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Preparation, characterization and spectroscopy of the europium diphenylphosphinate complex

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Abstract

The purpose of this work is to study the preparation and spectroscopic behavior of the europium diphenylphosphinate complex – $Eu(DPP)_3$. Elemental and thermogravimetric analysis, powder X-ray diffractometry, and infrared spectroscopy were applied to characterize the formula of the final product and the sixfold coordination of the Eu^{3+} ion. Excitation and emission spectra have been recorded at liquid nitrogen and room temperatures. The $^5D_0 \rightarrow {}^7F_2$ transition intensity decreases when T decreases in comparison to the $^5D_0 \rightarrow {}^7F_1$ transition intensity. Molecular mechanic calculations were developed in order to obtain the spatial coordinates of the Eu^{3+} and ligand ions. The simple overlap model was used to calculate the total splitting of the $^5D_0 \rightarrow {}^7F_1$ transition, $^5D_0 \rightarrow {}^7F_0/{}^5D_0 \rightarrow {}^7F_2$ intensity ratio and the intensity parameters, Ω_λ ($\lambda=2$ and 4). Good agreements between theoretical predictions and experimental results have been obtained with $g=2/3$ as the effective charge and $\alpha=0.8\times10^{-24}$ cm^3 as the isotropic polarizability of the oxygen. © 1998 Elsevier Science S.A.

Keywords: Europium diphenylphosphinate complex; Luminescence; UV–Vis–IR spectroscopy; Intensity parameters

1. Introduction

The luminescence of europium coordination compounds is of great interest in relation to their peculiar characteristics, e.g. high emission efficiency, long lifetime and line-like emission bands in the visible region [1]. However, when organic molecules are used as ligands, the exploration of these features is normally hindered by the high hygroscopicity and consequently, kinetic lability of the system [2]. During the last few years the development of new complexes using encapsulating ligands has allowed us to obtain kinetically inert complexes, in which luminescence properties were optimized [3].

The diphenylphosphinic acid reacts promptly with lanthanides resulting in insoluble, non-hygroscopic, thermodynamically stable and kinetically inert complexes [4]. Additionally, it exhibits a large absorption band in the UV region due to phenyl groups [5], which indicates that such a ligand can be a good candidate in producing the antenna effect.

The aim of this paper is to describe the preparation, characterization and luminescence spectroscopy of the europium diphenylphosphinate-$Eu(DPP)_3$-complex, as a possible light converting molecular device (LCMD). Molecular mechanics simulation was used to obtain the spatial positions of the Eu^{3+} and the ligand ions [6,7], and the simple overlap model (SOM) [8] was used to discuss the $^5D_0 \rightarrow {}^7F_1$ transition splitting (ΔE_{0-1}), the $^5D_0 \rightarrow {}^7F_0/{}^5D_0 \rightarrow {}^7F_2$ (I_{0-0}/I_{0-2}) intensity ratio and intensity parameters, Ω_λ ($\lambda=2$ and 4), of this system.

2. Experimental

Europium diphenylphosphinate was prepared by mixing 0.2 M europium chloride and 0.1 M diphenylphosphinic acid methanolic solutions (molar ratio 1:4) at 40°C. The $EuCl_3$ solution was prepared by dissolving Eu_2O_3 in hydrochloric acid. Water was replaced by methanol through successive evaporations and the solution was dehydrated using a few drops of 2,2-dimethoxypropane. The final concentration of Eu^{3+} was 0.2 M and the acid concentration was approximately 0.1 M.

In order to analyze phosphorus and europium, the sample was dissolved in nitric acid and the determination was made by inductive coupling plasma in a Spectra spectrometer. Carbon and hydrogen were determined by an elemental analyzer Perkin Elmer 2400.

The X-ray powder diffraction pattern was obtained in a

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Siemens D5000 diffractometer by using Cu Kα radiation. Differential thermal analysis (DTA) and thermogravimetric (TG) curves were obtained in a TA Instruments SDT 2960 thermoanalyser. The sample was decomposed in dynamic atmospheric air at a heating rate of 20 °C min^{-1}. The IR spectra were obtained by using a Nicolet Impact 400 spectrometer and samples as KBr pellets, at room temperature. Excitation and emission spectroscopy of polycrystalline samples were performed at liquid nitrogen and room temperatures by using a spectrofluorometer Spex 212L.

