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Spectroscopic studies of lanthanide picrate complexes with *N*,*N*-dimethylacetamide. Structure of the La compound

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Abstract

Emission and excitation spectra were recorded for the complexes Ln(pic)$_3$.3(DMA) (pic=picrate, DMA=*N*,*N*-dimethylacetamide, Ln=La, Eu, Gd, Sm, Lu). The Eu and Sm complexes exhibit f–f characteristic luminescence spectra, while the other present broad emission bands are due to picrate anion luminescence. Both emission and excitation spectra of the Eu compound point to a small participation of the $^5D_1$ state in the emission process. Lifetimes for these luminescences were measured. Their values (in the range of ms) suggest a strong mixing of the singlet and triplet states of the ligands, as well as a fast transfer to the $^5D_0$ and $^4G_{5/2}$ states of Eu and Sm, respectively. For the Sm complex doped with Eu, small variations in the lifetimes were observed. Luminescence quantum yields were also determined. Single-crystal X-ray analysis of the La complex shows a D_{3h} symmetry around the central ion.

Keywords: Lanthanum; *N*,*N*-dimethylacetamide; Picrate

Addition compounds between lanthanide salts and *N*,*N*-dimethylacetamide (DMA) have been studied [1–8]. Lanthanide picrate complexes with DMA, with compositions Ln(pic)$_3$.3(DMA) were synthesized. According to the X-ray powder patterns, three types of diffractograms were obtained: La–Pr; Nd–Yb, Y; and Lu. The structure of the Sm compound, belonging to the second isomorphous series, was determined [9]. The emission spectrum of the Eu compound was observed as a function of temperature, evidencing a D_{3h} symmetry around the Eu^{3+} ion and showing a phase transition at 172 K [10]. In this paper, a spectroscopic study of the Eu and Sm compounds, which present lanthanide f–f luminescence, as well as some other representative compounds (La, Gd, Lu), which show picrate luminescence, are reported. In an attempt to study the first isostructural series of these compounds, X-ray analysis of La(pic)$_3$.3(DMA) was carried out and its structure is described.

1. Experimental

Emission and excitation spectra were recorded on a Hitachi MPF-4 spectrofluorimeter with modifications [11]. Emission lifetimes were measured on an Edinburgh FL 900 spectrofluorimeter equipped with a pulsed hydrogen lamp (40 kHz, 1 ns FWHM). This very short excitation time precluded the use of deconvolution procedures for calculating the emission lifetimes. Emission quantum yields were determined using the method developed by Wrighton [12] on a Hitachi MPF-4 spectrofluorimeter.

Single-crystal X-ray diffraction analysis of the La compound was carried out on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo Kα radiation. Most of the calculations were performed on a VAX computer with SHELX 76 [13], SHELXS 86 [14] and ORTEP [15] programs.

The synthesis and characterization of the compounds have already been described in a previous paper [9]. Doped samarium compounds were synthesized with 1 and 2 wt. % hydrated europium picrate added to the Sm salt prior to the complex synthesis.

2. Results and discussion

In a previous paper [10] the characteristic f–f emission spectrum of the complex Eu(pic)$_3$.3(DMA) was presented, pointing out to a D_{3h} symmetry around the Eu^{3+} ion. Fig.

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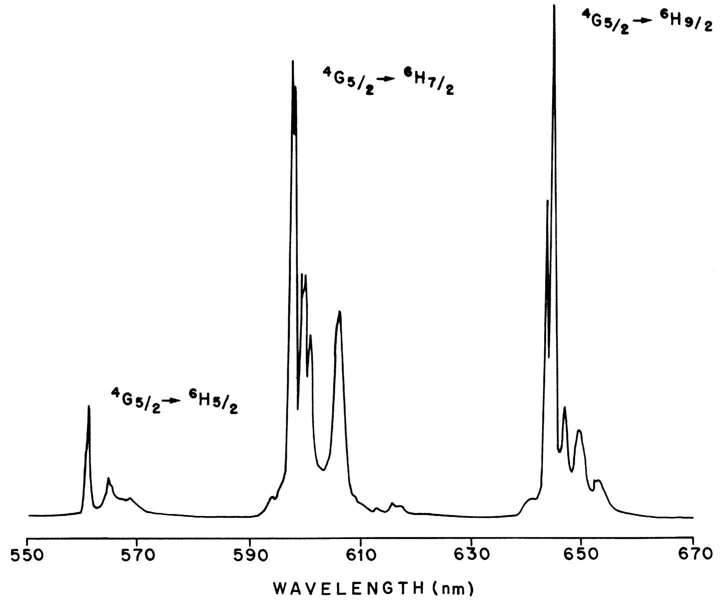

Fig. 1. Emission spectrum of the Sm compound.

