found: C, 45.50; H, 3.04; N, 2.70; Eu, 13.54%. IR (cm⁻¹, Nujol): $\bar{\nu}$ = 1643 (m), 1606 (s), 1576 (m), 1535 (m), 1462 (s), 1412 (m), 1377 (w), 1354 (w), 1304 (s), 1234 (m), 1186 (s), 1059 (w), 1030 (w), 932 (w), 856 (w), 785 (s), 745 (m), 717 (s), 642 (m), 606 (w), 581 (m), 523 (w), 488(w), 388 (w).

2.2.4. [Eu(DBM)₃(DMA)]

Single crystals of this compound were obtained from a reaction of [Eu(DBM)₃(H₂O)] (1.00 g, 1.19 mmol) in acetone (20 mL) with the dimethylacetamide ligand (0.2594 g, 2.98 mmol). After evaporation of the solvent, yellow single crystals were obtained, which were washed with distilled water and dried in vacuum desiccators. Yield: 1.04 g (96.09%). *Anal. Calc.* for C₄₉H₄₂EuNO₇: C, 64.76; H, 4.66; N, 1.54; Eu, 16.72. Found: C, 64.86; H, 4.86; N, 1.53; Eu, 16.68%. IR (cm⁻¹, Nujol): $\bar{\nu}$ = 1624 (s), 1595 (s), 1547 (s), 1518 (s), 1460 (s), 1381 (s), 1307 (s), 1219 (m), 1182 (m), 1067 (m), 1024 (m), 972 (w), 935 (w), 845 (w), 812 (w), 783 (m), 754 (m), 723 (s), 689 (s), 606 (m), 513 (m), 480 (m), 447 (m), 428 (m).

2.2.5. [Eu(DBM)₃(DMF)]

Yield: 1.00 g (93.84%). *Anal. Calc.* for C₄₈H₄₀EuNO₇: C, 64.43; H, 5.29; N, 1.57; Eu, 16.98. Found: C, 64.54; H, 4.99; N, 1.81; Eu, 16.84%. IR (cm⁻¹, Nujol): $\bar{\nu}$ = 1661 (m), 1595 (s), 1546 (s), 1516 (s), 1458 (s), 1377 (s), 1308 (m), 1221 (m), 1178 (w), 1107 (w), 1065 (m), 1022 (m), 1000 (w), 937 (w), 783 (w), 756 (m), 721 (s), 787 (m), 608 (m), 515 (m), 449 (w), 420 (w), 382 (w).

2.2.6. [Eu(DBM)₃(DMBZ)]

Yield: 1.11 g (96.00%). Anal. Calc. for C₅₄H₄₄EuNO₇: C, 66.80; H, 4.57; N, 1.44; Eu, 15.65. Found: C, 64.54; H, 4.99; N, 1.81; Eu, 16.84%. IR (cm⁻¹, Nujol): $\bar{\nu}$ = 1678 (w), 1595 (s), 1547 (s), 1519 (s), 1456 (s), 1377 (s), 1308 (s), 1284 (m), 1211 (m), 1176 (m), 1066 (m), 1022 (m), 999 (w), 941 (w), 860 (w), 812 (w), 783 (m), 756 (m), 721 (s), 690 (s), 647 (w), 607 (w), 511 (w), 446 (w).

2.3. Apparatus

The carbon, hydrogen, and nitrogen percentages in the complexes were determined from elemental analyses, using a Perkin-Elmer model 240 microanalyzer, while the Eu(III) content was performed by complexometric titration with EDTA [23].

The infrared absorption spectra were recorded in KBr pellets in a Bomem model MB-102 spectrophotometer using the range of 400 up to 4000 cm⁻¹. Thermogravimetric analyses (TGA) were performed by using a thermobalance TGA-50 Shimadzu under a uniform air flow rate of 50 mL min⁻¹ from room temperature to 900 °C, with a heating rate of 5 °C min⁻¹.

X-ray crystallography data were collected on an Oxford Diffraction Gemini S Kappa CCD diffractometer with a graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 123(2) K. Data were processed using the WinGX system [24]. The structure of the [Eu(DBM)₃(DMA)] complex was solved by SIR2002 [25]. The structure refinement was carried out with the SHELXL-97 [26]. The molecular representation was made using ORTEP3 [27], and the geometrical parameters were calculated using a PLATON system [28,29].

The excitation and emission spectra at room (~298 K) and liquid nitrogen temperature were collected at an angle of 22.5° (front face) in a spectrofluorimeter (SPEX-Fluorolog 2) with a double-grating 0.22 m monochromator (SPEX 1680) and a 450 W Xenon lamp as an excitation source. In order to eliminate the second-order diffraction of the source radiation, a cut-off filter was used in the measurements. All spectra were recorded by using a detector mode correction. The luminescence decay curves of the emitting levels were measured using a phosphorimeter SPEX 1934D accessory coupled to the spectrofluorometer. The luminescence instruments were fully controlled by a DM3000F spectroscopic computer program, and the spectral intensities were automatically corrected for the photomultiplier response.

3. Results and discussion

3.1. Characterization of the complexes

The percentages of the Ln(III) ions were determined by complexometric titration with EDTA, where the Ln-complexes were dissolved in methanol using xylenol orange as an indicator. These data together with the results of the elemental analysis of C, H, and N reveal the general formulas [Ln(TTA)₃·L₂] and [Ln(DBM)₃·L] for the complexes. Although the same synthetic route had been applied to obtain the complexes, the Ln-TTA-complexes with DMF were only obtained as a monohydrated one, presenting the formula [Ln(TTA)₃·DMF·H₂O]. Similar quaternary complexes presenting formula [Ln(Nic)₃·DMF·H₂O], where Nic is the ligand pyridine-3-carboxylate, were synthesized by Yan and Xie [19].

