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On the use of theoretical tools in the study of photophysical properties of the new $Eu(fod)_3$ complex with diphenbipy

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Abstract

The synthesis, characterization, spectroscopic, and fluorescence properties of $Eu(fod)_3 \cdot 2H_2O$ and $Eu(fod)_3 \cdot$ diphenbipy (fod = 6,6,7,7,8,8, 8-heptafluoro-2,2-dimethyl-3,5-octadionate, diphenbipy = 4,4′-diphenyl-2,2′-dipyridyl) are described. New spectroscopic studies of these complexes are presented based on theoretical and experimental analyses of the intensity parameters, Ω_2 and Ω_4, and on the maximum splitting of the $^7F_1$. The geometries calculated by Sparkle/AM1 model was used to calculate the $^7F_1$ manifold splitting (ΔE_{0-1}) and the intensity parameters Ω_2, Ω_4 based on the Simple Overlap Model (SOM). The reconciliation among the data from the theoretical $^7F_1$ manifold splitting, and the intensity parameter certifies the reliability of the models used in the theoretical calculations.
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1. Introduction

High luminescent europium (III) complexes with β-diketones and *o*-phenantroline-*N*-oxide ligands have been synthesized and suggested as promising light conversion molecular devices (LCMD) [1]. For the obtainment of an efficient LCMD it is necessary the optimization of the luminescence process [2] that consists in an initial stage, where the light in the UV region is absorbed by the ligands (antenna effect [3]). After this the energy is transferred, generally from the triplet state of the ligand to the excited state of the lanthanide ion, and in the last stage the excited lanthanide ion decays to the ground state via photon emission in the visible region.

Some recent papers, where theoretical tools were used for the design of new europium complexes with a high quantum yield have been published by our group [4,5]. The development of a new Sparkle/AM1 model [6] which demands a lower computational effort makes possible the theoretical project of lanthanide complexes with high luminescence since it permits to treat a great number of lanthanide complexes in a relatively short period of time. Additionally, this new version is capable of calculating the coordination polyhedron of Pr^{+3} [7], Eu^{+3}, Gd^{+3}, Tb^{+3} [6], Dy^{+3} [8], Tm^{+3} [9] and Yb^{+3} [10] ions complexes with the same accuracies of the ab initio/effective core potential calculations [6].

The Sparkle/AM1 model, as tool for design of new LCMDs, has been applied in an intense way to calculate the ground state geometry of the lanthanide complexes [11–13]. These geometries are used to predict some spectroscopic properties, such as singlet and triplet energies, and electronic spectra of lanthanide complexes [11–13]. With these quantities it is possible to build rate equations that involve the energy transfer mechanism to calculate the quantum yields [4] for these complexes.

In this Letter, we report the synthesis, characterization and spectroscopic properties of the $Eu(fod)_3 \cdot$ diphenbipy (fod = 6,6,7,7,8,8, 8-heptafluoro-2,2-dimethyl-3,5-octadionate, diphenbipy = 4,4′-diphenyl-2,2′-dipyridyl). Theoreti-

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cal tools such as Sparkle/AM1 model (used for predicting the ground state geometries) and Simple Overlap Model (SOM) [14] (used to calculate the $^7F_1$ manifold splitting (ΔE_{0-1}) and the intensity parameters Ω_2, Ω_4) have been used to explain the influence of the ligand field in the studied complexes.

2. Experimental details

2.1. Sample

The $Eu(fod)_3 \cdot 2H_2O$ complex and diphenbipy were purchased from Aldrich and used as received. The complex $Eu(fod)_3 \cdot$ diphenbipy was prepared adding 40 ml of a warm ethanolic solution of diphenbipy (1 mmol) to an ethanolic solution containing 1 mmol of $Eu(fod)_3 \cdot 2H_2O$. The pure products were obtained by repeated crystallization from hexane and dried over P_2O_5 under reduced pressure (less than 1 mmHg). The purity of the compounds was achieved by CHN elemental analysis.

