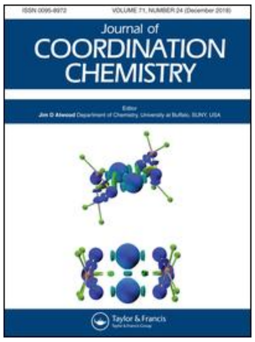

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# 1,3-Dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide as ligand for the preparation of luminescent lanthanide complexes

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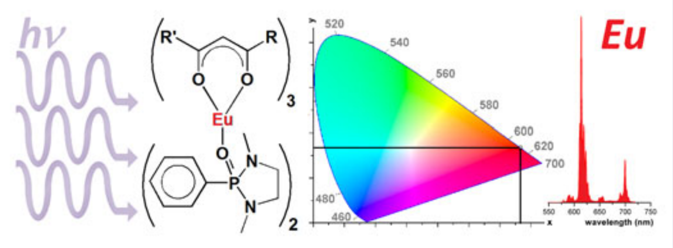
**ABSTRACT**

Europium(III) coordination compounds having general formula $[Eu(\beta\text{-dike})_3L_2]$ (β-dike = dibenzoylmethanate, tenoyltrifluoroacetonate; L = 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide) were isolated and characterized. The complexes exhibited bright red emission associated to the $^5D_0 \rightarrow ^7F_J$ transitions of the metal center upon excitation with near-UV light, with intrinsic quantum yields around 51% and 65%, respectively, for the dibenzoylmethanate and tenoyltrifluoroacetonate derivatives. More information about the behavior of 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide as an antenna-ligand towards trivalent lanthanide ions was obtained by its coordination to $[Ln(NO_3)_3]$ (Ln = Eu, Gd, Tb) metal fragments.



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Europium(III); gadolinium(III); terbium(III); photoluminescence; diazaphospholidine-2-oxide

## 1. Introduction

Luminescent trivalent lanthanide complexes are of interest for applications in advanced technologies [1–5], such as electronic devices [6, 7], electroluminescent materials [8, 9], and biological probes [10–12]. Because of the hard Lewis acid character of trivalent lanthanide ions [13], molecules containing the [P=O] fragment behave as good O-donor ligands towards these metal centers. Triphenylphosphine oxide (tppo) is the most common example, and several visible- and NIR-emitting lanthanide complexes with triphenylphosphine oxide and anionic ligands in the coordination

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sphere are reported [14–25]. The structurally related chelating phosphine oxide bis(2-(diphenylphosphino)phenyl)ether (dpepo), once coordinated to [Eu($\beta$-diketonate)$_3$], afforded luminescent complexes with quantitative excited-state energy transfer from the ligands to the metal ion, leading to exceptionally high photoluminescence quantum yields in solution and in poly(methyl methacrylate) [26].

Hexamethylphosphoramide (hmpa) is another simple molecule able to coordinate trivalent lanthanide ions [27–42]. Nitrato complexes of Eu(III) with hmpa exhibit triboluminescence [43–45] and the luminescence of Tb(III) and Gd(III) nitrato complexes with hmpa and dibenzoylmethanate was studied [46]. The complexes [Ln(depma)(NO$_3$)$_3$(hmpa)$_2$] (depma = 9-diethylphosphono-methylanthracene; Ln = Dy, Gd) are recent examples of magneto-optic materials [47].

Despite the fact that molecules based on the 1,3-diazaphospholidine-2-oxide skeleton resemble phosphoramide and phosphine oxide ligands, their coordination chemistry towards lanthanide ions is poorly explored. To the best of our knowledge, no Ln(III) coordination compound with this species was reported, despite the fact that 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide and related species were proposed as efficient extraction agents for group 3 and lanthanide ions [48]. As a part of our research on new luminescent metal complexes with phosphoramide and arylphosphonic diamide ligands [49, 50], in this manuscript we report the synthesis and photophysical characterization of new Ln(III) complexes with 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide.

## 2. Experimental

### 2.1. Materials and methods

Commercial solvents (Aldrich) were purified as described [51]. Lanthanide oxides and chlorides were purchased from Chempur. All the other reagents (Aldrich, Alfa Aesar) were used as received. The syntheses of the lanthanide complexes were carried out under inert atmosphere, working in a glove-box (MBraun Labstar with MB 10 G gas purifier) filled with $N_2$ and equipped for inorganic syntheses. [Ln(NO$_3$)$_3$(H$_2$O)$_3$] (Ln = Eu, Gd, Tb) nitrato complexes were prepared following a reported procedure [52].

Elemental analyses (C, H, N) were carried out at the University of Padua using a Fison EA1108 microanalyzer. Magnetic susceptibilities were measured on solid samples at 298 K with a MK1 magnetic susceptibility balance (Sherwood Scientific Ltd.) and corrected for diamagnetic contribution by means of tabulated Pascal's constants [53]. Melting point measurements were carried out with a Büchi B 535 instrument. IR spectra were collected from 4000–400 cm$^{-1}$ using a Perkin-Elmer Spectrum One spectrophotometer. The air-sensitive samples were prepared in a glove-box using an air-tight sample holder with KBr windows. $^1$H, $^{31}$P{$^1$H}, and $^{19}$F NMR spectra were recorded on a Bruker AVANCE 400 spectrometer using CDCl$_3$ and DMSO-d$_6$ as solvents. The partially deuterated fraction of the solvent was quoted with respect to tetramethylsilane and used as an internal reference for $^1$H spectra. $^{31}$P{$^1$H} chemical shifts are reported with respect to 85% H$_3$PO$_4$, with downfield shifts considered positive. $^{19}$F chemical shifts are referred to CFCl$_3$.