The infrared spectral data of the Ln- β -diketonate complexes with the tertiary amide ligands (except those of the [Ln(TTA)₃·DMF·H₂O] complexes) as compared with those of the hydrated precursors (figures not shown) do not present a broad band around 3500 cm⁻¹ assigned to the O-H stretching of the H₂O molecules, indicating a complete substitution of the water molecules by the tertiary amide ligands in the first coordination sphere of the Ln(III) ion. The comparison between the infrared spectra of the free and

coordinated amide ligands shows a downward shift of the amide I band ν (C=O) from a higher (~1676 cm⁻¹) to lower wave number (~1600 cm⁻¹). These results suggest that the bonding of the amide ligands to the Ln(III) ions occurs through the oxygen atoms.

3.2. Description of structure of the [Eu(DBM)₃(DMA)] complex

Single crystals of the [Eu(DBM)₃(DMA)] complex acceptable for the X-ray diffraction analysis were growing up via slow evaporation of a mixture of the starting materials, [Eu(DBM)₃(H₂O)] complex, and DMA, using acetone as a solvent. The intensity data were taken using 123 K as temperature. Details of the data collection and refinement parameters of the structure are presented in Table 1.

The crystal structure (Fig. 1a) shows that the Eu³⁺ ion is seven coordinate to six oxygen atoms from three chelating DBM ligands, O(1–6), and one from the DMA ligand, O(7). The DMBA ligand is disordered in the crystal structure, they are in two positions with 0.5 of occupation factors. A similar structural DMA disorder has been observed in the lanthanide complexes by Yan and Chen [21]. The crystal structure presents non conventional intermolecular hydrogen bonds type C–H...O, between C(43)–H(43)...O(4) [1 – x, 1 + y, z (symmetry operation)] with dC...O = 3.420(4) Å, and angle equal to 157°. This non conventional interaction produces an infinite two dimensional chain, in the (100) plane. In the β -diketonate chelate rings, the mean bond for the carbon–carbon (C–C) is 1.38 Å, and the C–C–C mean bond angle of 121°, respectively, is consistent with the delocalization of the π -electrons in the chelate ring system in β -diketonates [28–31]. It is interesting to notice that phenyl rings are twisted from the plane defined by the chelating rings, but the twist angles are noticeably different, as can be seen in Fig. 1a. In order to better demonstrate the twist effect, the DBM ligands in the [Eu(DBM)₃(DMA)] complex are labeled as **A**, **B**, and **C** (Fig. 1a). The phenyl rings in the molecules **A**, **B**, and **C** are twisted from the chelating ring of 9.5° and 23.9°, 22.3° and 47.1°, and 24.2° and 20.9°, respectively. It is important to note that the twist effect observed in the [Eu(DBM)₃(DMA)] complex is more pronounced than that presented in the hydrated complex reported by Zalkin and Templeton [32] and Lennartson et al. [33]. This behavior indicates that the tertiary amide DMA provides a higher steric hindrance onto the coordinated DBM ligands than the coordinated water molecules; therefore, the phenyl groups are orientated in order to minimize steric repulsion among

Table 1

Crystal Data and Details of the Structure Determination for the [Eu(DBM)₃(DMA)] complex.

Formula	C ₄₉ H ₄₂ EuNO ₇
Formula weight	908.80
Crystal system	triclinic
Space group	P $\bar{1}$
a, b, c (Å)	10.2580(3), 10.3843(2), 22.3517(5)
α , β , γ (°)	78.906(2), 78.049(2), 63.239(2)
V (Å ³)	2066.41(9)
Z, D _{calc} (g/cm ³)	2, 1.461
μ (Mo K α) (mm ⁻¹)	1.571
F(000)	924
Crystal size (mm)	0.18 × 0.20 × 0.24
T (K)	123
λ (Mo K α) (Å)	0.71073
θ (°) min: max	2.7:30.3
hkl max: min	–14:13; –14:14; –29:31
Total, Unique Data, R(int)	26471, 10963, 0.035
Observed data [I > 2.0 σ (I)]	8929
Nref, Npar	10963, 544
R, wR ₂ , S	0.0295, 0.0514, 0.92
Max. and Avg. shift/error	0.00, 0.00
Min. and Max. Resd. Dens. (e/Å ³)	–0.66, 0.64