2.2. Measurements

The elemental analysis was measured by means of a CHNS–O analyzer Flash 1112 Series EA Thermo Finnigam. The infrared spectra were recorded from 4000 to 400 cm^{-1} using a spectrophotometer model BRUKER IFS 66 with conventional KBr technique. The absorption spectra were recorded on a Perkin–Elmer UV–Visible spectrophotometer Lambda 6 model 2688–002. The luminescence spectra at room temperature and 77 K were obtained in an ISS PC1™ Spectrofluorometer. The excitation device is equipped with a 300 W xenon lamp and a holographic grating. The emission is collected in a 25 cm monochromator with resolution of 0.1 nm equipped with a photomultiplier. The excitation and emission slit width were 0.5 mm, both monochromators having 1200 grooves/mm.

3. Theoretical details

3.1. Geometry optimization and calculation of the transition energies

The ground state geometry of the $Eu(fod)_3 \cdot 2\,H_2O$ and $Eu(fod)_3 \cdot$ diphenbipy complexes were calculated with the Sparkle/AM1 model [6], implemented in the MOPAC93r2 package [15]. The MOPAC keywords used were: PRECISE, GNORM = 0.25, SCFCRT = 1.D-10 (in order to increase the SCF convergence criterion) and XYZ (the geometry optimizations were performed in Cartesian coordinates).

For $Eu(fod)_3 \cdot 2H_2O$ and $Eu(fod)_3 \cdot$ diphenbipy complexes we have calculated their singlet and triplet excited states using configuration interaction single (CIS) based on the intermediate neglect of the differential overlap/spectroscopic (INDO/S) technique [16,17] implemented in ZINDO package [18]. We have used a point charge of +3e to represent the trivalent europium ion.

3.2. Intensity parameters

From the emission spectrum, we have determined the value of the experimental $^7F_1$ manifold splitting as well as the experimental intensity parameters Ω_2 and Ω_4 by using the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively, and by expressing the emission intensity $I = \hbar\omega A_{rad} N$ in terms of the areas under the emission curve. Here, $\hbar\omega$ is the transition energy, A_{rad} is the corresponding coefficient of spontaneous emission and N is the population of the emitting level ($^5D_0$). The magnetic dipole $^5D_0 \rightarrow {}^7F_1$ allowed transition was taken as reference. The A_{rad} is given by

$$A_{rad} = \frac{4e^2\omega^3}{3\hbar c^3}\chi \sum_{\lambda} \Omega_{\lambda} \langle {}^7F_J \| U^{(\lambda)} \| {}^5D_0 \rangle^2. \qquad (1)$$

The appropriate reduced matrix elements of Eq. (1) were taken from [19], and an average index of refraction of 1.5 was used in the Lorentz local field correction, χ. The procedure for the calculation of the theoretical $^7F_1$ manifold splitting intensity parameters, Ω_λ, is described in [20].

4. Results and discussion

The analytical data are in accordance with the proposed formulae of $Eu(fod)_3 \cdot$ diphenbipy, the UV–Vis absorption spectrum has shown three bands in 207, 251 and 288 nm (Table 1). The free diphenbipy shows two bands in 208 and 250 nm. The inexistence of the band in 250 nm (characteristic of the diphenbipy ligand) in the spectrum of the $Eu(fod)_3 \cdot 2H_2O$ complex and the presence of this band in the spectrum of $Eu(fod)_3 \cdot$ diphenbipy, is indicative that the water molecules are substituted by diphenbipy ligand in the first sphere of coordination of the Eu^{+3} ion.

The IR data show that the band due to the νCN is shifted to lower frequencies (about 1343.40 cm^{-1}) as compared to the free ligand (1584.12 cm^{-1}) band due to the coordination of this ligand by means the CN group of diphenbipy. The spectrum also shows that there is no coordination of water molecules in this complex because in our observation the water molecules is lost upon heating at 90 °C in vacuum over P_2O_5.