1,3-Dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide (L) was obtained from reaction of O=$PCl_2Ph$ with *N*,*N*′-dimethylethylenediamine in the presence of triethylamine [54] using $CH_2Cl_2$ as solvent. Spectroscopic data of the ligand: $^1H$ NMR ($CDCl_3$, 298 K), $\delta$: 7.78–7.38 (m, 5H, Ph), 3.47–3.31 (m, 2H,$CH_2$), 3.31–3.14 (m, 2H,$CH_2$), 2.52 (d, 6H, $J_{PH}$ = 10.0 Hz, $CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K), $\delta$: 29.65. IR (KBr), $cm^{-1}$: 1188 s ($\nu_{P=O}$). UV-VIS ($CH_2Cl_2$, 298 K), nm: < 300. $^1H$ NMR data are comparable to those reported [54], and the $^{31}P$ NMR chemical shift is in line with that given [48].

## 2.2. Synthesis of [Eu(β-dike)$_3$L$_2$]

The complexes [Eu($\beta$-dike)$_3$L$_2$] ($\beta$-dike = dibenzoylmethanate (dbm), tenoyltrifluoroacetonate (tta); L = 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide) were prepared by dissolving 1.5 mmol of dibenzoylmethane (0.336 g) or tenoyltrifluoroacetone (0.333 g) in THF (20 mL), subsequently reacted with potassium *tert*-butoxide (0.168 g, 1.5 mmol). After 2 h, the solution thus obtained was slowly added to anhydrous $EuCl_3$ (0.129 g, 0.5 mmol) in 20 mL of THF and the reaction mixture was left under stirring at room temperature for 4 h. A THF solution (10 mL) containing 1.0 mmol of L (0.210 g) was then added and the mixture was kept overnight under stirring at room temperature. After filtration, the solvent was removed under reduced pressure and dichloromethane (25 mL) was added. The solution was purified by centrifugation, then the solvent was evaporated and diethylether (5 mL) was added. The yellowish solid that separated out was collected by filtration and dried under vacuum. Yield = 75% ($\beta$-dike = dbm), 80% ($\beta$-dike = tta).

## 2.3. Characterization of [Eu(dbm)$_3$L$_2$]

Anal. Calcd for $C_{65}H_{63}EuN4O_8P_2$ (1242.13 g $mol^{-1}$, %): C, 62.85; H, 5.11; N, 4.51. Found (%): C, 62.61; H, 5.53; N, 4.49. M.P. (°C) 125 (dec.). $\chi^M{}_{corr}$ (c.g.s.u.) $3.9 \times 10^{-3}$. IR (KBr), $cm^{-1}$: 1596–1409 s ($\nu_{dbm}$), 1185 sh, 1161 m ($\nu_{P=O}$). $^1H$ NMR (DMSO-$d_6$, 298 K), $\delta$: 7.70–7.44 (m, 10H, P-Ph), 7.20 (s, 2H, $\beta$-dike-CH), 7.19 (s, 1H, $\beta$-dike-CH), 6.82 (t, 6H, $J_{HH}$ = 7.4 Hz, $\beta$-dike-Ph), 6.67 (dd, 12H, $J_{HH}$ = 6.3 Hz, $J_{HH}$ = 7.4 Hz, $\beta$-dike-Ph), 5.72 (d, 12H, $J_{HH}$ = 6.3 Hz, $\beta$-dike-Ph), 3.30–3.23 (m, 4H, N-$CH_2$), 3.23–3.15 (m, 4H, N-$CH_2$), 2.36 (d, 12H, $J_{PH}$ = 10.0 Hz, N-Me). $^{31}P\{^1H\}$ NMR (DMSO-$d_6$, 298 K), $\delta$: 28.1 (FWHM = 30 Hz).

## 2.4. Characterization of [Eu(tta)$_3$L$_2$]

Anal. Calcd for $C_{44}H_{42}EuF_9N_4O_8P_2S_3$ (1235.92 g $mol^{-1}$, %): C, 42.76; H, 3.43; N, 4.53. Found (%): C, 42.58; H, 3.45; N, 4.49. M.P. (°C) 78 (dec.). $\chi^M{}_{corr}$ (c.g.s.u.) $4.2 \times 10^{-3}$. IR (KBr), $cm^{-1}$: 1616–1302 s ($\nu_{tta}$), 1182 s, 1136 s ($\nu_{P=O}$). $^1H$ NMR (DMSO-$d_6$, 298 K), $\delta$: 7.72–7.45 (m, 10H, P-Ph), 7.43 (s, 3H, $\beta$-dike-thioph), 6.51 (s, 3H, $\beta$-dike-thioph), 6.35 (s, 3H, $\beta$-dike-thioph), 3.79 (s, 3H, $\beta$-dike-CH), 3.29-3.22 (m, 4H, N-$CH_2$), 3.22–3.15 (m, 4H, N-$CH_2$), 2.37 (d, 12H, $J_{PH}$ = 10.0 Hz, N-Me). $^{31}P\{^1H\}$ NMR (DMSO-$d_6$, 298 K), $\delta$: 28.1 (FWHM = 170 Hz). $^{19}F$ NMR (DMSO-$d_6$, 298 K), $\delta$: –78.3.

