ACADEMIC PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Solid State Chemistry 171 (2003) 183–188

JOURNAL OF SOLID STATE CHEMISTRY

http://elsevier.com/locate/jssc

Synthesis, sparkle model, intensity parameters and spectroscopic studies of the new Eu(fod)$_3$phen-NO complex

M.E. de Mesquita,[a,*] S.A. Júnior,[b] N.B.C. Júnior,[a] R.O. Freire,[a] F.R.G. e Silva,[c] and G.F. de Sá[b]

[a] Departamento de Química, Universidade Federal de Sergipe, 49.100-000, São Cristóvão, SE, Brazil
[b] Departamento de Química Fundamental, Universidade Federal de Pernambuco, 50.590-470, Recife, PE, Brazil
[c] Departamento de Química, Universidade Federal do Rio Grande do Norte, 59072-970, Natal-RN, Brazil

Received 6 June 2002; received in revised form 1 August 2002; accepted 17 November 2002

Abstract

We report the synthesis, characterization, spectroscopic properties, structure prediction and intensity parameters of the Eu(fod)$_3$phen-NO (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octadionate and phen-NO = 1,10-phenanthroline N-oxide). Both the elementary analysis and the IR vibrational data are consistent with the formula of the cited complex. The absorption spectrum in ethanol shows a maximum at 272 nm, which is shifted from 293 nm in relation to Eu(fod)$_3$. This is an indication of the coordination of phen-NO. The emission spectra at room temperature and at 77 K show a very high intensity for the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition, pointing to a highly polarizable chemical environment around the Eu^{3+} ion. The complex has a decay time, τ, lower than the Eu(fod)$_3$2H$_2$O. It can be attributed to a considerable resonance of the ligand triplet with the excited levels of the lanthanide ion. The sparkle and INDO/S-CI models were used to calculate the structure and electronic spectrum of this complex. Good agreement between theoretical and experimental UV absorption spectra has been obtained. Structural data were used to perform theoretical predictions of the Judd–Ofelt intensity parameters ($\Omega_\lambda, \lambda = 2, 4$), the $^5D_0 \rightarrow {}^7F_0/{}^5D_0 \rightarrow {}^7F_2$ intensity ratio and $^5D_0 \rightarrow {}^7F_1$ transition splitting using the simple overlap model. The satisfactory results obtained are an indication that the models used can lead to reliable prediction of the structure and $4f-4f$ intensities.

Keywords: Luminescence; Intensity parameters; Sparkle model

1. Introduction

The design of luminescent lanthanide complexes has been intensively studied in the past decade, in particular with regard to the applications to highly efficient light conversion molecular devices (LCMD) as described by Lehn [1]. This interest is motivated by the possibility to use such complexes as luminescent materials, as solvent extraction agents, NMR shift reagents, as well as laser materials [2,3]. To function as an LCMD several processes must be present: (I) Ligand absorption, (II) an efficient ligand to metal energy transfer, (III) efficient luminescence of the metal ion.

Besides the synthesis and experimental investigation of the photophysical properties of new lanthanide complexes, our group has been successfully developing theoretical models to determine the coordination geometry of lanthanide complexes [4–7], the position and nature of the ligand excited states in the correspondent complexes [4–7], the $4f-4f$ intensity parameters [4–7], the ligand-to-lanthanide ion energy transfer rates [4], and the luminescence quantum yields [5]. The synthesis and characterization of Ln(fod)$_3$ with 1-10-phenanthroline (phen) and 2,2′bipyridyl(bipy) have been reported in the literature [8].

In the present paper we will describe the synthesis, characterization, spectroscopic, and photophysical properties theoretically and experimentally, as well the structure and quantum yield (q) calculations of the new Eu(fod)$_3$phen-NO complex (fod = 6,6,7,7,8,8,

---

*Corresponding author. Fax: +55-79-212-6684.
E-mail address: mesquita@ufs.br, re@infonet.com.br (M.E. de Mesquita).