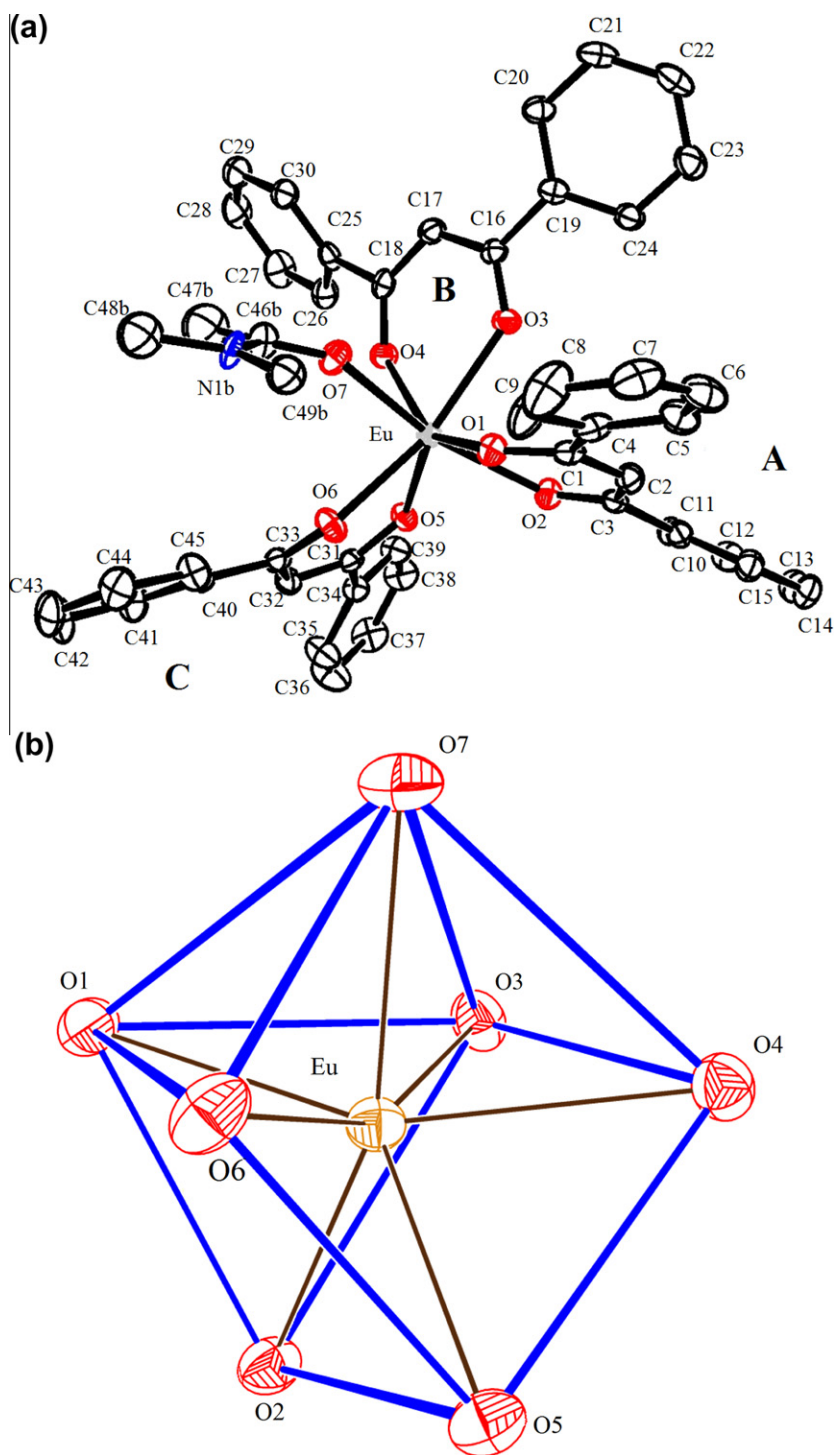


Fig. 1. (a) ORTEP3 drawing (50% of probability) displaying the X-ray structure of the [Eu(DBM)₃(DMA)] complex, the H atoms and the DMA disorder are omitted for clarifying and (b) coordination polyhedron of Eu³⁺ ion in the [Eu(DBM)₃(DMA)].

the ligands. Twists of the DBM anion were also reported in Refs. [34,35]. Another significant structural difference between [Eu(DBM)₃(DMA)] and the hydrated complexes is the weak intermolecular interactions.

The seven-coordinated {EuO₇} polyhedron can be described as a C_{2v} distorted monocapped trigonal prism, in which the C₂ axis crosses the oxygen atom from DMA (Fig. 2b), being the capping ligand for the amide oxygen atom. Table 2 presents the distances from the Eu(1) center to oxygen atoms and the angles

O(x)–Eu(1)–O(x') (where x = 1, 2, 3, 4, 5, and 6) in the first coordination sphere. The interatomic distances Eu(1)–O(x) have an average value of 2.3 Å.

3.3. Thermogravimetric data

Thermogravimetric (TG) curves of the TTA and DBM-complexes recorded from 25 to 900 °C are presented in Fig. 2a and b, respectively. As can be seen in Fig. 2a, the TG curve for the hydrated

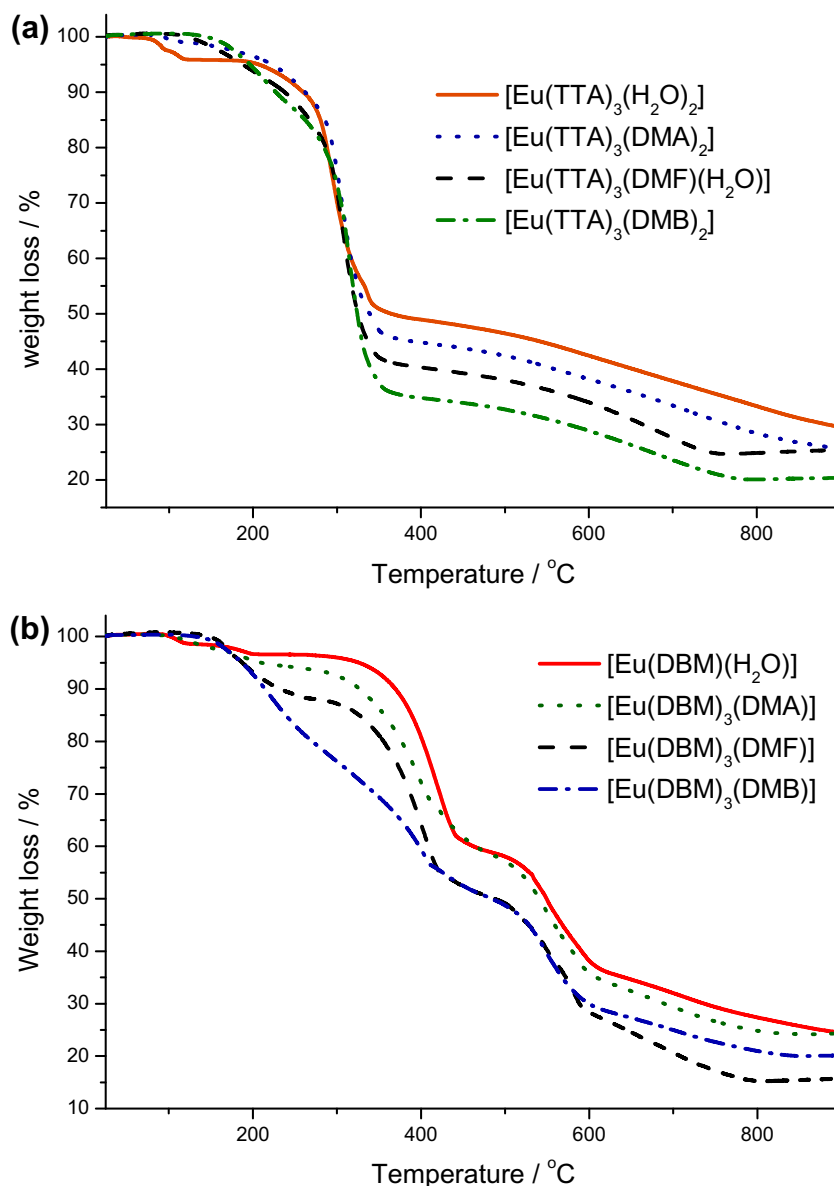


Fig. 2. TG curves of the complexes (a) [Gd(TTA)₃L₂] and (b) [Gd(DBM)₃L] (where L = H₂O, DMA, DMF, and DMB). The complex containing TTA and DMF ligands presents the formula [Gd(TTA)₃(DMF)(H₂O)].