### 2.5. Coordination of 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide to $[Ln(NO_3)_3]$ (Ln = Eu, Gd, Tb)

The reaction between the $[Ln(NO_3)_3(H_2O)_3]$ precursors (1.0 mmol; Ln = Eu, 0.392 g; Ln = Gd, 0.397 g; Ln = Tb, 0.399 g) and two equivalents of L (0.420 g) were carried out in THF (25 mL) at room temperature under inert atmosphere (glove box). Stirring was continued overnight, then the solvent was evaporated at reduced pressure and the resulting solid was triturated with diethylether (10 mL), filtered and dried under vacuum.

### 2.6. Characterization of nitrato-derivatives

IR (M = Eu, solid), $cm^{-1}$: 1455 s, 1438 s ($\nu_{N=O}$), 1305 s ($\nu^{as}{}_{ONO}$), 1154 s ($\nu_{P=O}$). IR (M = Gd, solid), $cm^{-1}$: 1456 s, 1439 s ($\nu_{N=O}$), 1307 s ($\nu^{as}{}_{ONO}$), 1154 s ($\nu_{P=O}$). IR (M = Tb, solid), $cm^{-1}$: 1457 s, 1439 s ($\nu_{N=O}$), 1309 s ($\nu^{as}{}_{ONO}$), 1154 s ($\nu_{P=O}$).

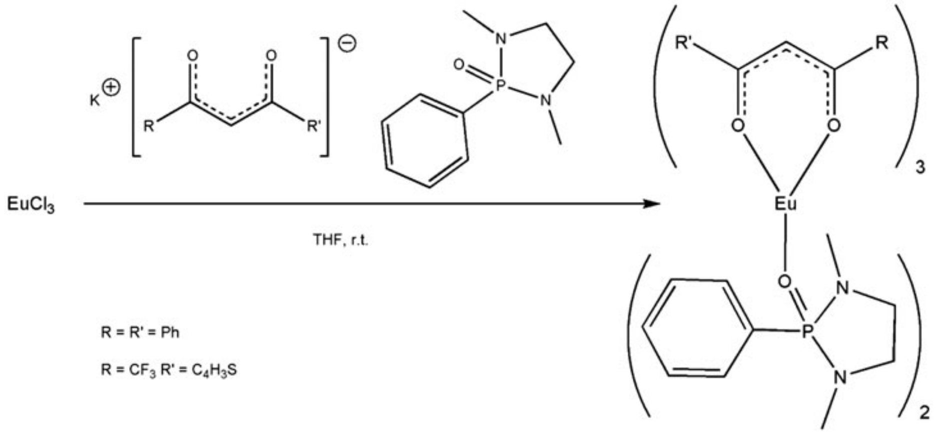
### 2.7. Photoluminescence measurements

Absorption spectra in solution were collected using a Perkin-Elmer Lambda 35 spectrophotometer. Emission (PL) spectra of air-sensitive samples were recorded under inert atmosphere (glove box) from 400–1035 nm with an OceanOptics Flame-T spectrometer coupled with an optical fiber, a collimating lens and a longpass filter, using UV led (280–375 nm) excitation sources. When necessary, samples were cooled at 200 K with cold $N_2$ gas coming from a liquid nitrogen evaporator. Photoluminescence emission (PL) and excitation (PLE) measurements of air-stable compounds were carried out at room temperature on solid samples by a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer. A continuous-wave xenon arc lamp was used as source, selecting the excitation wavelength by a double Czerny–Turner monochromator. A single grating monochromator coupled to a photomultiplier tube was used as detection system for optical emission measurements. Excitation and emission spectra were corrected for the instrumental functions. Time-resolved analyses were performed in multichannel scaling modality (MCS) by using a pulsed UV led source ($\lambda_{emission} = 377$ nm). The intrinsic quantum yields ($Q^{Eu}_{Eu}$) were estimated from the $\tau$ values on the basis of Equation (1), where $n$ indicates the refractive index of the sample. The value of 1.5 is assumed for solid state samples in this work for comparative purposes; it is worth noting that refractive index may differ depending on the nature of the compound. $I(^5D_0 \rightarrow {}^7F_J)/I(^5D_0 \rightarrow {}^7F_1)$ is the ratio between the total integrated emission from the Eu($^5D_0$) level to the $^7F_J$ manifold and the integrated intensity of the transition $^5D_0 \rightarrow {}^7F_1$ [55].

$$Q^{Eu}_{Eu} = 14.65 n^3 I \frac{(^5D_0 \rightarrow {}^7F_J)}{I(^5D_0 \rightarrow {}^7F_1)\tau(s)} \tag{1}$$

### 2.8. Computational details

The computational geometry optimizations of the $[Eu(\beta\text{-dike})_3L_2]$ complexes were carried out without symmetry constraints using the hybrid-GGA DFT functional EDF2 [56],