0022-4596/03/$ - see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0022-4596(02)00206-2

8-heptafluoro-2,2-dimethyl-3,5-octadionate and phen-NO = 1,10-phenanthroline N-oxide). The sparkle model for lanthanide complex within the AM1 approach (SMLC/AM1) [9,10], was used to calculate the geometry of this complex. From the determined geometry, sparkle was replaced by a point charge, +3e, to account for the charge of the lanthanide ion. The electronic spectrum of the complexed ligands coordinated to the lanthanide was then calculated by the INDO/S-CI method [11]. Furthermore, the theoretical and experimental intensities of the $^5D_0 \rightarrow ^7F_{0,1,2,4}$ transitions of the Eu(III) ion in the complex Eu(fod)$_3$phen-NO are analyzed and discussed. The experimental analysis of the Ω_2 and Ω_4 intensity parameters will be made through the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ transitions taking as reference the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition. The theoretical analysis of these parameters is based on the simple overlap model (SOM) for the ligand field and the average energy denominator method to treat the forced electric dipole contribution to the intensities. The dynamic coupling mechanism is also taken into account on the basis of the point dipole ligand polarization approximation [12].

2. Experimental details

2.1. Synthesis

The Eu(fod)$_3$ complex and 1,10-phenanthroline monohydrate 99.99% were purchased from Aldrich and used as received. The ligand phen-NO was prepared following the method reported by Corey et al. [13], and was characterized by C, H, N microanalysis, melting point, IR vibrational and UV–visible spectroscopic analysis and gas chromatography. The complex Eu (fod)$_3$phen-NO was prepared by adding 40 mL of a warm ethanolic solution of phen-NO (1 mmol) to an ethanolic solution containing 1 mmol of Eu(fod)$_3$2H$_2$O. The pure product was obtained by repeated crystallization from ethanol and dried over P$_2$O$_5$ under reduced pressure (less than 1 mm Hg). The chemical analytical data for the complex indicates that the formula of the complex corresponds to Eu(fod)$_3$phen-NO as expected. The complex was characterized by means of chemical analysis, IR vibrational and UV–visible absorption spectroscopy, luminescence spectroscopy, and excited state lifetimes.

2.2. Spectroscopic measurements

The IR spectrum was recorded using a KBr pellet and a spectrophotometer (4000–400 cm^{-1}), BRUKER model IFS 66. The absorption spectrum was recorded on a Perkin Elmer LAMBDA 6 UV–visible spectrophotometer.

For the excitation and luminescence spectra the sample was excited using a 150 W xenon lamp. The appropriate wavelengths were selected by a 0.25 monochromator (Jobin Yvon model H-10). The emission spectra were analyzed using a Jobin Yvon double monochromator, model U-1000 and the fluorescence signal detected by a water-cooled RCA C31034-02 photomultiplier was processed by a Jobin Yvon Spectralink system. The signal excitation spectra were recorded by an EG&G Princeton Applied Research Boxcar, a Gated Integration model 4422 and processed by a model 4402. The lifetime measurement was made at 298 K using a nitrogen laser for excitation model VSL-337ND of Laser Science Inc. and the same Boxcar system for data acquisition described previously [14]. The quantum yield of the Eu^{3+} complex was determined by comparison with standard phosphors (Y$_2$O$_3$:Eu), the efficiencies of which have previously been determined by absolute measurements. This method provides absolute efficiencies while avoiding absolute measurements and has been described in detail [15].

3. Theoretical details

3.1. Ligand-rare earth ion energy transfer rate

The procedure to obtain the ligand-rare earth ion energy transfer rates follows three steps. For step (i) the SMLC/AM1 (sparkle model for lanthanide compounds/Austin Model 1) method [16] has been used to determine the molecular structure of the Eu(fod)$_3$phen-NO complex. The set of parameters for the sparkle species has been presented elsewhere [9] and includes the Gaussian functions for the core–core repulsion interaction according to the AM1 method [9]. For step (ii) the INDO/S-CI (intermediate neglect of differential overlap/singlet–configuration interaction) method [17] implemented in the ZINDO program [18] has been used to calculate the transition energies and oscillator strength of the ligands in the presence of a 3+ point charge [9]. By using the results obtained in steps (i) and (ii), the energy transfer rates between the ligands and the lanthanide ion in step (iii) were obtained with a model recently developed in our group which includes the direct and exchange Coulomb interactions in the perturbation operator [19,20].