3. Theoretical background

The $^5D_0 \rightarrow {}^7F_1$ transition splitting and the I_{0-0}/I_{0-2} ratio are treated through the SOM as described in the literature [8–11]. The theoretical expression of the intensity parameters Ω_λ (λ=2, 4 and 6) is [12],

$$\Omega_\lambda = (2\lambda + 1)\sum_{t,p} \frac{|B_{\lambda tp}|^2}{(2t+1)} \tag{1}$$

in which

$$\begin{aligned} B_{\lambda tp} = {} & \frac{2}{\Delta E}\langle r^{t+1}\rangle \theta(t,\lambda)\gamma_p^t \\ & - \rho(2\beta)^{\lambda+1}\left[\frac{(\lambda+1)(2\lambda+1)}{2\lambda+1}\right]^{1/2}\langle r^\lambda\rangle \\ & \times \langle f\|C^{(\lambda)}\|f\rangle \Gamma_p^t \delta_{t,\lambda+1} \end{aligned} \tag{2}$$

with λ=2,4 and 6, t=1, 3, 5 and 7, $-t \leq p \leq t$, depending on symmetry restrictions. The radial integrals $\langle r^\lambda\rangle$ (λ=2, 4 and 6) are taken from Freeman-Desclaux (FD) [13] and $\langle r^8\rangle$ is extrapolated via $\langle r^k\rangle = 0.884e^{0.02425k^{2.5454}}$, because this function reproduces the FD values within an average relative deviation less then 6%.

The forced electric dipole mechanism is in the first term of Eq. (2). In this contribution, both ΔE and $\theta(t, \lambda)$ are given in Ref. [14], and the SOM is applied to develop γ_p^t, the odd part of the ligand field parameter [11,12].

The dynamic coupling (DC) contribution is in the second term of Eq. (2). We call attention to the SOM factor, $\rho(2\beta)^{\lambda+1}$, that has been recently introduced [15,16], replacing both the Steinheimer shielding correction [17] and Karayianis-Morrison radial expansion factor [18].

Molecular mechanics calculation was performed by using the HyperMM+$^{\text{TM}}$ program through a modified MM2 force field (named MM+) [6,7,19,20], and the Polack-Ribiere minimum energy search procedure [21].

4. Results and discussion

Analyses. Found/calculated for $C_{36}H_{11}O_6P_3Eu$–Eu(DPP)$_3$,(%): C, 53.35/53.81; H, 3.72/3.76; P, 13.2/11.6; Eu, 20.3/18.9.

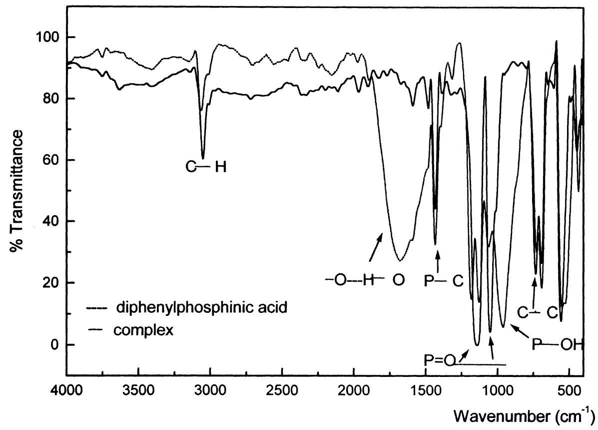

Fig. 1. IR spectra of the DPP Acid (dotted line) and Eu(DPP)$_3$ (full line).

In Fig. 1 the proposed assignments to the diphenylphosphinic acid absorption peaks [22,23] are shown. Among the observed features in the spectra of free ligand and complex we considered as coordination effects are: (i) vanishing of the bands relative to O–H and P–O(H) bonds, (ii) shifting of band position relative to another stretching mode P–O(H) (1065 to 1054 cm^{-1}), (iii) overlapping and position shift of two bands assigned to P=O (1180 to 1160 cm^{-1}).

The interplanar distances (Table 1) indicate that the compound obtained has the same structure as the one obtained by Dustan and Vicentini [4].

TG and DTA curves (Fig. 2) indicate the absence of water in the coordination site, in agreement with the IR spectral analysis data. The compound is thermostable up to about 400°C.

In the excitation spectra (Fig. 3) the strong band at 273

Table 1
X-ray data

d(A)	I/I_0	d(A)	I/I_0	d(A)	I/I_0	d(A)	I/I_0
12.01	100.0	4.31	44.1	3.24	18.2	2.85	23.0
6.93	23.8	3.85	30.2	3.13	25.9	2.62	15.8
4.54	46.8	3.51	34.5	3.03	25.1	2.58	17.1

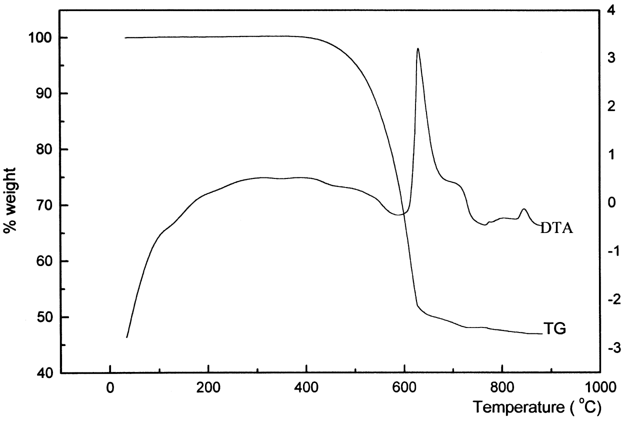

Fig. 2. TG and DTA curves.