1 presents the emission spectrum of the Sm compound, where the transitions $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ appear.

It can be observed that the peaks in the $^4G_{5/2}\rightarrow{}^6H_{7/2}$ transition are split into two components, in contrast with the europium doped compound, where these peaks are single. This splitting is probably due to a zero-phonon resonance effect, which accounts for an abnormal number of lines in several lanthanide compounds' absorption and emission spectra [16].

For the other lanthanides studied, the complexes are not luminescent at room temperature and present broad band emissions at 77 K, due to the picrate anions. For the Gd compound, this emission has a maximum at 550 nm (18 182 cm^{-1}); the La compound presents a plateau-like maximum from 510 to 540 nm (19 608 to 18 519 cm^{-1}); the Lu complex presents a maximum at 500 nm (20 000 cm^{-1}).

The excitation spectra of the La, Gd and Lu compounds at 77 K present broad absorption bands with maxima at ca. 390 nm (25 641 cm^{-1}).

The excitation spectrum of the Eu compound (also at 77 K), in addition to this broad band, due to absorption by the picrate anions, presents two weak bands due to the transitions $^5D_1\leftarrow{}^7F_0$ at 526.5 nm (19 011 cm^{-1}) and $^5D_1\leftarrow{}^7F_1$, at 535.5 nm (18 692 cm^{-1}), evidencing the participation of the $^5D_1$ level of the Eu^{3+} ion in the energy transfer process.

At 77 K, the $^5D_1\leftarrow{}^7F_0$ absorption is stronger than $^5D_1\leftarrow{}^7F_1$ while at 293 K these intensities are reversed, showing an increase of the $^7F_0$ population at low temperature (as expected). These transitions, however, are weak in comparison to the picrate absorption bands.

We were also able to detect, in the Eu compound, a very weak $^5D_1\leftarrow{}^7F_1$ emission band, split into two components at 534.0 and 534.8 nm (18 726 and 18 698 cm^{-1}). The weakness of this transition as compared to the emissions of the $^5D_0$ level shows that the role of the $^5D_1$ level in the overall energy transfer process is a minor one. It is known that when the $^5D_1$ level is populated, it transfers energy very efficiently to the $^5D_0$ level, causing strong emission from the latter [17]. Anyway, from the position of the

Table 1
Luminescence lifetimes and quantum yields for Eu($^5D_0\rightarrow{}^7F_2$) and Sm ($^4G_{5/2}\rightarrow{}^6H_{9/2}$) compounds

Compound	$^5D_0\rightarrow{}^7F_2$(1)		$^4G_{5/2}\rightarrow{}^6H_{9/2}$ (2)		$\phi_{293\ K}$
	$\tau_{77\ K}$ (ms)	$\tau_{293\ K}$ (ms)	$\tau_{77\ K}$ (ms)	$\tau_{293\ K}$ (ms)	
$Eu(pic)_3.3DMA$	2.2	1.3	–	–	0.03 (1)
$Eu(pic)_3.11H_2O$	3.4	3.8	–	–	–
$Sm(pic)_3.3DMA$ (1% Eu)	2.4	3.1	2.8	3.5	0.0004 (2)
$Sm(pic)_3.3DMA$ (2% Eu)	2.5	3.1	2.9	3.5	0.0002 (2)
$Sm(pic)_3.3DMA$	–	–	3.8	3.5	0.0002 (2)

picrate excited state (around 19 200 cm^{-1}), both $^5D_0$ and $^5D_1$ levels can be efficiently populated. This energy does not present significant variation for the different lanthanide central ions, as observed in the emission spectra.

In Table 1 the luminescence lifetimes and quantum yields of the emissions $^5D_0 \rightarrow {}^7F_2$ (Eu) and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (Sm) compound (this last neat and Eu-doped) are shown; Table 2 presents the picrate emission lifetimes for the La, Gd and Lu compounds.