Table 2

Selected bond lengths (Å) and angles (°) around the europium ion for the [Eu(DBM)₃(DMA)] complex.

Bond lengths			
Eu–O1	2.337(2)	Eu–O2	2.313(2)
Eu–O3	2.343(1)	Eu–O4	2.349(2)
Eu–O5	2.343 (2)	Eu–O6	2.342(1)
Eu–O7(DMA)	2.341(2)		
Bond angles			
O1–Eu–O2	73.50(6)	O1–Eu–O3	81.13(5)
O1–Eu–O4	149.13(6)	O1–Eu–O5	134.28(6)
O1–Eu–O6	88.43(5)	O1–Eu–O7	83.91(6)
O2–Eu–O3	82.24(6)	O2–Eu–O4	116.40(6)
O2–Eu–O5	76.78(6)	O2–Eu–O6	112.82(6)
O2–Eu–O7	155.66(6)	O3–Eu–O4	72.04(5)
O3–Eu–O5	128.07(5)	O3–Eu–O6	158.51(6)
O3–Eu–O7	85.49(6)	O4–Eu–O5	75.91(6)
O4–Eu–O6	111.32(5)	O4–Eu–O7	79.13(6)
O5–Eu–O6	72.08(5)	O5–Eu–O7	126.87(6)
O6–Eu–O7	74.71(6)		

[Eu(TTA)₃(H₂O)₂] complex displays the first weight loss event up to 120 °C that corresponds to 4.3% of the initial weight. These data agree with the loss of the two water molecules. The TG curve of the [Eu(TTA)₃-DMF-H₂O] complex presents a weight loss (2%) in the temperature range of 25–120 °C, which is attributed to the dehydration process. All of the TTA-amide complexes show weight losses starting around 120 up to 250 °C, which can be assigned to the release of amide ligands. This event is followed by an abrupt weight loss until a temperature of about 400 °C, which might be attributed to the decomposition of the Eu(TTA)₃ system. The decomposition process was completed around 850 °C, resulting in a white Eu₂O₃ as the final product (approximately 20% of the original weight).

The TG curves of the Eu-DBM complexes (Fig. 2b) with amide ligands do not show any weight loss until further heating to 150 °C, which suggests that these compounds are anhydrous. The weight losses that occur in the range from 150 to 260 °C can be attributed to losses of amide ligands. After three consecutive weight losses until 850 °C, Eu₂O₃ was obtained as the final product.

3.4. Theoretical geometries of the complexes

The geometries of the europium complexes were obtained by using an improved version of the semiempirical *Sparkle Model for the Calculation of Lanthanide complexes* (SMC), implemented into the MOPAC6 package, according to the procedure described in Refs. [36]. The theoretical geometries of the $[\text{Eu}(\text{DBM})_3\text{L}]$ complexes were optimized using the experimental structural data of the $[\text{Eu}(\text{DBM})_3(\text{DMA})]$ complex as starting geometry. Thus, the input geometries of the $[\text{Eu}(\text{DBM})_3(\text{DMF})]$ and $[\text{Eu}(\text{DBM})_3(\text{DMB})]$ complexes were obtained by substitution of the methyl in the acetyl amide moiety by H and phenyl groups, respectively. Since X-ray structural data were not obtained for the $[\text{Eu}(\text{TTA})_3\text{L}_2]$ complexes, the input geometries for this kind of compounds were obtained by using the HYPERCHEM program [37].

The theoretical geometry obtained for the complex $\text{Eu}(\text{DBM})_3(\text{DMA})$ agrees with the experimental one. The coordination polyhedra obtained via the SMC method for all of the Eu–DBM–amide complexes might be described as distorted monocapped trigonal prisms, while the eight-coordinate $\{\text{EuO}_8\}$ polyhedra for all

of the Eu–TTA–amide systems are better described as distorted dodecahedrons.

3.5. Luminescence study of the lanthanide complexes

The excitation spectra of the Eu(III) TTA and DBM complexes in the solid state were recorded from 250 to 590 nm at a liquid nitrogen temperature, on monitoring the emission intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (Fig. 3). These spectra are dominated by the broad bands in the spectral interval from 250 to 500 nm that are assigned to the centered singlet–singlet β -diketonate ligand transitions. This result indicates that the luminescence from Eu(III)– β -diketonate–amide complexes is a consequence of the sensitization of the europium excited state by energy transfer from the ligands. Besides, the spectra show narrow bands due to excitation from the $^7\text{F}_0$ ground state to $^5\text{L}_6$ (overlapped by the centered ligand transitions), $^5\text{D}_3$ (~448 nm), $^5\text{D}_2$ (~464 nm), $^5\text{D}_1$ (~525 nm), and $^5\text{D}_0$ (~579 nm) excited states. The spectrum of the complex containing the DMB amide is quite different from the spectra of the other complexes, indicating a higher disturbance caused by this ligand in comparison with the otherwise complexes, probably because of its steric effects.

Fig. 4 shows the emission spectra of the TTA and DBM Eu-complexes, under excitation at 350 nm. These spectra consist of sharp bands assigned to the intraconfigurational $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions ($j = 0-4$), being the band attributed to the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ dominating. Several less intense bands are also observed in the range of 500–570 nm, which correspond to the transitions: $^5\text{D}_1 \rightarrow ^7\text{F}_0$ (526 nm), $^5\text{D}_1 \rightarrow ^7\text{F}_1$ (536 nm), and $^5\text{D}_1 \rightarrow ^7\text{F}_2$ (557 nm). The emission spectra of the Eu–TTA–amide complexes (Fig. 4a) present similar profiles, indicating that the DMA and DMF ligands distort the structure of the diketonate ligands in a similar way conducting very close site symmetry around the Eu^{3+} ion. On the other hand, the steric hindrance due the DMB ligand is higher than those from the other amide ligands, which cause a more pronounced distortion in the complexes, lowering the symmetry around the metal ion, which is in agreement with the excitation spectra features just discussed. The phosphorescence broad band from diketonate ligands is not present in any spectra, which suggests that the intramolecular ligand-to-metal energy transfer is very efficient.