3.2. Quantum yield

The numerical solution of the rate equations describing the kinetics of the $4f-4f$ luminescence was carried out according to the model developed in Ref. [21]. These numerical solutions of the rate equations yield the time dependence of the energy level populations, which reach the steady-state regime after 10^{-6}–10^{-5} s. These steady-state populations were then used to calculate the emission quantum yield which is given by the following equation.

$$q = \frac{A_T\eta_2}{\phi\eta_1}, \tag{1}$$

where the sub-indices 1 and 2 indicate the ground state and the emitting level ($^5D_0$), in the complex, A_T is the sum of the coefficient for spontaneous emission for the $^5D_0 \rightarrow {}^7F_{0,1,2,4}$ transitions and ϕ is the pumping rate.

4. Results and discussion

The IR spectrum of the Eu(fod)$_3$phen-NO complex provides evidence that the metal ion is coordinated to via the NO group. The N–O stretching frequencies shift from 1273 and 1257 to 1344 and 1279 cm^{-1}, respectively. The coordination is also confirmed by the UV–visible absorption spectrum. Furthermore, the vibrational spectrum shows there are no water molecules coordinated to the Eu^{3+} ion. If it is assumed that other phenanthroline is also coordinated the coordination number would be 8 for this complex, the same as for the Eu(fod)$_3$phen previously studied [8].

The absorption spectrum of Eu(fod)$_3$2H$_2$O recorded in ethanol shows an intense band in the UV region with a maximum at 290 nm [22], but it has shifted to a lower wavelength (272 nm) with a higher intensity in the new Eu(fod)$_3$phen-NO complex.

The luminescence spectrum of solid Eu(fod)$_3$phen-NO at 298 K is shown in Fig. 1. The luminescence spectrum of the Eu^{3+} ion in the complex is due to the transition from the $^5D_0$ excited state to the ^7F ground state manifold. The substitution of water for phen-NO in the first coordination sphere of the europium complex results in an increase in the intensities of the Eu^{3+} ion transitions, as is most evident for the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition. The high intensity can be associated with the low symmetry of the site. Some evidence of this low splitting of the $^5D_0 \rightarrow {}^7F_1$ transition is shown in the spectrum of the Eu(fod)$_3$phen-NO complex shown in Fig. 1. In the analogous Eu(fod)$_3$phen complex, the square-antiprismatic coordination may be assigned to the eight coordinate adducts. The SMLC optimization with AM1 method predicts C_1 for the point group of the Eu(fod)$_3$phen-NO complex.

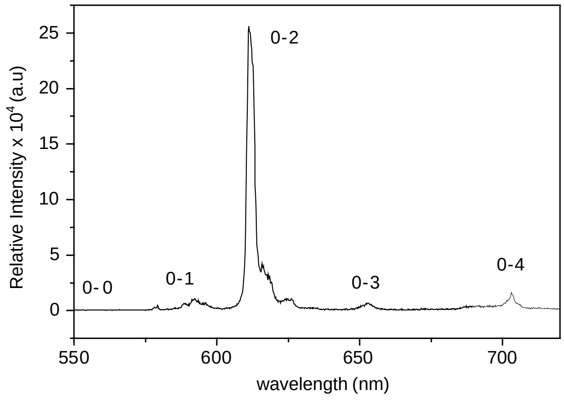

Fig. 1. Luminescence spectra ($\lambda_{exc} = 370$ nm) of Eu(fod)$_3$phen-NO in the solid at 300 K.

Table 1
Spheric atomic coordinates for coordination polyhedron of the Eu(fod)$_3$phen-NO complex

Átoms	r (Å)	θ (°)	ϕ (°)
Eu	0	0	0
O$_1$-fod	2.381	90	0
O$_2$-fod	2.418	90	245.878
O$_3$-fod	2.395	62.185	276.241
O$_4$-fod	2.379	86.385	210.197
O$_5$-fod	2.391	144.452	138.108
O$_6$-fod	2.378	145.858	287.114
N$_1$-phen-NO	2.745	69.958	320.379
O$_7$-phen-NO	2.402	17.944	256.852

Although no crystal structure was obtained, the application of the SMLC/AM1 model for other system has been satisfactory [6,10,11]. We have thus applied it to the predict ion of the geometry of Eu(fod)$_3$phen-NO, and have used this as the input geometry into INDO/S-CI in order to predict the electronic absorption spectrum.

Table 1 shows the atomic coordinates for the coordination polyhedron of the complex as determined by the sparkle model. The coordination sphere is composed of the six bonding oxygens from the three fod ligands and one oxygen and one nitrogen from the phen-NO. The polyhedron of the complex is a distorted square-antiprism as shown in Fig. 2.