All emission curves are single exponentials, suggesting fast energy transfer from the picrates to the central ions. The picrate emission lifetimes order of magnitude (ms) point out clearly to a significative mixing of singlet and triplet emitting states. Since these states are already mixed, this accounts for the non occurrence of a paramagnetic ion effect (Gd^{3+}) on the lifetime values.

The $^5D_0 \rightarrow {}^7F_2$ emission of Eu(pic)$_3$.3(DMA) is faster than Eu(pic)$_3$.11H$_2$O. This is probably due to the presence of large ligand molecules coordinated to the central ion, opening possibly internal conversion non-radiative channels for energy relaxation. It can also be observed that at 77 K the emission lifetime of Eu(pic)$_3$.3(DMA) is longer than at room temperature, pointing out to non-radiative relaxation processes that are more relevant at higher temperatures.

With relation to the samarium(III) compounds, the emission lifetimes of the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition did not show significant variations when the compound was doped with europium, except at 77 K. In the doped samples, these lifetimes are shorter and constant with relation to Eu concentration. On the other hand, in these doped compounds the Eu emission lifetimes are longer, suggesting that there is some energy transfer from the Sm ions, as opposed to room temperature, where no apparent energy transfer seems to occur.

The emission quantum yields presented in Table 1 show that non-radiative relaxation processes play a very significant role in those compounds. These quenching processes seem to be more significative in the case of the Sm^{3+} compounds and may be related to the existence, in this ion, of a $^7F_{9/2}$ level, that opens a cross-relaxation non-radiative channel to the $^4G_{5/2}$ level.

The X-ray structural analysis carried out in the La compound showed that the coordination polyhedron around the metallic ion is a tricapped trigonal prism (Fig. 2) with the oxygens O11, O31, O21, O4, O6 and O5 forming the trigonal prism and the oxygens O121, O211 and O311 forming the caps. This polyhedron is identical (within experimental error) to the observed for the Sm compound [9]. The symmetry is D_{3h}, in agreement with the one suggested by emission spectroscopy for the Eu compound [10] and the coordination number is 9. Tables 3

Table 2
Emission lifetimes at 77 K, picrate luminescence

Compound	$\tau_{77\ \mathrm{K}}$ (ms)
La(pic)$_3$.3DMA	3.3
Gd(pic)$_3$.3DMA	3.7
Lu(pic)$_3$.3DMA	3.9
La(pic)$_3$.11H$_2$O[a]	3.4
Gd(pic)$_3$.11H$_2$O[a]	3.5
Lu(pic)$_3$.8H$_2$O[a]	3.0

[a] Ref. [18].

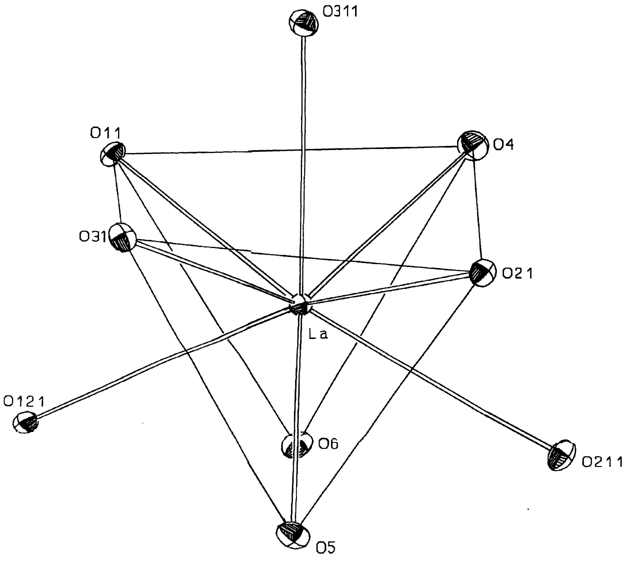

Fig. 2. Coordination polyhedron of La(pic)$_3$.3DMA.

