



Positron annihilation studies in binary solid solutions and mechanical mixtures of lanthanide dipivaloylmethanate complexes



F. Fulgêncio^{a,*}, F.C. Oliveira^b, D. Windmüller^a, M.H. Araujo^a, A. Marques-Netto^a, J.C. Machado^{a,1}, W.F. Magalhães^{a,*}

^a Departamento de Química, ICEx, Universidade Federal de Minas Gerais – UFMG, C.P. 702, CEP 31270-901 – Belo Horizonte, MG, Brazil

^b Grupo de Pesquisa em Nanociências e Nanomateriais, Centro Federal de Educação Tecnológica de Minas Gerais (CEFET-MG), Campus Timóteo, Timóteo, MG, Brazil

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To the memory of our colleague José Caetano Machado, passed away on July 27th 2014.

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ABSTRACT

Measurements using positron annihilation lifetime (PALS) and Doppler broadening annihilation radiation lineshape (DBARLS) spectroscopies were performed in several lanthanide dipivaloylmethanate complexes, $\text{Ln}(\text{dpm})_3$ where $\text{Ln} = \text{Sm}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Yb}^{3+}$ and $\text{dpm} = 2,2,6,6\text{-tetramethyl-3,5-pentanedionate}$, and also on their binary solid solutions and mechanical mixtures, biphasic systems, of the general formula $\text{Ln}_{1-x}\text{Eu}_x(\text{dpm})_3$. Expressive positronium formation was observed in all $\text{Ln}(\text{dpm})_3$ complexes, except in $\text{Eu}(\text{dpm})_3$ complex. The results indicate formation of solid solutions in the Sm^{3+} , Gd^{3+} and Tb^{3+} systems, where total inhibition of positronium formation was observed. A Stern–Volmer type equation, $I_3/I_3 = 1 + kx$, was used to fit the data, enabling the calculation of the inhibition constants, k . A mechanical mixture behavior, with linear variation of I_3 between the I_3 values of the pure complexes, was observed in systems containing Ho^{3+} , Er^{3+} and Yb^{3+} complexes, where no effective solid solution formation occurred due to differences between the crystalline structures of these complexes and $\text{Eu}(\text{dpm})_3$. No positronium quenching reactions were observed in the solid solutions. DBARLS results confirmed those of PALS, evidencing that the positron annihilation spectroscopies are useful techniques to characterize the formation of solid solutions. PALS measurements at 80 K were performed in the $\text{Sm}_{1-x}\text{Eu}_x(\text{dpm})_3$ and $\text{Gd}_{1-x}\text{Eu}_x(\text{dpm})_3$ solid solutions. The results indicate that, despite a contraction in the crystalline structures, the solid solution structure remains intact at low temperatures. The temperature dependence of the inhibition constant do not seem to be understood from the positronium formation spur model and might be related to intra and intermolecular energy and charge transfer processes in the solid solutions, which is currently being studied.

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1. Introduction

In past years, numerous investigations have been carried out on different lanthanide complexes with organic ligands due to their photoluminescence properties. Luminescence investigation of Ln^{3+} β -diketonate complexes has increased in the last two decades since these complexes can be used as light conversion molecular devices (LCMD) [1,2] due to the high ultraviolet absorption coefficient of the β -diketonates and an efficient energy transfer from the β -diketonate ligand to the trivalent lanthanide ion (antenna effect) [3,4]. In particular, $\text{Tb}(\text{dpm})_3$ arouses interest due to its strong green luminescence [5] and, although $\text{Eu}(\text{dpm})_3$ present

low luminescence intensity at room temperature, it has received considerable attention in the literature because of its use as an NMR shift reagent [6]. On the other hand, Ho/Yb and Er/Yb systems are being largely studied due to the presence of up-conversion processes [7–12].

Studies of positron annihilation on Ln^{3+} binary solid solutions are particularly interesting since their luminescence properties differ from the simple mixture of the isolated complexes. It has been previously observed that in the $\text{Tb}_{1-x}\text{Eu}_x(\text{dpm})_3$ solid solutions, the presence of the $\text{Eu}(\text{dpm})_3$ complex, which has low energy ligand to metal charge transfer states (LMCTS), quenches the Tb^{3+} luminescence due to an energy transfer from the $\text{Tb}^{3+} \text{ } ^5\text{D}_4$ state to de $\text{Eu}^{3+} \text{ } ^5\text{D}_0$ state, and then to the charge transfer states, as well as inhibits the Ps formation [13]. A $\text{Tb}(\text{dpm})_3$ luminescence quenching by $\text{Eu}(\text{dpm})_3$ was also observed when the two isolated complexes were dissolved in common solvents [14].