**Scheme 1.** Synthesis of [Eu(β-dike)$_3$L$_2$] complexes.

in combination with the split-valence polarized 6–31G(d,p) basis set for light atoms and the scalar quasirelativistic 4f-in-core pseudopotential ECP52MWB for europium, with the associated valence basis set [57–59]. Because of the inclusion of the 4f$^6$ shell of Eu(III) in the pseudopotential, the "restricted" formalism was applied. The stationary points were characterized by IR simulations (harmonic approximation) [60]. Calculations were performed with Spartan '16 (Wavefunction Inc.), build 2.0.3 [61, 62], running on Intel Xeon-bases x84-64 workstations. The geometries of the first coordination spheres were compared with ideal geometries by means of the SHAPE software, version 2.1 [63].

## 3. Results and discussion

$\beta$-Diketonate complexes having general formulas [Eu($\beta$-dike)$_3$L$_2$], where $\beta$-dike is dibenzoylmethanate (dbm) or tenoyltrifluoroacetonate (tta), were obtained by reacting EuCl$_3$ with the $\beta$-diketone, previously deprotonated with potassium *tert*-butoxide, and then with 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide, as depicted in Scheme 1.

The complexes thus isolated are stable in air at room temperature. Despite the fact that we were unable to obtain crystals suitable for X-ray diffraction, the characterization data support the formation of the desired products. In particular, elemental analyses agree with the proposed formulations and the molar magnetic susceptivities are in line with the expected value for Eu(III) derivatives at room temperature [13]. The IR spectra show, besides the typical vibrations of the $\beta$-diketonate ligands, the $\nu_{PO}$ stretch in the range 1186–1136 cm$^{-1}$, close to the value observed for the free ligand. The $^1$H NMR spectrum in DMSO-d$_6$ of the dbm complex exhibits resonances of the phenyl substituents at 6.8, 6.7 and 5.7 ppm, similar to those recorded for other europium complexes containing the [Eu(dbm)$_3$] fragment in DMSO-d$_6$ solution [64, 65]. These signals are replaced by three resonances around 7.4, 6.5, and 6.3 ppm in the tta derivative, comparable to the thiophene-related $^1$H NMR signals of other [Eu(tta)$_3$]

complexes [66, 67]. The $\beta$-dike CH resonances fall at 7.2 ppm for the dbm derivative and at meaningfully lower chemical shift value, around 3.8 ppm, for the tta complex, in agreement with literature outcomes [64–67]. The presence of the –$CF_3$ substituent in the tta complex is confirmed by the $^{19}$F NMR singlet at −78.3 ppm. $^{19}$F NMR chemical shifts around −80 ppm are commonly reported for the tta ligand coordinated to Eu(III) [66–68]. The 1,3-diazaphospholidine-2-oxide ligand can be detected in the $^{1}$H NMR spectrum by the N-Me resonance around 2.36 ppm, with $^{3}J_{PH}$ coupling constant of 10 Hz. The doublet is scarcely shifted with respect to the free ligand and the coupling constant is not affected by the interaction with Eu(III). Two second-order multiplets are also present in the range 3.30–3.15 ppm, attributable to the [N-$CH_2$-$CH_2$-N] fragment of the five-membered cycle. Also in this case the resonances are close to those recorded for free 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide. The presence of two groups of signals is associated to the lack of equivalence of the protons in *E* and *Z* position with respect to the *P*-bonded phenyl ring. The aromatic substituent is associated to a series of signals in the high frequency region of the $^{1}$H NMR spectra. Integration data support the formation of eight-coordinate complexes with three $\beta$-diketonate and two [O=P]-donor ligands. Only one singlet is present in the $^{31}P\{^{1}H\}$ NMR spectra, broadened with respect to the free ligand because of paramagnetic relaxation, suggesting that 1,3-diazaphospholidine-2-oxide interacts with the Eu(III) center in DMSO-$d_6$ solution. The FWHM (full width at half maximum) values are 30 and 170 Hz, respectively, for the dbm and tta derivatives, while the FWHM value for the free ligand is 3 Hz. The higher broadening in $[Eu(tta)_3L_2]$ with respect to $[Eu(dbm)_3L_2]$ agrees with the lower steric bulk of tta, that allows a stronger coordination of L. Broad $^{31}$P NMR resonances are common for ligands with [O=P] donor moieties coordinated to Eu(III), as occurs for example for $[Eu(tta)_3(O{=}PPh_3)_2]$ and related species [68]. The scarce chemical shift variation with respect to the free ligand suggests fast L/DMSO-$d_6$ exchange in the Eu(III) coordination sphere of the complexes here described [69–71].

The DFT-optimized geometries of the $[Eu(\beta\text{-dike})_3L_2]$ complexes, depicted in Figure 1, support the formation of eight-coordinate compounds, with two 1,3-diazaphospholidine-2-oxide ligands coordinated to Eu(III) with comparable bond lengths. As deduced from the $^{31}$P NMR data, the Eu-O(L) distances are slightly shorter (2.322–2.354 Å) in the tta derivative with respect to the dbm complex (2.395–2.420 Å) as a consequence of the lower steric crowding. The bond lengths related to coordination of dbm and tta are in line with data reported for several other Eu(III) $\beta$-diketonate complexes [72]. The first coordination spheres of both the complexes are asymmetric ($C_1$). The analysis carried out with the SHAPE software (Table 1) indicates that the geometries more similar to the $[EuO_8]$ fragment of $[Eu(dbm)_3L_2]$ are the square antiprism and the triangular dodecahedron, while in the case of $[Eu(tta)_3L_2]$ the first coordination sphere resembles the biaugmented trigonal prism.