Analysis of the emission bands corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions for the $[\text{Eu}(\text{TTA})_3(\text{amide})]$ complexes shows that these bands split in a number of components expected by both the coordination polyhedral obtained via X-ray diffraction and theoretical structural data. In this case, $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions exhibit two more closely spaced higher-energy components, which are compatible with a pseudo- C_{3v} symmetry around the Eu^{3+} ion.

Emission spectra of the $[\text{Eu}(\text{DBM})_3(\text{amide})]$ complexes display a nearly identical pattern, but more splitting than in the precursor hydrated complex, reflecting the distortion of the amide coordination.

In order to evaluate the efficiency of luminescence of the europium complexes, the luminescence quantum yield (q) and the intrinsic quantum efficiency (η) of the Eu^{3+} ion were experimentally determined [1,38,39].

The values of η were calculated from the ratio $A_{\text{rad}}/A_{\text{total}}$, where A_{rad} and A_{total} are radiative and total rates assigned to the decay processes of the $^5\text{D}_0$ emitting level, respectively. In this case, the A_{rad} values were obtained by summing the radiative spontaneous coefficients due to the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions, while A_{total} ones were determined from the lifetime values of the $^5\text{D}_0$ emitting level (τ) by considering the reciprocal relation between these properties ($A_{\text{total}} = 1/\tau$). Further specific details about these parameters are reported in the literature [1].

The quantum efficiency of the $^5\text{D}_0$ emitting level (η) for the β -diketonate complexes are presented in Table 3. The data reveal

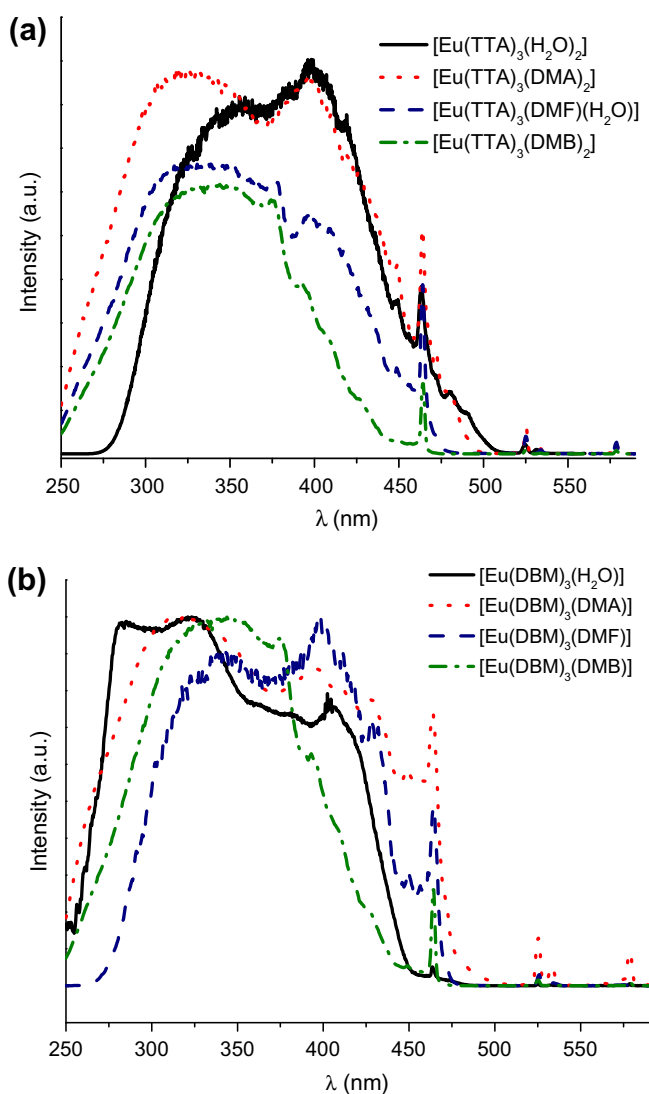


Fig. 3. Excitation spectra of the europium complexes recorded at nitrogen liquid temperature with emission monitored on the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition: (a) $[\text{Eu}(\text{TTA})_3\text{L}_2]$ and (b) $[\text{Eu}(\text{DBM})_3\text{L}]$ (where $\text{L} = \text{H}_2\text{O}$, DMA, DMF, and DMB). The complex containing TTA and DMF ligands presents the formula $[\text{Eu}(\text{TTA})_3(\text{DMF})(\text{H}_2\text{O})]$.