Table 3
Summary of data collection and crystal parameter

Formula	C$_{30}$H$_{33}$LaN$_{12}$O$_{24}$
Molecular weight	1084.57
Crystal system	monoclinic
Space group	$P2_1/c$
Cell constants	
a (Å)	15.065 (3)
b (Å)	15.255 (2)
c (Å)	19.174 (5)
β (°)	99.15 (2)
Volume V (Å^3)	4350 (3)
Molecules per cell (Z)	4
Density (calcd.) D_c (g cm^{-3})	1.656
Radiation λ (Mo Kα) (Å)	0.71073
Crystal size (mm)	0.50×0.50×0.40
T (K)	293
Linear absorption coeff. μ (mm^{-1})	1.08
Scan technique	$\omega/2\theta$
θ range for data collection (°)	0–27
Number of reflections measured	7722
Number of unique reflections	7502
Number of reflections above 3σ (I)	3740
Minimized function	$\Sigma\ w(\lvert F_0\rvert - \lvert F_c\rvert)^2$
Weighting scheme	$[\sigma^2(F_0)+0.0003\lvert F_0\rvert^2)^{-1}$
$R=\Sigma\ (\lvert F_0\rvert - \lvert F_c\rvert)/\Sigma\ \lvert F_0\rvert$	0.0494
$w_R=[\Sigma\ w(\lvert F_0\rvert - \lvert F_c\rvert)^2/\Sigma\ w\lvert F_0\rvert^2]^{1/2}$	0.0522
h_{min}, h_{max}; k_{min}, k_{max}; I_{min}, I_{max}	−19, 18; 0, 19; 0, 24
Max, min residuals ρ (e Å^{-3})	0.70, −0.53

Unit cell parameters by least-squares refinement of the setting angles of 25 reflections with 8.82<θ<15.46°.

Table 4
Distances (Å) and angles (°) around the La ion

		La	–	O (11)	2.427 (6)
		La	–	O (121)	2.700 (7)
		La	–	O (21)	2.481 (6)
		La	–	O (211)	2.732 (6)
		La	–	O (31)	2.430 (7)
		La	–	O (311)	2.740 (7)
		La	–	O (4)	2.413 (7)
		La	–	O (5)	2.447 (7)
		La	–	O (6)	2.416 (6)
O (11)	–	La	–	O (121)	63.2 (2)
O (11)	–	La	–	O (21)	139.0 (2)
O (11)	–	La	–	O (211)	146.3 (2)
O (11)	–	La	–	O (31)	76.6 (2)
O (11)	–	La	–	O (311)	71.7 (2)
O (11)	–	La	–	O (4)	84.1 (2)
O (11)	–	La	–	O (5)	133.3 (2)
O (11)	–	La	–	O (6)	82.3 (2)
O (121)	–	La	–	O (21)	137.1 (2)
O (121)	–	La	–	O (211)	122.6 (2)
O (121)	–	La	–	O (31)	66.9 (2)
O (121)	–	La	–	O (311)	117.1 (2)
O (121)	–	La	–	O (4)	140.2 (2)
O (121)	–	La	–	O (5)	70.8 (2)
O (121)	–	La	–	O (6)	69.9 (2)
O (21)	–	La	–	O (211)	63.0 (2)
O (21)	–	La	–	O (31)	82.5 (2)
O (21)	–	La	–	O (311)	67.3 (2)
O (2l)	–	La	–	O (4)	82.5 (2)
O (21)	–	La	–	O (5)	74.5 (2)
O (21)	–	La	–	O (6)	134.3 (2)
O (211)	–	La	–	O (31)	137.1 (2)
O (211)	–	La	–	O (311)	119.4 (2)
O (211)	–	La	–	O (4)	73.2 (2)
O (211)	–	La	–	O (5)	68.2 (2)
O (211)	–	La	–	O (6)	71.3 (2)
O (31)	–	La	–	O (311)	61.6 (2)
O (31)	–	La	–	O (4)	129.3 (2)
O (31)	–	La	–	O (5)	79.0 (2)
O (31)	–	La	–	O (6)	136.7 (2)
O (311)	–	La	–	O (4)	67.8 (2)
O (311)	–	La	–	O (5)	127.3 (2)
O (311)	–	La	–	O (6)	143.3 (2)
O (4)	–	La	–	O (5)	140.9 (2)
O (4)	–	La	–	O (6)	84.5 (2)
O (5)	–	La	–	O (6)	89.3 (2)

and 4 present crystal parameters and distances and angles around the La^{3+} ion. The unit cell has 4 molecules of the compound.

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