Absorption and photoluminescence data of the $\beta$-diketonate complexes are summarized in Table 2. As observable in Figure 2, dichloromethane solutions of the compounds are characterized by strong absorptions in the near-UV range. Solid-state photoluminescence measurements showed that the excitation of the coordinated ligands with wavelengths below 480 nm causes the emission from the Eu(III) center

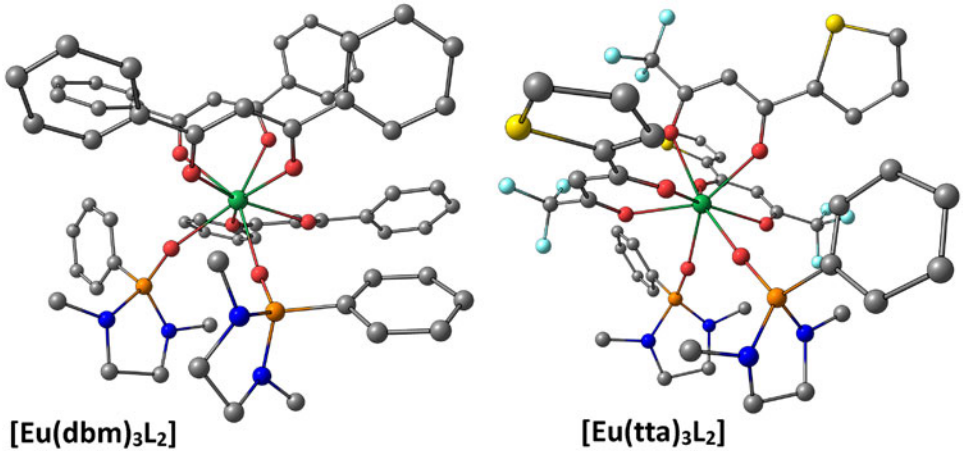


**Figure 1.** DFT-optimized structures of the [Eu(β-dike)$_3$L$_2$] complexes. Hydrogens are omitted for clarity. Color map: Eu, green; C, grey; O, red; N, blue; F, light blue; P, orange; S, yellow. Selected computed bond lengths for [Eu(dbm)$_3$L$_2$], Å: Eu-O(dbm) 2.333, 2.377, 2.353, 2.373, 2.359, 2.364; Eu-O(L) 2.395, 2.420. Selected computed bond lengths for [Eu(tta)$_3$L$_2$], Å: Eu-O(tta) 2.342, 2.369, 2.355, 2.376, 2.324, 2.450; Eu-O(L) 2.322, 2.354.

**Table 1.** Output of the SHAPE software for the [Eu(β-dike)$_3$L$_2$] complexes.

| | OP | HPY | HBPY | CU | SAPR | TDD | J26 | J14 | BTPR | J84 | TT |
|---|---|---|---|---|---|---|---|---|---|---|---|
| [Eu(dbm)$_3$L$_2$] | 31.02 | 23.59 | 15.83 | 9.401 | 0.944 | 0.978 | 15.15 | 29.27 | 1.542 | 3.675 | 10.24 |
| [Eu(tta)$_3$L$_2$] | 31.66 | 23.28 | 15.89 | 10.53 | 1.346 | 1.434 | 14.23 | 29.16 | 1.071 | 3.677 | 11.18 |

OP $D_{8h}$, octagon; HPY $C_{7v}$, heptagonal pyramid; HBPY $D_{6h}$, hexagonal bipyramid; CU $O_h$, cube; SAPR $D_{4d}$, square antiprism; *TDD* $D_{2d}$, triangular dodecahedron; J26 $D_{2d}$, Johnson gyrobifastigium; J14 $D_{3h}$, Johnson elongated triangular bipyramid; *BTPR* $C_{2v}$, biaugmented trigonal prism; J84 $D_{2d}$, Snub disphenoid; TT $T_d$, triakis tetrahedron.