The luminescence spectra of the $Eu(fod)_3 \cdot 2H_2O$ and $Eu(fod)_3 \cdot$ diphenbipy complexes in the solid state are

Table 1
Photophysical data for $Eu(fod)_3 \cdot 2H_2O$ and $Eu(fod)_3 \cdot$ diphenbipy complexes in the solid state[a] and solution[b]

Complex	Absorption[b]	Luminescence[a]	
	λ_{max} (nm)	λ_{emis} (nm)	λ_{exc} (nm)
$Eu(fod)_3 \cdot 2H_2O$	291	611	340
$Eu(fod)_3 \cdot$ diphenbipy	288	612	340

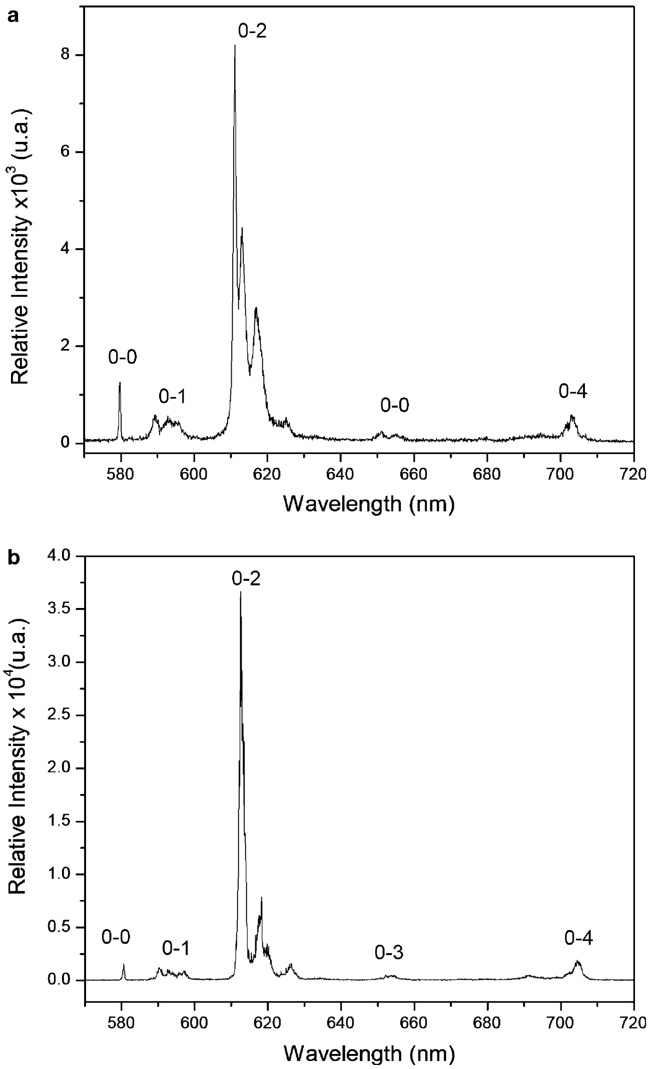

Fig. 1. Emission spectra of: (a) $Eu(fod)_3 \cdot 2H_2O$ and (b) $Eu(fod)_3 \cdot$ diphenbipy complexes in the solid state, at 77 K.

shown in Fig. 1a and b, respectively. The presence of the $^5D_0 \rightarrow {}^7F_0$ transition can be used as a good diagnostic of the crystallinity and purity of the compounds of [21]. Since the band is not splitted by the ligand field effect, any splitting observed is necessarily due to a multiplicity of Eu^{+3} sites. However, a single symmetrical peak is observed in both complexes, which strongly indicates that only one Eu^{+3} site is present in both samples. The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is 11.98 to the complex $Eu(fod)_3 \cdot$ diphenbipy complex, which is higher than that of the complex with water (7.96). These data indicate that the intensity of the $^5D_0 \rightarrow {}^7F_2$ is markedly enhanced by complexing with diphenbipy (Fig. 1b). The complex $Eu(fod)_3 \cdot$ diphenbipy shows a very lower symmetry for the Eu^{+3} ion than that for the $Eu(fod)_3 \cdot 2H_2O$, because the transitions $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_0$ have considerable intensities and the $^7F_1$ and $^7F_2$ manifolds are clearly totally split. The substitution of water molecules by diphenbipy ligand in the $Eu(fod)_3 \cdot 2H_2O$ complex increases the luminescence intensities because it is well known that fluorescence from the $^5D_0$ level of the Eu^{+3} ion is strongly quenched by coupling with the OH vibration [22].