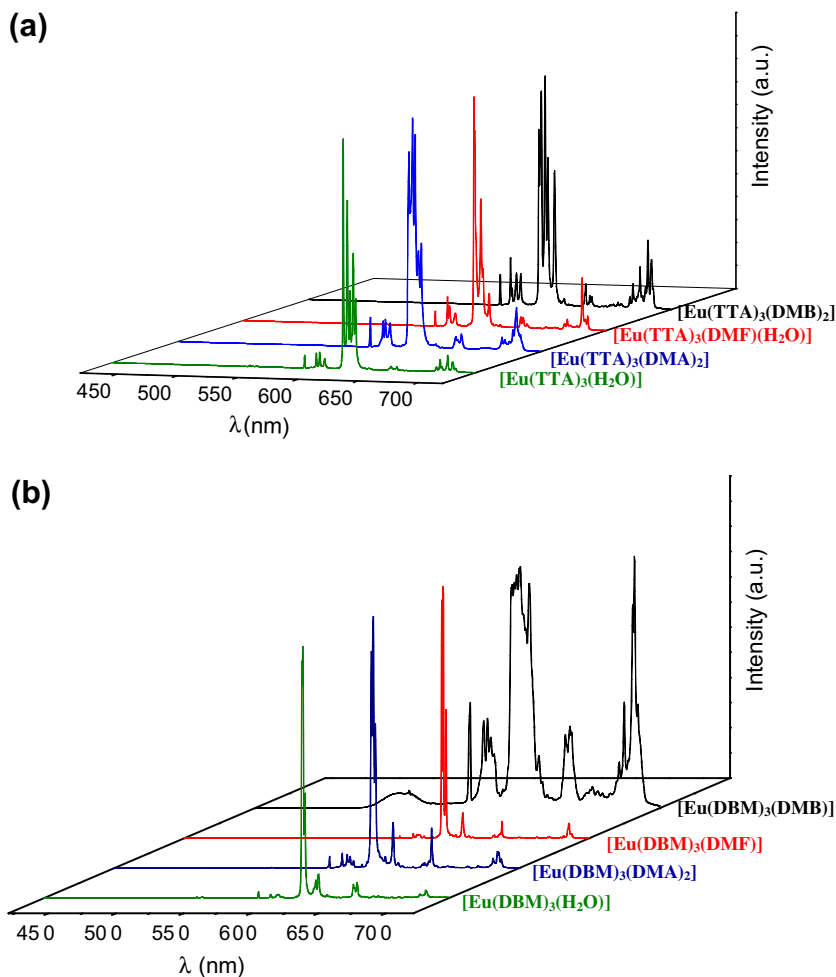


Fig. 4. Emission spectra of the europium complexes recorded at nitrogen liquid temperature with excitation monitored at 350 nm: (a) $[\text{Eu}(\text{TTA})_3\text{L}_2]$ and (b) $[\text{Eu}(\text{DBM})_3\text{L}]$ (where $\text{L} = \text{H}_2\text{O}$, DMA , DMF and DMB). The complex containing TTA and DMF ligands presents the formula $[\text{Eu}(\text{TTA})_3(\text{DMF})(\text{H}_2\text{O})]$.

Table 3

Experimental intensity parameters for the $[\text{Eu}(\text{TTA})_3\text{L}_2]$ and $[\text{Eu}(\text{DBM})_3\text{L}]$ complexes, where $\text{L} = \text{H}_2\text{O}$, DMA , DMF , and DMB .

Complexes	Ω_2	Ω_4	A_{rad}	A_{nrad}	A_{tot}	η (%)	q_{exp} (%)	q_{calc} (%)
$[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]^{\text{a}}$	33.0	4.6	1110	2730	3846	29	23	28
$[\text{Eu}(\text{TTA})_3(\text{DMA})_2]$	36.9	9.3	1295	498	1793	72	78	71
$[\text{Eu}(\text{TTA})_3(\text{DMF})(\text{H}_2\text{O})]$	23.8	9.1	904	651	1555	58	45	57
$[\text{Eu}(\text{TTA})_3(\text{DMB})_2]$	36.4	7.6	1255	269	1524	82	81	81
$[\text{Eu}(\text{DBM})_3(\text{H}_2\text{O})]$	19.9	4.4	716	2129	2845	25	–	25
$[\text{Eu}(\text{DBM})_3(\text{DMA})]$	51.0	6.7	1752	1189	2941	60	45	59
$[\text{Eu}(\text{DBM})_3(\text{DMF})]$	44.3	6.8	1491	947	2438	61	43	60
$[\text{Eu}(\text{DBM})_3(\text{DMB})]$	46.5	8.6	1488	2442	3930	38	–	–

^a Ref. [1].

that the substitution of water molecules by the tertiary amides significantly increases the quantum efficiency of the europium complexes. The Eu–TTA-complex with DMF was only obtained in the monohydrated form $[\text{Eu}(\text{TTA})_3(\text{DMF})(\text{H}_2\text{O})]$. The lowest value of η determined for this complex ($\eta = 58\%$) is owing to the presence of only one water molecule in the first coordinated sphere of the Eu(III) ion [40].

Experimental Judd–Ofelt intensity parameters for the Eu(III) ion in the complexes are determined by the following Eqs. (1) and (2)

$$\Omega_i = \frac{4e^2\omega^3 A_{0i}}{3hc^3\chi\langle^7F_4\|U^{(i)}\|^5D_0\rangle^2} \quad (1)$$

where A_{0i} are the coefficients of spontaneous emission, χ is the Lorentz local field correction term that is given by $\chi = n(n^2 + 2)^2/9$ with the refractive index $n = 1.5$, and matrix elements $\langle^7F_4\|U^{(i)}\|^5D_0\rangle^2$ are described in Ref. [41]. In this work, the Ω_6 parameter was not experimentally determined due to the low intensity of the $^5D_0 \rightarrow ^7F_6$ transition.

Table 3 presents the experimental intensity parameters for the TTA and DBM-complexes with the tertiary amide ligands. Among the TTA and DBM complexes, the highest values of the intensity parameter Ω_2 are observed for those complexes with DMA and DBM ligands. Since this parameter is usually related to the degree of covalent character of the lanthanide metal ion–ligand bond [1], the results can be explained in terms of the inductive effect of

the substituting CH₃ and phenyl in the DMA and DBM, respectively, which increase the polarizability of the oxygen atom coordinated to the europium ion. In addition, it is also seen that the complexes with DBM present values of Ω_2 parameters higher than those with TTA. Based on the dynamic-coupling model, this behavior may be also due to ligand polarizability, considering that the phenyl groups make the DBM ligand more polarizable than the trifluoromethane substituent in the TTA anion.

Experimental singlet and triplet energies of the ligands in the complexes were applied to calculate the energy transfer processes of the ligand-to-lanthanide ion and to investigate the luminescent properties of Eu(III) compounds. In this case, the experimental singlet energies were assumed as the energy corresponding to maxima absorbance in the absorption spectra (assigned to the $\pi \rightarrow \pi^*$ transitions). In contrast, triplet energies were estimated as the energy corresponding to the shortest wavelength (0–0 phonon transition) on the basis of the phosphorescence spectra of the gadolinium complexes recorded at 77 K, under an excitation at 377 nm (Fig. 5) [1,9,23].