**Table 2.** Absorption and photoluminescence data of the [Eu(β-dike)$_3$L$_2$] complexes.

| Compound | Data |
|---|---|
| [Eu(dbm)$_3$L$_2$] | UV-VIS (CH$_2$Cl$_2$, r.t.), nm: 396, 347 max, 250. PL (solid, $\lambda_{\text{excitation}} = 300$ nm, r.t.), nm: 579 ($^5D_0 \rightarrow {}^7F_0$, 0.4%), 588, 591, 597 ($^5D_0 \rightarrow {}^7F_1$, 4.7%), 611, 613, 618, 623, 626 ($^5D_0 \rightarrow {}^7F_2$, 74.2%), 649, 651, 653, 656 ($^5D_0 \rightarrow {}^7F_3$, 5.0%), 690, 699, 703 ($^5D_0 \rightarrow {}^7F_4$, 15.7%). PLE (solid, $\lambda_{\text{emission}} =$ 614 nm, r.t.), nm: $<$ 480, 464 ($^5D_2 \leftarrow {}^7F_0$). $\tau$ (solid, $\lambda_{\text{excitation}} = 377$ nm, $\lambda_{\text{emission}} = 613$ nm), µs: 482. $Q_{\text{Eu}}^{\text{Eu}}$= 51%. CIE 1931: $x = 0.666$, $y = 0.334$. |
| [Eu(tta)$_3$L$_2$] | UV-VIS (CH$_2$Cl$_2$, r.t.), nm: 343 max, 270. PL (solid, $\lambda_{\text{excitation}} = 400$ nm, r.t.), nm: 579 ($^5D_0 \rightarrow {}^7F_0$, 0.6%), 589, 592, 595 ($^5D_0 \rightarrow {}^7F_1$, 4.6%), 611, 614, 617 ($^5D_0 \rightarrow {}^7F_2$, 75.0%), 650, 654 ($^5D_0 \rightarrow {}^7F_3$, 3.9%), 690, 701 ($^5D_0 \rightarrow {}^7F_4$, 15.9%). PLE (solid, $\lambda_{\text{emission}} = 614$ nm, r.t.), nm: $<$ 480 (ligands excitation), 464 ($^5D_2 \leftarrow {}^7F_0$). $\tau$ (solid, $\lambda_{\text{excitation}} = 377$ nm, $\lambda_{\text{emission}} = 613$ nm), µs: 610. $Q_{\text{Eu}}^{\text{Eu}}$= 65%. CIE 1931: $x = 0.665$, $y = 0.334$. |

(Figure 2). Direct excitation of Eu(III) is also present in the PLE spectra, corresponding to the $^5D_2 \leftarrow {}^7F_0$ transition centered at 464 nm [73]. The PL spectra display only the typical $^5D_0 \rightarrow {}^7F_J$ bands, the most intense occurring for $J = 2$. The $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ intensity ratio ranges from 15.8 (β-dike = dbm) to 19.2 (β-dike = tta) and the $^5D_0 \rightarrow {}^7F_1$ transition is separated into three peaks because of the Stark effect. These data suggest low symmetry of the first coordination sphere, with 2 the maximum possible rotational symmetry order, in agreement with the results of DFT calculations. The occurrence of only one $^5D_0 \rightarrow {}^7F_0$ transition supports the presence of only one Eu(III) emitting center, even if such information is not conclusive [73].