As we can observe in Fig. 2, the coordination polyhedron of the $Eu(fod)_3 \cdot 2H_2O$ complex is formed by six oxygens from the β-diketones ligands and two oxygens from water molecules. For the $Eu(fod)_3 \cdot$ diphenbipy complex the coordination polyhedron is composed by six oxygens from the β-diketones ligands and two nitrogens from the diphenbipy ligand. Tables 2 and 3 show the Sparkle/AM1 spherical coordinates of the $Eu(fod)_3 \cdot 2H_2O$ and $Eu(fod)_3 \cdot$ diphenbipy, respectively.

The optimized geometry obtained from the Sparkle/AM1 model is shown in Fig. 2.

The experimental and theoretical values of the $\Delta E_{0\text{–}1}$ and Ω_λ ($\lambda = 2,4$) are shown in Table 4. The $\Delta E_{0\text{–}1}$ calculation is used in order to obtain the value of the charge factor g, which enters into the Ω_λ expression, because the $\Delta E_{0\text{–}1}$

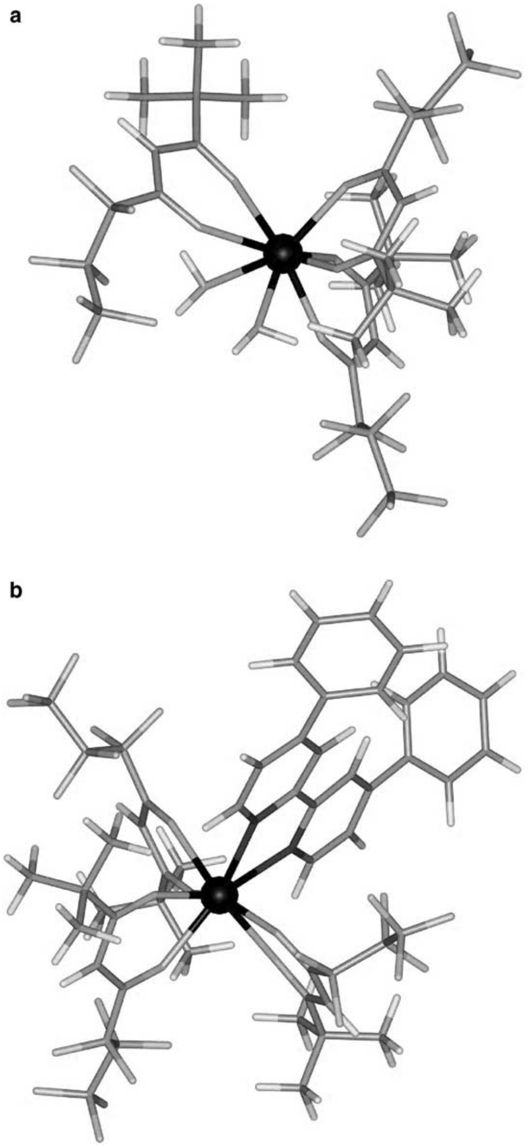

Fig. 2. Calculated ground state geometry of (a) $Eu(fod)_3 \cdot 2H_2O$ and (b) $Eu(fod)_3 \cdot$ diphenbipy complexes.