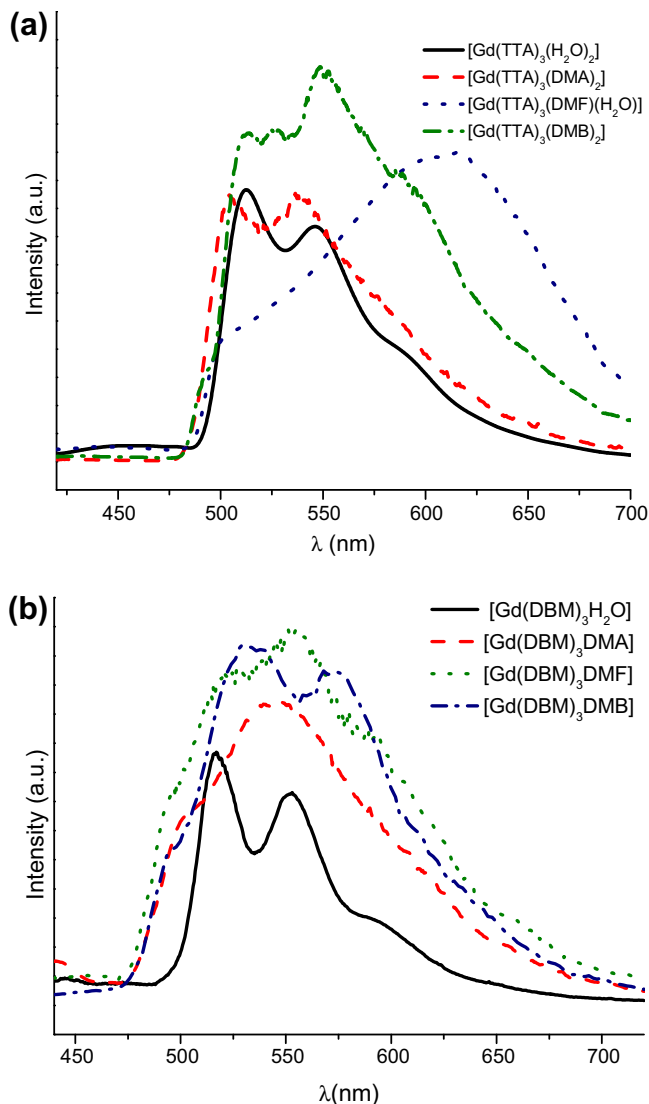


Fig. 5. Phosphorescence spectra of the gadolinium complexes recorded at nitrogen liquid temperature with excitation monitored at 350 nm: (a) [Gd(TTA)₃L₂] and (b) [Gd(DBM)₃L] (where L = H₂O, DMA, DMF and DMB). The complex containing TTA and DMF ligands presents the formula [Gd(TTA)₃(DMF)(H₂O)].

The energy values (singlet; triplet states) for the Gd-diketonate complexes are the following (in cm⁻¹): [Gd(TTA)₃(H₂O)₂] (29498; 20325); [Gd(TTA)₃(DMA)₂] (29240; 20921); [Gd(TTA)₃(DMF)(H₂O)] (29498; 20747); [Gd(TTA)₃(DMB)₂] (29283; 20833); [Gd(DBM)₃·H₂O] (29718; 20534); [Gd(DBM)₃DMA] (29718; 21186); [Gd(DBM)₃DMF] (29762; 21186); [Gd(DBM)₃DMB] (29369; 21277).

3.6. Intramolecular β -diketonate-to-Eu³⁺ energy transfer

In order to obtain information about intramolecular β -diketonate to Eu(III) ion energy transfer in the complexes, the energy transfer W_{ET} rates were calculated according to the theoretical model previously described in the literature [1].

In this work, the following ligand-to-metal energy transfer pathways are considered: $S_1 \rightarrow {}^5D_4$, $T \rightarrow {}^5D_1$ and $T \rightarrow {}^5D_0$, which are based on the relative energy position of the donor ligand and acceptor Eu³⁺ states. Table 4 shows the values of the energy transfer and back-energy transfer rates of the complexes. According to the selection rules for the ligand-to-europium ion energy transfer process, the $S_1 \rightarrow {}^5D_4$ (Eu³⁺) pathway is dominated by the 2²-multipolar mechanism, while the $T \rightarrow {}^5D_1$ and $T \rightarrow {}^5D_0$ ones are mainly due to the exchange mechanism.

Among the energy transfer rates (Tables 4 and 5), low values are obtained for the $S_1 \rightarrow {}^5D_4$ channel ($\sim 9.1 \times 10^6$ s⁻¹), indicating that the 2²-multipolar mechanism plays a few roles in the energy transfer from the TTA or DBM ligands to Eu³⁺ ion. On the other hand, the $T \rightarrow {}^5D_1$ and $T \rightarrow {}^5D_0$ pathways have energy transfer rates ($\sim 1.0 \times 10^{10}$ s⁻¹) around four orders of magnitude higher than the latter, indicating that direct ligand-to-metal energy transfer is dominated by the exchange mechanism. Although the $T \rightarrow {}^5D_1$

Table 4

Energy transfer rates from ligand states (singlet and triplet) to europium levels ²⁵⁺¹L_J (Eu³⁺) in the [Eu(TTA)₃(L)₂] complexes, where L = H₂O, DMA, DMF, and DMB ligands.

Complexes	Non-radiative transitions	Energy transfer rates (s ⁻¹)	Back-transfer rates (s ⁻¹)
[Eu(TTA) ₃ (H ₂ O) ₂]	$S \rightarrow {}^5D_4$	9.17×10^6	1.08×10^3
	$T \rightarrow {}^5D_1$	2.21×10^{10}	5.60×10^7
	$T \rightarrow {}^5D_0$	1.15×10^{10}	3.93×10^3
[Eu(TTA) ₃ (DMA) ₂]	$S \rightarrow {}^5D_4$	9.55×10^6	3.86×10^3
	$T \rightarrow {}^5D_1$	1.92×10^{10}	2.84×10^6
	$T \rightarrow {}^5D_0$	8.43×10^9	1.68×10^2
[Eu(TTA) ₃ (DMF)(H ₂ O)]	$S \rightarrow {}^5D_4$	8.99×10^6	1.06×10^3
	$T \rightarrow {}^5D_1$	2.01×10^{10}	6.82×10^6
	$T \rightarrow {}^5D_0$	9.28×10^9	4.24×10^2
[Eu(TTA) ₃ (DMB) ₂]	$S \rightarrow {}^5D_4$	9.54×10^6	3.14×10^3
	$T \rightarrow {}^5D_1$	1.97×10^{10}	4.43×10^6
	$T \rightarrow {}^5D_0$	8.85×10^9	2.69×10^2

Table 5

Energy transfer rates from ligand states (singlet and triplet) to europium levels ²⁵⁺¹L_J (Eu³⁺) in the [Eu(DBM)₃L] complexes, where L = H₂O, DMA, and DMF ligands.