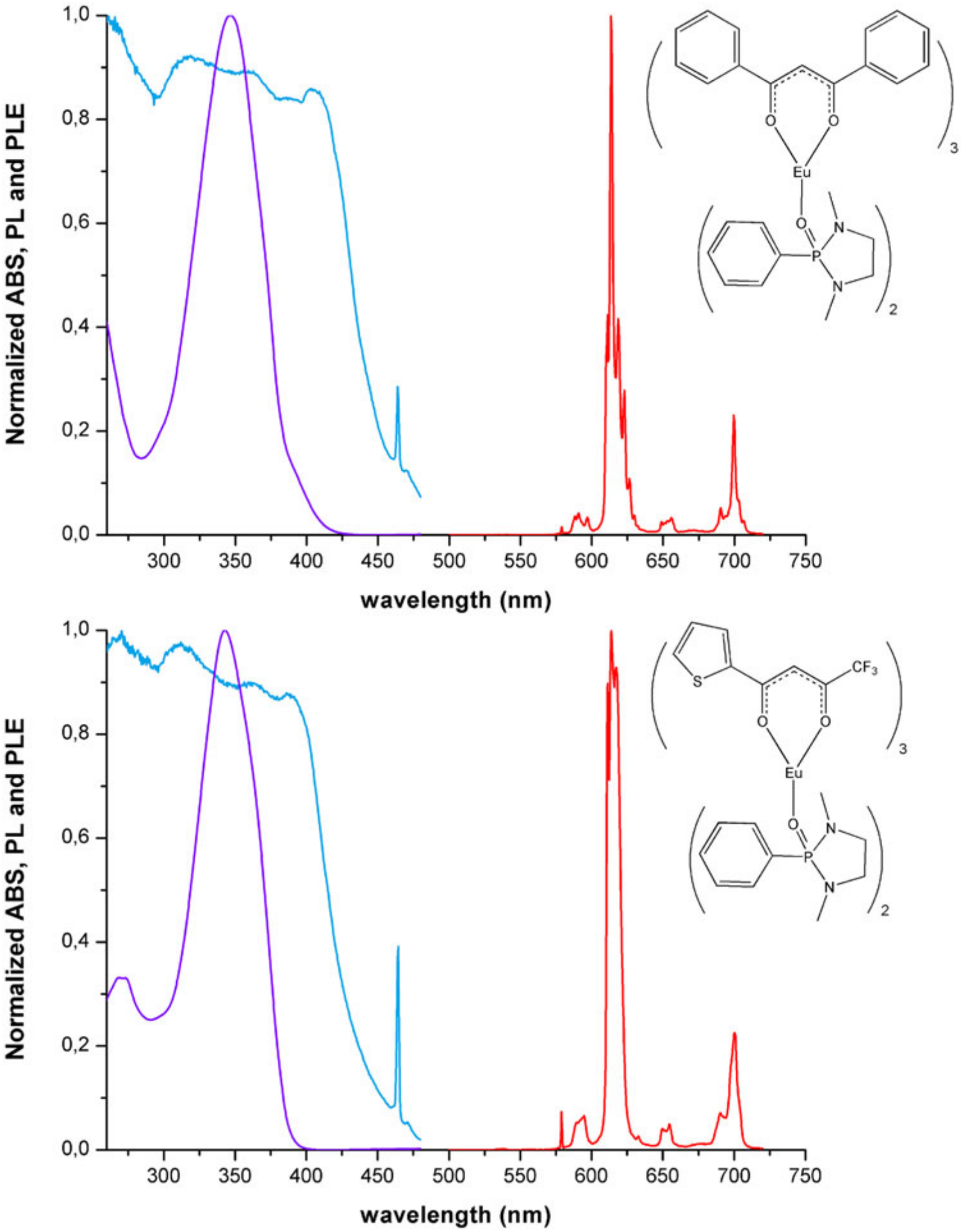


Figure 2. Normalized absorption ($CH_2Cl_2$ solution, violet line), emission (solid, red line) and excitation (solid, light blue line) spectra of the $[Eu(\beta\text{-dike})_3L_2]$ complexes.

Emissions of all the compounds fall in the reddish orange region of the CIE 1931 chromaticity diagram with unitary color purity [74], as shown in Figure 3. The lifetimes ($\tau$) were determined from the mono-exponential interpolation of the luminescence decay curves, reported in Figure 3. The measured $\tau$ values are 482 and 610 μs, respectively, for solid $[Eu(dbm)_3L_2]$ and $[Eu(tta)_3L_2]$. The lifetime of the tta derivative is comparable to that reported for $[Eu(tta)_3(ptso)_2]$ (ptso = p-tolyl sulfoxide), 598 μs [75].

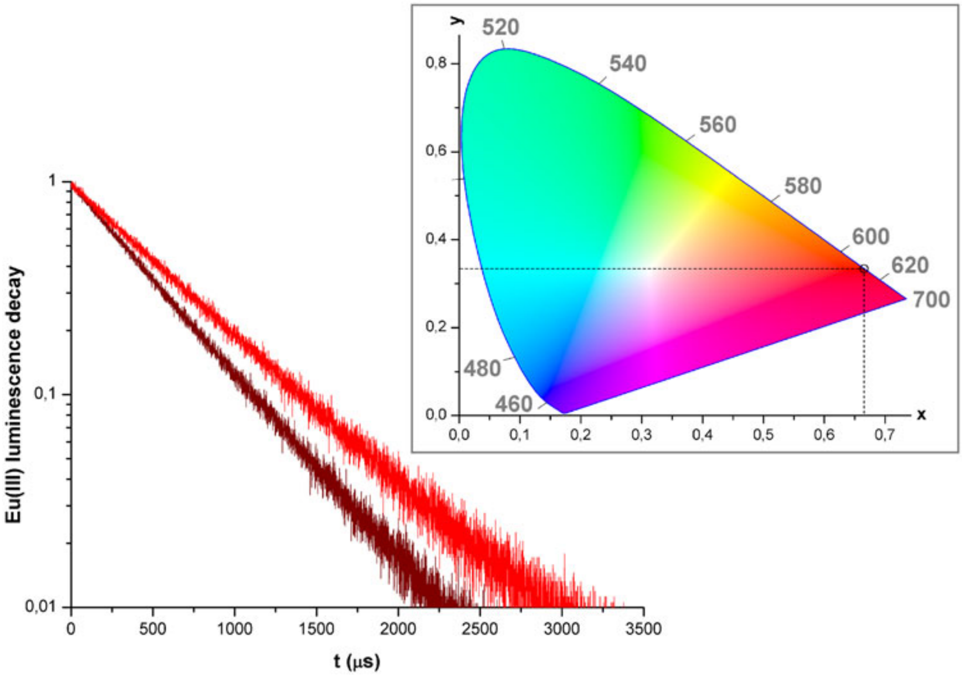


**Figure 3.** Semi-log plot of the luminescence decay curves of the [Eu(β-dike)$_3$L$_2$] complexes. β-dike = dbm, wine line; β-dike = tta, red line. Solid samples, $\lambda_{excitation}$ = 377 nm, $\lambda_{emission}$ = 613 nm, r.t. Inset: CIE 1931 chromaticity coordinates.

The $Q_{Eu}^{Eu}$ values calculated on the basis of Equation (1) are 51% and 65%, respectively, for the dibenzoylmethanate and tenoyltrifluoroacetonate derivatives.

Further information about the sensitization of Ln(III) luminescence by the 1,3-diazaphospholidine-2-oxide ligand was obtained by coordination to [Ln(NO$_3$)$_3$] (Ln = Eu, Gd, Tb) metal fragments. The compounds isolated from the 1: 2 reaction between [Ln(NO$_3$)$_3$(H$_2$O)$_3$] and L rapidly decompose in the presence of moisture and their complete characterization is beyond the scope of this work. IR data agree with the presence of nitrato ligands $k^2$-coordinated to Ln(III) [76]. Moreover, the coordination of L is highlighted by the stretchings relative to the P=O bonds around 1154 cm$^{-1}$.