Table 2
Spherical atomic coordinates for the Sparkle/AM1 coordination polyhedron of the $Eu(fod)_3 \cdot 2H_2O$ complex

Atom	R (Å)	θ (°)	ϕ (°)
Eu^{3+}	0.00	0.00	0.00
O (fod) (1.258, 2.2)	2.38	85.57	7.85
O (fod) (1.258, 2.2)	2.38	82.65	70.39
O (fod) (1.258, 2.2)	2.38	69.62	278.10
O (fod) (1.258, 2.2)	2.38	70.37	212.66
O (fod) (1.258, 2.2)	2.38	145.27	131.98
O (fod) (1.258, 2.2)	2.38	152.31	298.21
O (H_2O) (1.258, 0.6)	2.39	81.97	135.98
O (H_2O) (1.258, 0.6)	2.39	4.53	188.52

The charge factors and the polarizability appear beside the ion (g, α in 10^{-24} Å^3).

Table 3
Spherical atomic coordinates for the Sparkle/AM1 coordination polyhedron of the $Eu(fod)_3 \cdot$ diphenbipy complex

Atom	R (Å)	θ (°)	ϕ (°)
Eu^{3+}	0.00	0.00	0.00
O (fod) (1.918, 3.36)	2.39	87.70	1.97
O (fod) (1.918, 3.36)	2.39	91.03	63.90
O (fod) (1.918, 3.36)	2.39	71.19	279.21
O (fod) (1.918, 0.03)	2.38	80.42	215.27
O (fod) (1.918, 3.36)	2.39	143.99	141.53
O (fod) (1.918, 0.03)	2.38	150.87	293.34
N (diphenbipy)(3.188, 0.03)	2.51	60.86	136.92
N (diphenbipy) (3.188, 0.03)	2.51	11.94	23.36

The charge factors and the polarizability appear beside the ion (g, α in 10^{-24} Å^3).

Table 4
Experimental and theoretical values of the intensity parameters Ω_2 and Ω_4 in 10^{-20} cm^2, the splitting of the $^7F_1$ manifold, ΔE_{0-1} in the $Eu(fod)_3 \cdot 2H_2O$ and in the $Eu(fod)_3 \cdot$ diphenbipy complexes

	$Eu(fod)_3 \cdot 2H_2O$		$Eu(fod)_3 \cdot$ diphenbipy	
	Experimental	Theoretical	Experimental	Theoretical
Ω_2	10.9×10^{-20}	10.9×10^{-20}	17.9×10^{-20}	17.9×10^{-20}
Ω_4	2.1×10^{-20}	2.1×10^{-20}	2.6×10^{-20}	2.6×10^{-20}
ΔE_{max} (cm^{-1})	190.4	190.3	184.5	184.5

has a very well-established analytical expression. The theoretical calculations have reproduced the experimental values of the $^7F_1$ manifold in both complexes using the charge factors appearing in Tables 2 and 3. The very high value of the Ω_2 for $Eu(fod)_3 \cdot$ diphenbipy reflects the hypersensitive behavior of the $^5D_0 \rightarrow {}^7F_2$ transition. In our calculations, it was possible to distinguish between the forced electric dipole and the dynamic coupling mechanism. We found that this latter largely dominates because it was not possible to fit theoretically the experimental intensity parameters data without entering this contribution into the Ω_λ equation [23]. This can be seen by means of the polarizability values achieved for the ligating oxygen and nitrogen ions (see Tables 2 and 3).

5. Conclusion

We have synthesized the europium diphenbipy complex. The coordination was determined from the chemical analytical data and from the changes in the IR, UV–Vis spectra observed after the substitution of the two water molecules in the first sphere of the coordination of Eu^{+3} ion by the diphenbipy ligand.

The substitution of the water molecules by diphenbipy in the $Eu(fod)_3 \cdot 2H_2O$ complex has led to an increase in the intensity of the luminescence which can be associated to the low symmetry on the site.

The high value of the Ω_2 intensity parameter for the complex with diphenbipy reflects the hypersensitive behavior of the $^5D_0 \rightarrow {}^7F_2$ transition and indicates that the Eu^{+3} ion is in a high polarizable chemical environment.

The reconciliation among the data from the theoretical $^7F_1$ manifold splitting, and the intensity parameter certifies the reliability of the models used in the theoretical calculations.

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