Photoluminescence of Europium(III) Dithiocarbamate Complexes: Electronic Structure, Charge Transfer and Energy Transfer

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For the first time, we observed photoluminescence in Eu(III) dithiocarbamate complexes at room temperature—more specifically in [Eu(Et_2NCS_2)$_3$phen], [Eu(Et_2NCS_2)$_3$bpy] and the novel [Eu(Ph_2NCS_2)$_3$phen], where phen stands for 1,10-phenanthroline and bpy for 2,2′-bipyridine. Correlations between the electronic structure of the dithiocarbamate ligands on one hand, and covalency, intensity, and ligand field spectroscopic parameters on the other, could be established. Moreover, the relative values of the emission quantum efficiencies obtained for these complexes, as well as their dependence with temperature, could be satisfactorily described by a theoretical methodology recently developed [*J. Chem. Phys.* **2005**, *122*, 054109].

1. Introduction

Sulfur is a comparatively weak donor toward Ln(III) ions, but in favorable circumstances coordination does occur, especially in the case of bidentate negative ligands.[1] One important class of Ln(III)−sulfur complexes is the adducts of dithiocarbamate anions, which have been studied sporadically since the 1960s.[2] Recently, there has been a resurgence of interest in these compounds for a variety of uses, both in structural,[3] thermodynamical[4] and spectroscopic studies[3,5] and for practical applications, such as in nanotechnology and microelectronics.[6] These compounds can be prepared with various dithiocarbamates (RR′NCS_2^-, where R and R′ can be a wide variety of groups), as anionic complexes (tetrakis complexes) or as neutral complexes, generally with adduct molecules that are Lewis bases. These are usually neutral molecules, generally mono- or bidentate, and include sulfoxides, 2,2′-bipyridine, 1,10-phenanthroline, etc.[3−5] The resulting adducts have generally coordination number 8, possess solubility in some organic solvent and in some cases possess sufficient volatility that they can be sublimated and deposited as thin films.[6,7]

An important characteristic of the dithiocarbamate lanthanide complexes, first described by C. K. Jϕrgensen in the 1960s,[8] is that they present ligand-to-metal charge transfer (LMCT) states of very low energy. In compounds in which the LMCT state coincides in energy with the metal ion and/or ligand excited states in the near UV−visible spectral region, it may constitute an important channel for depopulation of the lanthanide excited states, leading to luminescence quenching.[9−11] Such is the case of dithiocarbamate complexes of Eu(III), because Eu(III), among all trivalent lanthanide ions, is the one most easily reducible to oxidation state II. Probably due to this reason, their photoluminescence properties have not been properly addressed in the literature of lanthanide spectroscopy, although there are many reports exploring diverse aspects of the spectroscopy of these compounds. One rare exception was the paper of Kobayashi et al., which reports the photoluminescence of Na[Eu($S_2CN(CH_3)_2$]·3.5H_2O at 4.2 K.[12]

The spectroscopy of lanthanide coordination compounds has been developed since the 1930s to the present time almost exclusively in terms of coordination compounds with O or N as directly coordinated atoms.[1,13] However, detailed photoluminescence studies of sulfur-coordinated compounds with the purpose of correlating intensity parameters, intramolecular energy transfer rates, emission quantum efficiencies and luminescence quenching via LMCT states, with the electronic structure of the ligands is still lacking in the literature.

In this paper, static and dynamic photoluminescence properties of the complexes [Eu(Et_2NCS_2)$_3$phen], [Eu(Et_2NCS_2)$_3$bpy], and of the new complex [Eu(Ph_2NCS_2)$_3$phen] are presented. The electronic energy level structure of these complexes is described both from semiempirical INDO/S-CI molecular orbital calculations and by phosphorescence spectra of similar Gd(III) complexes, which has an ionic radius close to the Eu(III) one but does not present emissions in the visible spectral region. Moreover, the positions of the LMCT states in the Eu(III) complexes are analyzed in terms of their dependence on the electronic structure of the free ligands, described both by heuristic means and also with the help of semiempirical and ab initio molecular orbital calculations. The efficiencies of the luminescence process in the Eu(III) dithiocarbamate complexes are finally analyzed in terms of their dependence on the energy transfer rates from the ligands and 4f states to the LMCT states, calculated via a theoretical methodology recently developed.[14]