From the emission spectrum shown in Fig. 1, we have determined 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 allowed transition $^5D_0 \rightarrow {}^7F_1$ was taken as the reference. The A_{rad} are given by

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

The appropriate reduced matrix elements of Eq. (2), were taken from Ref. [23], and an average index of refraction equal to 1.5 was used in the Lorentz local field correction which enters in the expressions for the coefficients of spontaneous emission. The procedure for the calculation of the theoretical intensity parameters, Ω_λ, are described in Refs. [7,12].

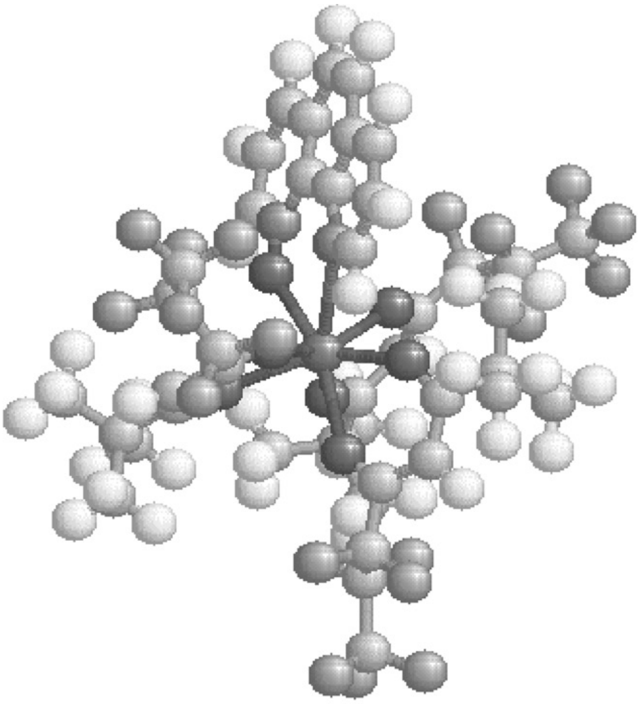

Fig. 2. Calculated ground state geometry of the complex Eu(fod)$_3$ phen-NO.

Table 2
Experimental and theoretical values of the Ω_2, Ω_4 and A_{rad} obtained from emission spectrum of the Eu(fod)$_3$phen-NO complex

	A_{rad} (s^{-1}) ($^5D_0 \rightarrow {}^7F_{4,2,1,0}$)	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)
Experimental	872	24.5	13.4
Theoretical	—	22.9	2.76

Intensity parameters were calculated from the structural data in Table 1 and the theoretical procedure described in Ref. [4]. The polarizability, α, and the charge transfer factor, g, were treated as freely varying parameters. These quantities should act in the sense of reproducing the best effects of the chemical environment on the rare earth ion. Table 2 presents the values of the charge factors and polarizabilities used to obtain the Ω_2 and Ω_4 theoretical parameters. The g's and α's are restricted to ranges of physically acceptable values.

In Fig. 3 is shown a comparison between the experimental and the calculated spectra from the input geometry SMLC/AM1 to INDO/S-CI. The predicted spectrum fits the experimental one with respect to the number of main maxima and relative intensity, although displaying a systematic blue shift, which may be due mainly to solvent effects, which have not been considered in the calculation. The theoretical spectrum was calculated for a molecule in vacuum whereas the observed spectrum was obtained for ethanolic solutions of the complex.

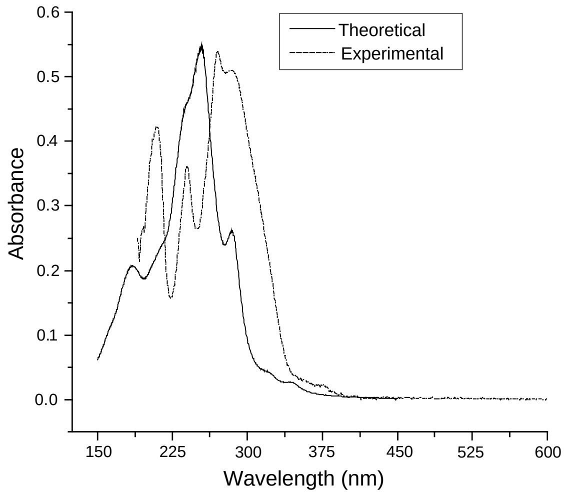

Fig. 3. The experimental and the calculated spectra from input geometry SMLC/AM1 to INDO/S-CI.

