# The influence of carboxilate, phosphinate and seleninate groups on luminescent properties of lanthanides complexes

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## ABSTRACT

The lanthanides(III) complexes $[Ln(bza)_3(H_2O)_n] \cdot mH_2O$, $[Ln(ppa)_3(H_2O)_n] \cdot mH_2O$ and $[Ln(abse)_3(H_2O)_n] \cdot mH_2O$ where $Ln = Eu^{3+}$, $Gd^{3+}$ or $Tb^{3+}$ were synthesized using sodium benzoate (Nabza), sodium phenylseleninate (Naabse) and sodium phenylphosphinate (Nappa) in order to verify the influence on coordination modes and the luminescence parameters when the carbon is exchanged by phosphorus or selenium in those ligands. The complexes' stoichiometries were determined by lanthanide(III) titration, microanalysis and TGA. The coordination modes were determined as bidentate bridging and chelate by the FT-IR. The triplet state energies of the ligands were obtained by two different approaches giving a difference of about $\sim 2000$ cm$^{-1}$ between them. The $[Eu(abse)_3(H_2O)]$ complex shows the higher degree of covalence which was verified by the centroid of $^5D_0 \rightarrow {}^7F_0$ transition (17,248 cm$^{-1}$). On the other hand the $[Ln(abse)_3(H_2O)_n] \cdot mH_2O$ complexes have an inefficient antenna effect verified by the low values of absolute emission quantum yields. The $[Ln(ppa)_3(H_2O)_n] \cdot mH_2O$ complexes have higher emission decay lifetime values among the complexes which is a result of the ability of this ligand to form coordination polymers avoiding water molecules in the first coordination sphere. The $[Eu(ppa)_3]$ complex has the highest point symmetry around europium(III) among the synthesized complexes, followed by the $[Eu(bza)_3(H_2O)_2] \cdot 3/2(H_2O)$ and $[Eu(abse)_3(H_2O)]$ complexes where europium(III) show similar point symmetries. As one may expect, the triplet state energy position would change the transfer and/or back energy transfer rates from ligand to metal. The calculation of these rates show that the back energy transfer rates are more affected than the transfer ones by changing the triplet state energy in the range of $\sim 2000$ cm$^{-1}$. The changes in the energy transfer rates from triplet state to europium(III) levels are not sufficient to significantly modify the population of the europium(III) $^5D_{0,1}$ levels and therefore the emission quantum yield.

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## 1. Introduction

The most part of lanthanides(III)-doped materials can be applied in several fields such as: displays, sensors, biomarkers, etc. [1–3] due to their luminescent properties. The lanthanides(III) emission may happen from the visible (Tb$^{3+}$ and Eu$^{3+}$, for example) to near infrared regions (Nd$^{3+}$ and Er$^{3+}$, for example). The emission spectra of lanthanides(III)-doped compounds are composed by narrow bands due to the intraconfigurational 4f-4f transitions that are forbidden by Laporte's rule and in some cases they are also forbidden by Spin's rule. The presence of a non-symmetric electric field around lanthanide(III) ions due to inorganic or organic ligands [1–3] promotes the mixing of electronic states with opposite parities relaxing Laporte's rule. The complexes containing organic ligands are interesting for academic

studies and applications because the ligands play an important role in the properties of the complex such as: stability, solubility, interactions with biological groups and also emission efficiency. The energy pathway (excitation to emission) in lanthanide(III) complexes is a tricky process which involves energy transfer and back transfer rates between ligand states and lanthanide levels. The excitation may occur through the ligand states (fundamental to excited singlet states) followed by intersystem crossing (energy transfer from excited singlet to triplet states), energy transfer from ligand to lanthanide(III) excited levels and finally the emission occurs through the lanthanide f–f transitions, according to the traditional energy transfer from triplet states to lanthanide. The energy transfer also may happen via charge transfer or even directly from the excited singlet state; in both cases the energy transfer from the triplet state is ruled out [4,5]. The emission efficiency of the lanthanide(III) complex depends on: (i) the energy of the triplet state that should be above the lanthanide ion emitting level [4,6], being 2500 cm$^{-1}$ desirable in order to decrease the back energy transfer rate; (ii) the non-radiative

processes that are usually caused by the presence of O–H, N–H and C–H oscillators; (iii) the ligand field asymmetry and (iv) the transfer and back energy transfer rates between the ligand and the lanthanide ion [1,6].

Among several organic ligands used for preparing complexes of lanthanide(III) ions, the ligands containing the carboxylates are widely reported in the literature [7,8]. There are several reports concerning the structure as well as some luminescent properties of complexes containing this kind of ligand. The carboxylate ion may coordinate to the lanthanide(III) by several coordination modes such as: bidentate bridging, bidentate chelate, monodentate or mixed modes like bridging and chelate [7,8]. Ligands containing phosphinate and seleninate groups are not often reported in the literature. The lanthanide(III) complexes containing diphenyphosphinate (dpp) as coordination group were reported by Stucchi and co-workers [9,10]. The latter ligand has the ability to form stable bonds with lanthanides(III) ions and usually its lanthanide(III) complexes do not have water molecules in the first coordination sphere [9,10]. Malta and co-workers [11] reported on the synthesis and spectroscopic characterization of two lanthanide(III) complexes containing the ligands benzeneseleninic acid (abse) and 4-chloro-benzeneseleninic acid (abseCl). These authors reported on the influence of the addition of chlorine in the phenyl ring on the covalence of Ln–O bonds but did not explore the possible different coordination modes of the seleninate group. There is no report in the literature comparing the changes caused by the replacement of the carbon by phosphorus or selenium in a specific ligand molecular structure. The understanding of how the carboxylates, phosphinates or seleninates groups may change the chemical nature of coordination sphere, the point symmetry around lanthanide ions and the luminescent properties is important in order to plan futures complexes that show desirable properties, such as high emission quantum yields.