Complexes	Non-radiative transition	Energy transfer rates (s ⁻¹)	Back-transfer rates (s ⁻¹)
[Eu(DBM) ₃ (H ₂ O)]	$S \rightarrow {}^5D_4$	8.23×10^6	3.41×10^2
	$T \rightarrow {}^5D_1$	2.12×10^{10}	1.98×10^7
	$T \rightarrow {}^5D_0$	1.04×10^{10}	1.31×10^3
[Eu(DBM) ₃ (DMA)]	$S \rightarrow {}^5D_4$	8.32×10^6	3.44×10^2
	$T \rightarrow {}^5D_1$	1.77×10^{10}	7.41×10^5
	$T \rightarrow {}^5D_0$	7.20×10^9	40.7
[Eu(DBM) ₃ (DMF)]	$S \rightarrow {}^5D_4$	8.65×10^6	2.90×10^2
	$T \rightarrow {}^5D_1$	1.77×10^{10}	7.41×10^5
	$T \rightarrow {}^5D_0$	7.20×10^9	40.7

channel presents the highest values of W_{ET} (Table 4), it also exhibits the highest values of back-energy transfer rates. This behavior reflects the small difference ($\sim 1500\text{ cm}^{-1}$) between donor triplet and acceptor 5D_1 states. The calculated values of W_{ET} and W_{BET} reflect the optimum relative energy of the T and 5D_0 states that provides high values of W_{ET} and minimizes the back-energy transfer process. Consequently, this result suggests that the net excitation of Eu^{3+} ion in the complexes is significantly dependent on the $T \rightarrow ^5D_0$ channel.

The optical data in the Tables 4 and 5 suggest that no significant difference between the energy transfer processes exists for the complexes with TTA and DBM ligands. However, the W_{BET} values are higher in the complexes with the TTA ligand, which probably reflects the relative position of the donor and acceptor states. It is important to mention that the ligand-to- Eu^{3+} ion charge-transfer states have been neglected in the present calculations. Although this approximation could attribute more serious problems in some Eu^{3+} -complexes, it is considered less important in the diketonate complexes with neutral ligands.

From the energy transfer rates presented in Tables 4 and 5 and solving an appropriate set of rate equations in the stationary state, including radiative and non-radiative processes, luminescence quantum yields of the Eu^{3+} -diketonate complexes with neutral amide ligands have been calculated. The theoretical analysis was performed for the normalized populations of the ligand and metal ion states, according to the procedure described by de Sá et al. [1].

The calculated values of luminescence quantum yield are also summarized in Tables 4 and 5. The experimental quantum yield (q_{exp}) of the complexes in the solid state are determined according to the modified procedure developed by Brill and co-workers [38,39] with some experimental modifications [42]. In this work, magnesium oxide and sodium salicylate were used as reflectance and luminescent standard materials, respectively. The value of q_{exp} for $[\text{Eu}(\text{DBM})_3(\text{DMB})]$ complex was not determined owing to the hygroscopic behavior of the sample.

A comparison among the experimental values of quantum yield for the TTA complexes with amide ligands shows that $[\text{Eu}(\text{TTA})_3(\text{DMF})(\text{H}_2\text{O})]$ present the lowest value of q . As might be expected from vibronic considerations, the multiphonon relaxation by coupling to O–H(water) and C–H(DMF) vibrations quench more efficiently the luminescence of the Eu^{3+} ion. On the other hand, $[\text{Eu}(\text{TTA})_3(\text{DMA})_2]$ and $[\text{Eu}(\text{TTA})_3(\text{DMB})_2]$ complexes exhibit similar values of q_{exp} , as these two ligands do not present efficient quencher moieties close to the Eu^{3+} ion. The low values of q_{exp} determined for the complexes with the DBM ligand can be largely attributed to the presence of charge transfer state DBM-to- Eu^{3+} ion in lower energy, which was not considered in the calculations [43].

As can be seen, a reasonable agreement between the calculated (q_{calc}) and experimental quantum yield values was achieved. Besides, the better agreement was found for the complexes with the TTA ligand.

4. Conclusions

Six $\text{Eu}(\text{III})$ -diketonate complexes containing tertiary amides were synthesized and characterized. The characterization methods indicate that the complexes present the general formulas $[\text{Ln}(\text{TTA})_3\text{L}_2]$ and $[\text{Ln}(\text{DBM})_3\text{L}]$, where $L = \text{H}_2\text{O}$, DMA, DMF, and DMB, except the TTA-complex with DMF presents the formula $[\text{Eu}(\text{TTA})_3(\text{DMF})(\text{H}_2\text{O})]$. The site symmetry close to C_{2v} or C_{3v} determined on the basis of the photoluminescent spectrum for the $[\text{Eu}(\text{DBM})_3(\text{DMA})]$ compound is confirmed by the structure determined by single-crystal X-ray diffraction analysis and the SPARKLE theoretical method. The higher values of the intensity parameter, Ω_2 , obtained for the DBM complexes indicate that a

more polarizable chemical environment around the $\text{Eu}(\text{III})$ ion is in this system than in the TTA-complexes. The complexes containing tertiary amides coordinated with europium present high values of experimental quantum yield (q), which is similar to other Eu -diketonate complexes reported in the literature.

Acknowledgments

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Appendix A. Supplementary data

CCDC n° 854223 contains the supplementary crystallographic data for complex $[\text{Eu}(\text{DBM})_3(\text{DMA})]$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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