* Corresponding authors.

E-mail addresses: fefulgencio@gmail.com (F. Fulgêncio), welmag@ufmg.br (W.F. Magalhães).

¹ Diseased.

However, both luminescence and characterization studies of lanthanide solid solutions have been neglected. In this context, positron annihilation spectroscopies can be used as *in situ* nanoprobes to study Ln^{3+} complexes, their mechanical mixtures and solid solutions, for accessing the microstructure at a nanoscale level.

Positronium (Ps) is the bound state between a positron (e^+) and an electron (e^-). It is formed with two different spin states: *para*-positronium (*p*-Ps, singlet state) and *ortho*-positronium (*o*-Ps, triplet state), with intrinsic lifetimes 0.125 and 142 ns, respectively, in vacuum. In a material medium, the pick-off annihilation of the positron with electrons of the surroundings reduces the long *o*-Ps lifetime to a few nanoseconds.

The interactions between positrons and electrons can supply valuable information about physico-chemical properties of molecular solid systems [15–17]. The positron and Ps chemistry of solid coordination compounds has been studied by our group since the 1980s. These studies have evidenced the importance of the chemical properties of both ligand and central metal ion in Ps formation and its quenching [18–29]. The ligand effect can be seen when a metallic ion is complexed with different ligands, acetylacetonate (acac) and dipivaloylmethanate (dpm) for example, yielding different amounts of Ps [25,26]. Also, complexes with ligands containing highly electronegative groups do not form Ps [23]. The influence of the metallic ion on the Ps formation can be verified on both transition metal and lanthanide complexes. In transition metal complexes, ions like Fe^{3+} , Cr^{3+} and Co^{3+} do not form appreciable amount of Ps and also inhibit Ps formation and/or quench the Ps in liquid and solid solutions, but complexes with Al^{3+} , Ga^{3+} and In^{3+} form considerable amounts of Ps [24].

In lanthanide complexes, Ps formation has been observed in all trivalent ions complexes through the lanthanide series, except in the majority of the Eu^{3+} complexes [25–27]. The absence of Ps formation in most Eu^{3+} complexes can be explained due to the presence of low energy LMCTS [13,28–30]. Actually, Ps formation in Eu^{3+} complexes had not been reported until 2006, when Ps formation was observed in some highly luminescent Eu^{3+} complexes [28].

Luminescence and PALS studies showed that, when no Ps formation is observed, the Eu^{3+} complexes are not luminescent at 298 K, presenting low energy LMCTS. On the other hand, Eu^{3+} complexes that form Ps are luminescent at 298 K, presenting high energy LMCTS. Low energy LMCTS is an efficient path for depopulating the lanthanide excited states, leading to luminescence suppression and quenching and also to the absence of Ps formation [13,28,29]. A mechanism was proposed by our group to explain how LMCTS affects Ps formation [13,29].

In this work, positron spectroscopies studies were performed on lanthanide dipivaloylmethanates, binary solid solutions and mechanical mixtures of the general formula $\text{Ln}_{1-x}\text{Eu}_x(\text{dpm})_3$, where $\text{Ln} = \text{Sm}^{3+}$, Gd^{3+} , Tb^{3+} , Ho^{3+} , Er^{3+} and Yb^{3+} . Among all $\text{Ln}(\text{dpm})_3$ complexes studied, $\text{Eu}(\text{dpm})_3$ was the only one that present a considerably low Ps formation yields. The *o*-Ps intensity (I_3) for the $\text{Eu}(\text{dpm})_3$ complex is very small (less than 4%) while the other $\text{Ln}(\text{dpm})_3$ present I_3 ranging from 37% to 45%. For this reason, we decided to study if $\text{Eu}(\text{dpm})_3$ complex would be an inhibitor of Ps formation in solid solutions.

2. Experimental

The $\text{Ln}(\text{dpm})_3$ ($\text{Ln} = \text{Sm}^{3+}$, Gd^{3+} , Tb^{3+} , Ho^{3+} , Er^{3+} and Yb^{3+}) complexes were synthesized from the Ln^{3+} chloride, which were prepared from their oxides and hydrochloride acid, purchased from Aldrich and were characterized as described in the literature [31–36].

The binary solid solutions were obtained by dissolving appropriate amounts of two complexes (host and guest) in a common

solvent (hexane). The solution was then evaporated in air at room temperature yielding crystals of the solid solutions that were stored in a moisture-free recipient. The physical mixtures were prepared by mechanical grinding in an agate grail.