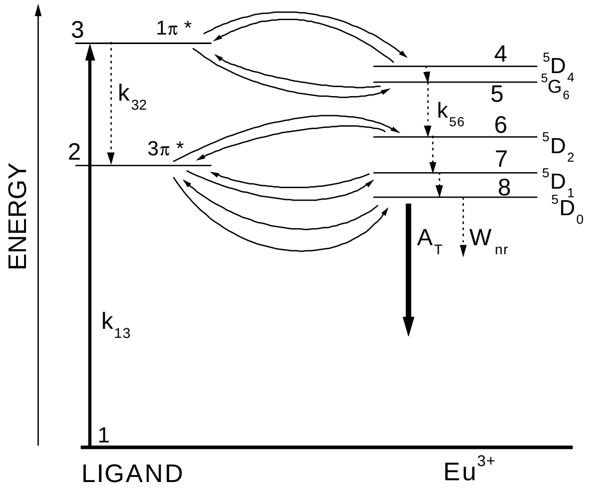

Fig. 4. Energy level diagram for the Eu(fod)$_3$phen-NO complex showing the most probable channels for the intramolecular energy transfer process. The solid and dashed arrows represent radiative (rate A_{rad}) and non-radiative (rate W_{nr}) processes, respectively. The pumping rate is k_{13} and k_{32} is the intersystem crossing rate.

An energy level diagram for the compound Eu(fod)$_3$ phen-NO is shown in Fig 4. The UV absorption takes place through the fod and phen-NO ligands. The experimental energies of the singlet and the theoretical energy of the triplet were used to set up the right part of the diagram shown in Fig. 4. In this model, ligand-to-metal energy transfer may occur through either the singlet or triplet ligand states. There are five 4f states that show appropriate resonance conditions with the ligand excited states. The choice of $^5D_0$, $^5D_1$, $^5D_2$, $^5G_6$ and $^5D_4$ results from favorable resonance conditions and from the selection rules discussed in Refs. [19,20]. The figure also labels the energy levels involved in the

Table 3
Calculated values for the energy transfer rates in the Eu(fod)$_3$phen-NO complex

Ligand state (cm^{-1})	$4f$ state (cm^{-1})	Transfer rate	Back-transfer rate
Triplet (22 711)→	$^5D_0$ (17 300)	$k_{28} = 3.46 \times 10^8$	$k_{82} \approx 0$
Triplet (22 711)→	$^5D_1$ (19 000)	$k_{27} = 1.376 \times 10^{10}$	$k_{72} = 288.1$
Triplet (22 711)→	$^5D_2$ (21 500)	$k_{26} = 2.18 \times 10^{7}$[a]	$k_{62} = 6.78 \times 10^4$
Singlet (27 027)→	$^5G_6$ (26 750)	$k_{35} = 2.56 \times 10^{6}$[b]	$k_{53} = 6.84 \times 10^5$
Singlet (27 027)←	$^5D_4$ (27 600)	$k_{43} = 9.79 \times 10^{6}$[b]	$k_{34} = 6.38 \times 10^5$

[a] Dipole-2^l pole mechanism.
[b] Dipole–dipole mechanism.

mechanism as well as transfer and transition rates involved (k_{ij}).