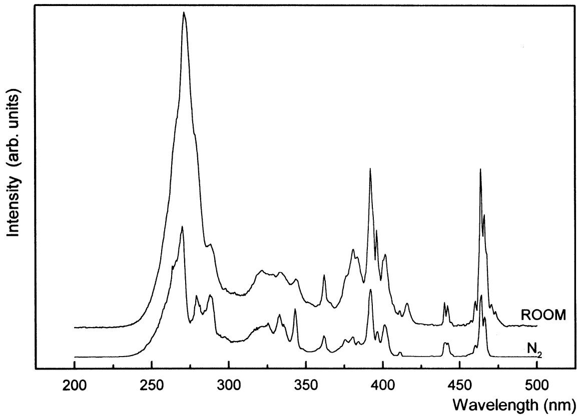

Fig. 3. Excitation spectra at liquid nitrogen and room temperatures (monitored at 593 nm).

nm was assigned as phenyl group absorption [5]. The set of sharp peaks from 300 nm are excited levels of the Eu^{3+} ion, except the one at 440 nm, which is assigned as the vibronic component (1160 cm^{-1}) due to P=O stretching associated with the $^7F_0 \rightarrow {}^5D_2$ transition. The higher intensity of Eu^{3+} band corresponding to excitation through the phenyl group shows that the energy transfer is operating (the antenna effect). In the emission spectra (Fig. 4) it may be observed that the Eu^{3+} ion $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$ transitions and that the I_{0-2}/I_{0-1} ratio decreases when the temperature decreases. The experimental values of the ΔE_{0-1} transition splitting, I_{0-0}/I_{0-2} ratio and intensity parameters Ω_2 and Ω_4 were then obtained.

In Table 2 the ligand ion coordinates obtained after the fitting procedure are given. The Eu^{3+} ion is at the origin of the reference frame.

The effective charge and isotropic polarizability for oxygen ions are 2/3 and 0.8×10^{-24} cm^3 respectively. This charge value may be understood by considering two electrons shared among the P–O and Eu–O bonds and the $O{=}P{-}O^-$ resonance. The isotropic polarizability is in the range of reasonable values [24].

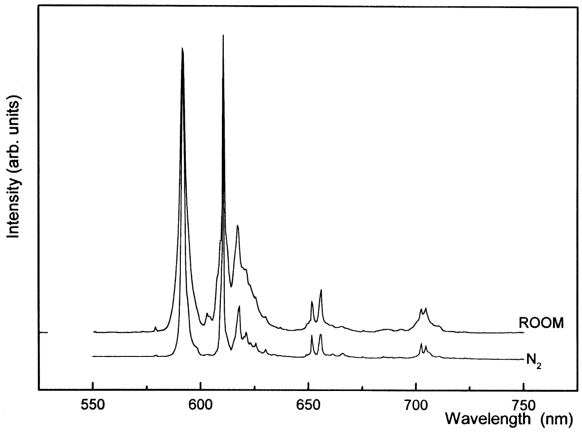

Fig. 4. Emission spectra at liquid nitrogen and room temperatures (excited at 273 nm).

Table 2
Spherical coordinates of the oxygen ions in the reference frame centered to the Eu^{3+} ion

R (Å)	θ (°)	ϕ (°)
2.5149	81.29	197.34
2.5151	57.10	315.54
2.5159	157.02	281.52
2.5160	109.52	40.10
2.5159	92.25	94.07
2.5155	53.78	145.85

Table 3
Experimental and theoretical ΔE_{0-1}(cm^{-1}), I_{0-0}/I_{0-2} and ratio intensity parameters (in units of 10^{-20} cm^2)

	Exp.	SOM
ΔE_{0-1}	170	149
I_{0-0}/I_{0-2}	3.7×10^{-3}	4.8×10^{-3}
Ω_2	1.28	1.13
Ω_4	0.075	0.088

In Table 3 the experimental results and theoretical predictions of ΔE_{0-1}, I_{0-0}/I_{0-2} and Ω_λ ($\lambda = 2$ and 4) are given.

5. Conclusion

Through the results obtained from different techniques it was possible to propose the formula of the final product as $Eu(DPP)_3$ and the six-fold coordination of the Eu^{3+} ion. The high efficiency of ligand-to-metal energy transfer mechanism observed in the excitation spectra and the thermal stability suggests the $Eu(DPP)_3$ complex as an interesting compound for LCMD application. A possible structure for the $Eu(DPP)_3$ complex was obtained by molecular mechanics simulation. The simple overlap model was then applied to calculate ΔE_{0-1}, I_{0-0}/I_{0-2} and $\Omega_{2,4}$ spectroscopic quantities and the theoretical predictions were in good agreement in comparison to experimental results. As the SOM has been applied to several systems with good predictions, this indicates that the molecular mechanics simulation reproduced the $Eu(DPP)_3$ complex structure.

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