The present work reports on possible changes of coordination modes and luminescent properties of lanthanides(III) complexes originated from the replacement of the carbon atom of a carboxylate ligand for selenium or phosphorus. The ligands benzoic acid (bza), phenylseleninic acid (abse) and phenylphosphinic acid (ppa) were chosen to study the influence of those different atoms on the complexes' chemical stoichiometries, coordination polyhedron, number of coordinated water molecules and energies of ligands' excited states. Theoretical Judd–Ofelt (JO) intensity parameters, energy transfer rates and the emission quantum yield were theoretically estimated using data of polar spherical coordinates of atoms of the complexes in the ground state geometries that were obtained from semi-empirical methods: Sparkle/AM1, Sparkle/PM3 and Sparkle/PM6. In order to evaluate the ground state geometry of the lanthanides(III) complexes the theoretical values of JO parameters were compared to the experimental ones. The influence of those ligands on the nature of chemical bonds between the oxygen and the lanthanides(III) ions is discussed as well.

## 2. Experimental section

The complexes were synthesized as follows: sodium hydroxide (NaOH) in a molar ratio 1:1 (L:OH), was added drop by drop in aqueous suspensions of the respective ligands (L=bza, abse and ppa) under stirring during 30 min at 70 °C. The complete dissolution of the ligands was an indicative of formation of their respective sodium salts. The aqueous solutions of the ligands' salts were separately added to an aqueous solution of lanthanide ($Ln^{3+}$=$Eu^{3+}$, $Gd^{3+}$ or $Tb^{3+}$) ions, with a pH value equal to 5.0, in a molar ratio 3:1 ($L:Ln^{3+}$). A white precipitate was formed immediately for all ligands. The complexes' suspensions were

stirred during 90 min at 80 °C for complete precipitation. After that time the solids were kept resting for 1 h, followed by filtration and washed with several portions of hot water. The solids were placed into a desiccator containing silica.

## 3. Characterizations

The chemical stoichiometries of the complexes were suggested by $Ln^{3+}$ titration using a standard 0.01 mol $L^{-1}$ EDTA solution, carbon and hydrogen microanalysis (Perkin Elmer 2400) and thermogravimetric analysis (TA instruments SDTQ600) that were carried out using a dynamic synthetic air atmosphere (100 mL $min^{-1}$) under a heating rate of 10 °C $min^{-1}$. Infrared spectroscopy (FT-IR Bomen FTLA 2000) data were obtained in transmission mode using KBr pellets.

The photoluminescence data were obtained in a Fluorolog-3 spectrofluorometer (Horiba FL3-22-iHR320), with double-gratings (1200 g/mm, 330 nm blazed) in the excitation monochromator and double-gratings (1200 g/mm, 500 nm blazed) in the emission monochromator. Anozone-free Xenon lamp of 450 W (Ushio) was used as a radiation source. The excitation spectra were obtained between 200–600 nm and they were corrected in real time according to the lamp intensity and the optical system of the excitation monochromator using a silicon diode as a reference. The emission spectra were carried out between 400–750 nm using the front face mode at 22.5°. All of them were corrected according to the optical system of the emission monochromator and the photomultiplier response (Hamamatsu R928P). The time resolved emission spectra were measured using a phosphorimeter system with a delay of 0.5 ms, in order to get only the emissions from triplet states of the ligands. The emission decay curves were obtained with a pulsed 150 W Xenon lamp using a phosphorimeter. The absolute quantum yields were measured using a Quanta-φ (Horiba F-309) integrating sphere equipped with an optical-fibers bundle (NA=0.22-Horiba-FL-3000/FM4-3000).

## 4. Determination of ground state geometries

For the determination of the complexes' ground state geometries the lanthanide ion was replaced by a $+3e$ point charge [12–14], the RHF wavefunctions were optimized using the Broyden–Fletcher–Goldfarb–Shanno procedure with a convergence criterion of 0.01 kcal $mol^{-1}$ Å$^{-1}$, semi empiricals AM1 or PM3 or PM6 with a convergence criteria of $10^{-6}$ kcal $mol^{-1}$ for the SCF. In Mopac2009 package [15] the following keywords were used: MODEL (AM1, PM3 or PM6), SPARKLE, XYZ, SCFCRT=1D-10, GEO-OK, BFGS, CHARGE= X, PRECISE, GNORM=0.10 and T=1D.

## 5. Results and discussion

As the first characterization the chemical formulae of the complexes were suggested from titration, carbon and hydrogen microanalysis. The results are shown in Table 1.

The amount of water molecules coordinated to the lanthanide ions were checked by thermogravimetric analysis (TGA). The TG curves are shown in the ESI (Fig. S1). The weight loss attributed to loss of water molecules coordinated to lanthanides(III) ions was calculated and determined experimentally from the TG data using the temperature range from 80–200 °C (Table 2).

Once the complexes' stoichiometries were determined the coordination modes of the ligand bza$^-$ were suggested by FT-IR and $\Delta\nu$, where $\Delta\nu = \nu_{as}(COO^-) - \nu_s(COO^-)$ [16,17]. The carboxylate coordination in complexes can be by several modes, such as: monodentate, bidentate bridging and/or bidentate chelate. For