Table 3 presents the theoretical values of the forward and back-transfer rates calculated. The arrows in this table indicate the direction of the energy transfer and the energy level labelling is presented in Fig. 4. The forward transfer rate to the $^5D_0$ level was calculated by assuming a thermal population factor equal to 0.17, at 300 K, for the $^7F_1$ manifold and an energy difference $\Delta = E(\text{triplet}) - [E(^5D_0) - E(^7F_1)]$. The parameters used in the calculations of the transfer rates were obtained from the luminescence spectra, lifetime measurements and sparkle model (structural data and ligand matrix elements). The parameters for Eu(fod)$_3$phen-NO were $R_L = 3.92$ Å (average value), $\gamma_{\text{triplet}} = 4000\,\text{cm}^{-1}$, $A_T = 872\,\text{s}^{-1}$ and the theoretical value used for the z-component of the electric dipole matrix element (Eq. (19) in Ref. [4]), was 4.38×10^{-36} (e.s.u.)^2 cm^2. The inverse of the $^5D_0$ (Eu^{3+}) level lifetime ($1/\tau$) was set to 2114 s^{-1}. In addition, the multipolar contributions to the transfer rates were calculated by using the following theoretical values for $\Omega_\lambda^{\text{e.d.}}$ (in $10^{-20}\,\text{cm}^2$): $\Omega_2^{\text{e.d.}} = 0.2, \Omega_4^{\text{e.d.}} = 0.23$ and $\Omega_6^{\text{e.d.}} = 0.39$. It should also be noticed that the back-transfer rates were calculated by multiplying the forward transfer rates by the Boltzmann factor $e^{-|\Delta|/k_B T}$ at room temperature. We also have assumed that the value of the non-radiative decay rate of the $4f-4f$ transitions within a $4f^N$ electronic configuration is $10^6\,\text{s}^{-1}$, which corresponds to the decay from the $^5D_1$ to the $^5D_0$ level .The following values for the screening factors were assumed for these compounds, $\sigma_2 = 0.6$, $\sigma_4 = 0.139$, $\sigma_6 = -0.1$ and $\sigma_0 = 0.989$ [9].

The energy transfer rates are higher for the $^5D_0$ and $^5D_1$ levels, where the exchange interaction dominates, than for the higher excited $4f$ levels, where the multipolar interactions are the most important ones. The multipolar interactions include the dipole–dipole and dipole-2^l-dipole mechanisms.

The measured emission quantum yield for the Eu^{3+} ion was 43% for the Eu(fod)$_3$phen-NO complex at room temperature. To compare theory with experiment, the numerical solution of the rate equations has been performed and the steady-state populations have been obtained for all the energy levels involved in the energy transfer process shown in Fig. 4. These populations were then employed in Eq. (1) to obtain the theoretical emission quantum yields. The calculations were performed by using the values of the energy transfer rates presented in Table 3 and also the following values of decay rates, $k_{21} = 10^5\,\text{s}^{-1}$, $k_{32} = 10^8\,\text{s}^{-1}$, $k_{31} = 10^6\,\text{s}^{-1}$ and $k_{13} = 10^4\,\text{s}^{-1}$ [21]. We found an optimum emission quantum yield of 41% for the Eu(fod)$_3$phen-NO complex, which is in good agreement with the experimental one.

The luminescence lifetime of solid Eu(fod)$_3$2H$_2$O showed a value of 0.62 ms compared with the new Eu(fod)$_3$phen-NO complex, for which obtained a decay time τ of 374 μs. The results clearly show that the substitution of the water molecules by phen-NO leads to lower decay times. This can be attributed to a considerable resonance of the ligand triplets (fod and phen-NO) with the excited levels of the Eu^{3+} ion in the Eu(fod)$_3$phen-NO complex making an energy back-transfer of the Eu→ligand. Furthermore the dominant non-radiative processes related to $^5D_0$ can be associated to an excited level of the charge transfer Eu←ligand [25].

5. Conclusions

The IR and UV–visible spectra as well as the luminescence measurements provide evidence that metal ion is coordinated to the ligands fod and phen-NO.

The low decay times of the Eu(fod)$_3$phen-NO complex can be associated with the energy back-transfer of the Eu→ligand. This can justify the lower quantum yield q compared with the similar complex [24].

We have studied theoretically the structure of the new Eu(fod)$_3$phen-NO complex using an improved version of the sparkle model [12]. The UV absorption spectrum was calculated through excited state levels obtained from the INDO/S-CI model. The absorption spectrum of the complex obtained has been reproduced well by the theory, providing confidence in the validity of the structure model used for the theoretical calculation [26]. The same numbers of peaks and the relative intensities sorted in the simulation of the absorption spectrum have stimulated the calculation of the Judd–Ofelt intensity parameters using the SOM. The results for Ω_λ indicate that the dynamic coupling mechanism is dominant and, therefore, that lanthanide ion is in a highly polarizable chemical environment.

Acknowledgments

The authors thank CNPq (Brazilian agency) and FAPESE (state agency) for financial support. One of us (M.E. Mesquita) thanks Prof. A. M. Simas for the possibility to use the ZINDO program.