PALS measurements were performed at 295 and 80 K, using a fast–fast coincidence system (ORTEC), with a time resolution of 230 ps given by ^{60}Co prompt curve. The low temperature measurements were performed using an OXFORD cryostat. The ^{22}Na (Perkin Elmer) positron source, with approximately 740 kBq ($20 \mu\text{Ci}$) activity, was sandwiched between two 7.6 μm thick Kapton foils, and the source correction was approximately 20%. The samples powders sandwiching the positron source are directly irradiated with polineutronics positrons going through the Kapton foils. The lifetime spectra, with minimum of six measurements for each sample, were resolved with four components using Positron-fit-Extended program [37,38], except for $\text{Eu}(\text{dpm})_3$, which was treated with three components due to its low *o*-Ps intensity. Lifetimes, τ_i , and associate intensities, I_i , were obtained, where $i = 1, 2, 3$ and 4 refer, respectively, to *p*-Ps, free positron, *o*-Ps not trapped into free volumes in the bulk material and *o*-Ps trapped in larger free volumes, where the free volumes here considered are any dynamic or static spaces, with low or zero electron density, which may vary from larger molecular interstices, with radius greater than nearly 0.3 nm, to mesopores. The equipment's resolution is 230 ps, making the *p*-Ps parameters (τ_1 and I_1) unreliable. To reduce the scattering of the other parameters, τ_1 was fixed at 120 ps, which is nearly the intrinsic *p*-Ps lifetime value. This procedure does not affect significantly the quality of the fitted spectra, as demonstrated by their reduced chi-squared near unity, and also reduce the correlations among the fitted parameters.

The DBARLS spectroscopy measurements were performed using a high pure Ge detector (ORTEC, model GEM-F5930) with a resolution of 1.23 keV at the 511 keV annihilation gamma energy, as determined by linear interpolation of the full width at half-maximum (FWHM) of the nuclear rays of $^{356.005}$ and $^{383.851}$ keV of ^{133}Ba and $^{569.670}$ keV of ^{207}Bi , simultaneously measured with the annihilation line for calibration purposes (55.7 eV/channel). The DBARLS parameters FWHM were determined by the Annpeak program [39] with ± 0.02 keV of experimental repeatability uncertainty as an average of three or more spectra per sample.

3. Results and discussion

3.1. PALS and DBARLS measurements on $\text{Ln}(\text{dpm})_3$ complexes at 295 K

Table 1 shows that all $\text{Ln}(\text{dpm})_3$ studied present a high Ps formation probability, I_3 (%), except for the $\text{Eu}(\text{dpm})_3$ complex. These results are in accordance with the literature [25].

The treatment of the spectra with 4 components provided a better reduced chi square (χ^2) when compared with 3 component treatments. According to Marques Netto et al. [25], the $\text{Ln}(\text{dpm})_3$ complexes presents *o*-Ps trapped in vacancies, making a four

Table 1

PALS and DBARLS parameters for the $\text{Ln}(\text{dpm})_3$ complexes ($\text{Ln} = \text{Sm}$, Eu , Gd , Tb , Ho , Er and Yb). PALS analysis with 4 components and τ_1 fixed at 0.120 ns, at (295 ± 1) K.

Complex	τ_4 (ns)	τ_3 (ns)	I_4 (%)	I_3 (%)	FWHM (keV)
$\text{Sm}(\text{dpm})_3$	3.7 ± 1.2	1.22 ± 0.04	3.5 ± 1.8	40.6 ± 1.6	2.70 ± 0.02
$\text{Eu}(\text{dpm})_3$	–	2.20 ± 0.55	–	2.4 ± 0.2	3.05 ± 0.02
$\text{Gd}(\text{dpm})_3$	2.8 ± 0.6	1.16 ± 0.10	4.3 ± 1.6	39.8 ± 1.5	2.67 ± 0.02
$\text{Tb}(\text{dpm})_3$	3.7 ± 0.4	1.27 ± 0.07	6.4 ± 1.2	39.6 ± 2.2	2.67 ± 0.02
$\text{Ho}(\text{dpm})_3$	4.2 ± 1	1.36 ± 0.09	4.7 ± 1.6	41.2 ± 1.5	2.64 ± 0.02
$\text{Er}(\text{dpm})_3$	3.4 ± 0.4	1.24 ± 0.06	7.3 ± 1.2	36.8 ± 1.7	2.63 ± 0.02
$\text{Yb}(\text{dpm})_3$	3.0 ± 0.7	1.32 ± 0.03	2.2 ± 0.8	45.4 ± 1.3	2.60 ± 0.02

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