The emission spectrum of the Eu(III) derivative, obtained by excitation with near-UV light (Figure 4), shows the typical bands associated to the $^5D_0 \rightarrow {}^7F_J$ transitions of the metal center, the most intense corresponding to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ centered at 619 nm. In the emission spectrum of the corresponding Gd(III) species a broad band with maximum at 505 nm and a shoulder around 445 nm can be detected, tentatively attributable to phosphorescence and fluorescence from the coordinated 1,3-diazaphospholidine-2-oxide ligand. The relative intensity of the highest-energy transition slightly decreases on cooling the sample (Figure 4). The triplet state (*T*) energy of the coordinated ligands estimated on the basis of the emission spectrum is around 21,500 cm$^{-1}$, well above the Eu(III) $^5D_0$ level, 17250 cm$^{-1}$, and also higher than the Tb(III) $^5D_4$ resonance level, 20,430 cm$^{-1}$ [1]. Despite the fact that the T – $^5D_4$ energy gap is below the value suggested by Latva *et al.* [77] for an efficient energy transfer, the coordination of 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide to Tb(III) nitrate afforded a

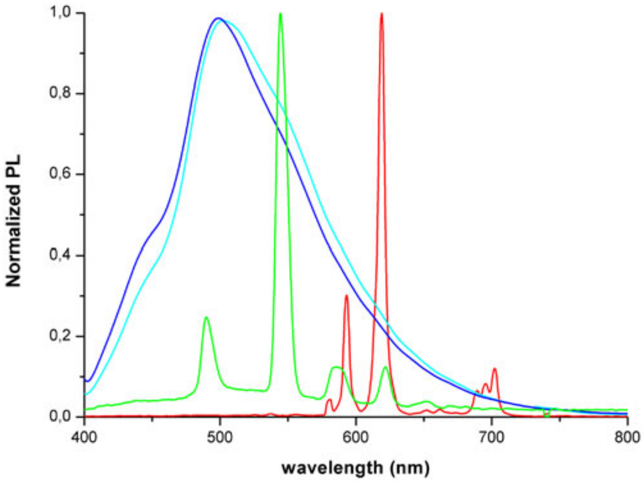


**Figure 4.** PL spectra of the Ln(III) nitrato complexes with 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide. Solid samples, inert atmosphere, $\lambda_{excitation} = 375$ nm. Ln = Eu, red line, r.t. Ln = Gd, blue line, r.t. Ln = Gd, cyan line, 200 K. Ln = Tb, green line, r.t.

**Table 3.** Photoluminescence data of the Ln(III) nitrato-complexes with 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide.

| Ln | Data |
|---|---|
| Eu | PL (solid, $\lambda_{excitation} = 375$ nm, r.t.), nm: 580 ($^5D_0 \rightarrow {}^7F_0$, 1.9%), 593 ($^5D_0 \rightarrow {}^7F_1$, 16.3%). 619 ($^5D_0 \rightarrow {}^7F_2$, 63.4%), 652 ($^5D_0 \rightarrow {}^7F_3$, 3.8%), 689, 695, 702 ($^5D_0 \rightarrow {}^7F_4$, 14.6%). |
| Gd | PL (solid, $\lambda_{excitation} = 375$ nm, 200 K), nm: 505 max ((ligands luminescence, FWHM: 4000 cm$^{-1}$), 445 sh (ligands luminescence). Triplet state: 21,500 cm$^{-1}$. |
| Tb | PL (solid, $\lambda_{excitation} = 375$ nm, r.t.), nm: 490 ($^5D_4 \rightarrow {}^7F_6$), 544 ($^5D_4 \rightarrow {}^7F_5$), 587 ($^5D_4 \rightarrow {}^7F_4$), 622 ($^5D_4 \rightarrow {}^7F_3$), 652 ($^5D_4 \rightarrow {}^7F_2$), 400–700 (ligands luminescence). |

green-emitting complex upon excitation with near-UV light, and in the PL spectrum the typical $^5D_4 \rightarrow {}^7F_J$ transitions of the metal center can be detected, the most intense centered at 544 nm and corresponding to $J = 5$ (Figure 4). The Tb(III) bands are superimposed to a broad phosphorescence band between 400 and 700 nm, comparable to that of the Gd(III) derivative, indicating that the T → $^5D_4$ energy transfer is not quantitative. Photoluminescence data of the nitrato-derivatives are summarized in Table 3.

## 4. Conclusion

In this article, we report some preliminary results about the application of 1,3-diazaphospholidine-2-oxide ligands in the field of visible-emitting lanthanide complexes, focusing attention on 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide. The collected data indicate that the ligand here studied is a promising candidate for the preparation of luminescent lanthanide derivatives, in particular considering Eu(III) as metal center. The introduction of different substituents in the 1,3-diazaphospholidine-2-oxide skeleton allows tuning of the electronic and steric features of this class of ligands. For this reason, the information summarized in this work could be helpful for the design of new antenna-ligands to be applied for the preparation of highly luminescent lanthanide derivatives.

## Disclosure statement

There are no conflicts to declare.

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