References

[1] J.-M. Lehn, Angew Chem. Int. Ed. Engl. 29 (1990) 1304.

[2] J.C. Bünzli, E. Moret, V. Foiret, K.J. Schenk, W. Mingzhad, J. Limpei, J. Alloys Compd. 207/208 (1994) 107.

[3] M. Li, P.R. Selvin, J. Am. Chem. Soc. 117 (1995) 8132.

[4] O.L. Malta, H.F. Brito, J.F.S. Menezes, F.R. Gonçalves e Silva, S. Alves Jr., F.S. Farias Jr., A.V.M. de Andrade, J. Lumin. 75 (1997) 255.

[5] O.L. Malta, H.F. Brito, J.F.S. Menezes, F.R. Gonçalves e Silva, C. de Melo Donegá, S. Alves Jr., Chem. Phys. Lett. 282 (1998) 233.

[6] H.J. Batista, A.V.M. de Andrade, R.L. Longo, A.M. Simas, G.F. de Sá, N.K. Ito, L.C. Thompson, Inorg. Chem. 37 (1998) 3542.

[7] G.B. Rocha, M.E. de Mesquita, A.M. Simas, G.F. de Sá, Mater. Sci. Forum 315 (1999) 400.

[8] K. Iftikhar, M. Sayeed, N. Ahmad, Inorg. Chem. 21 (1982) 80.

[9] A.V.M. de Andrade, N.B. da Costa Jr., R.L. Longo, O.L. Malta, A.M. Simas, G.F. de Sá, Mol. Eng. 7 (1997) 293.

[10] A.V.M. de Andrade, N.B. da Costa Jr., R.L. Longo, O.L. Malta, A.M. Simas, G.F. de Sá, Quím. Nova 21 (1998) 51.

[11] A.V.M. de Andrade, R.L. Longo, A.M. Simas, G.F. de Sá, J. Chem. Soc. Faraday Trans. 92 (1996) 1835.

[12] O.L. Malta, S.J.L. Ribeiro, M. Faucher, P. Porcher, J. Phys. Chem. Solids 52 (1991) 587.

[13] E.J. Corey, A.L. Borror, T. Flia, J. Org. Chem. 30 (1965) 88.

[14] M. Pietraszkiewicz, J. Karpink, A.K. Rout, Pure Appl. Chem. 65 (1993) 563; G.F. de Sá, W.M. de Azevedo, A.S.L. Gomes, J. Chem. Res. (S) (1994) 234.

[15] C. de Melo Donegá, S.J.L. Ribeiro, F.R. Gonçalves e Silva, G. Blasse, J. Phys. Chem. Solids 57 (1996) 1727.

[16] A.V.M. de Andrade, N.B. da Costa Jr., A.M. Simas, G.F. de Sá, Chem. Phys. Lett. 227 (1994) 349.

[17] J.E. Riedley, M.C. Zerner, Theor. Chem. Acta 32 (1973) 111.

[18] M.C. Zerner, ZINDO Manual, QTP, University of Florida, Gainesville, FL, 1990, p. 32611.

[19] O.L. Malta, J. Lumin. 71 (1997) 229.

[20] F.R. Gonçalves e Silva, O.L. Malta, J. Alloys Compd. 250 (1997) 427.

[21] O.L. Malta, F.R. Gonçalves e Silva, R. Longo, Chem. Phys. Lett. 307 (1999) 518.

[22] L.S. Villata, E. Wolcan, M.R. Feliz, A.L. Capparelli, J. Photochem. Photobiol. 115 (1998) 185.

[23] W.T, Carnall, H.Crosswhite, H.M. Crosswhite, Energy Level Structure and Transition Probabilities of the Trivalent Lanthanides in LaF3, Report-Argonne National Laboratory, 1977.

[24] C. de Melo Donegá, S.A. Júnior, G.F. de Sá, J. Alloys Compd. 250 (1997) 422.

[25] N. Sabbatini, M. Guardigli, J.-M. Lehn, Coord. Chem. Rev. 123 (1993) 201.

[26] G.F. de Sá, O.L. Malta, C. de, M. Donegá, A.M. Simas, R.L. Longo, P.A. Santa Cruz, E.F. da Silva Jr., Coord. Chem. Rev. 196 (2000) 165.