2. Experimental Section

2.1. Chemicals. Hydrated lanthanide chlorides and nitrates were prepared by dissolving lanthanide oxides in 1:1 chloridric acid and 1:1 nitric acid, respectively. 1,10-Phenanthroline monohydrate (Merck) was recrystallized in an ethanol/water mixture. 2,2′-Bipyridine (Aldrich) and diphenylamine (Merck) were used without further purifications. Diethylamine was distillated over metallic zinc powder. THF was dried with metallic sodium. The other solvents (Aldrich or Merck, reagent grade or better) were used as supplied.

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2.2. Lanthanide Complexes. *Synthesis of [Ln(Et$_2$NCS$_2$)$_3$phen].* A solution of diethylammonium diethyldithiocarbamate (3 equiv), which was prepared by the reaction of diethylamine with excess of CS$_2$ in acetone according to literature procedures,[15] in CH$_3$CN and a solution of 1,10-phenanthroline in CH$_3$CN (1 equiv) were, respectively, added to a solution of EuCl$_3$6H$_2$O (1 equic) in CH$_3$CN/EtOH (10:1, v/v). A small amount of white solid came out and was immediately filtered out of the mixture. The brick-red crystals were collected by filtration, washed with CH$_3$CN and air-dried. Anal. Calc for C$_{27}$H$_{38}$EuN$_5$S$_6$: C, 41.7; H, 4.9; N, 9.0. Found: C, 41.6; H, 4.8; N, 9.4. Similarly prepared was the compound [Gd(Et$_2$NCS$_2$)$_3$phen]. Anal. Calc for C$_{27}$H$_{38}$GdN$_5$S$_6$: C, 41.5; H, 4.9; N, 9.0. Found: C, 41.3; H, 4.8; N, 8.9.

Synthesis of [Ln(Et$_2$NCS$_2$)$_3$bpy]. A solution of sodium diethyldithiocarbamate trihidrated (3 equiv) was dissolved in hot CH$_3$CN and a solution of Eu(NO$_3$)$_3$6H$_2$O (1 equiv) in CH$_3$CN was added. After filtration to remove the precipitate, sodium nitrate was added to filtrate a solution of 1.1 equiv of 2,2′-bipyridine in triethylorthoformiate/CH$_3$CN (1:10, v/v). A small amount of white solid came out and was immediately filtered out of the mixture. The red crystals (prismatic form) were collected by filtration, washed with CH$_3$CN and air-dried. Anal. Calc for C$_{25}$H$_{38}$EuN$_5$S$_6$: C, 39.9; H, 5.0; N, 9.3. Found: C, 39.3; H, 4.7; N, 9.4. The procedure used in the synthesis of the complex [Gd(Et$_2$NCS$_2$)$_3$bpy] was the same used for [Gd(Et$_2$NCS$_2$)$_3$phen]. Anal. Calc For C$_{25}$H$_{38}$GdN$_5$S$_6$: C, 39.6; H, 5.0; N, 9.2. Found: C, 38.4; H, 4.7; N, 9.0.

Synthesis of [Ln(Ph$_2$NCS$_2$)$_3$phen]. A solution of (C$_6$H$_5$)$_2$NH (3 equiv) in dry THF was added to a suspension of KOC(CH$_3$)$_3$ in dry THF at (∼ −70 °C) over Ar flux. The formation of the amide anion could be verified by the change in color. To the resulting solution was added 6 equiv of CS$_2$. A yellow solid was formed, which was filtrated, washed with THF and dried in high vacuum. This solid was dissolved in hot CH$_3$CN and a solution of Eu(NO$_3$)$_3$6H$_2$O (1 equiv) in CH$_3$CN was added. After filtration to remove the precipitate, potassium nitrate was added to filtrate a solution of 1.1 equiv of 1,10-phenanthroline monohydrate in triethylorthoformiate/CH$_3$CN (1:10, v/v). A small amount of white solid came out and was immediately filtered out of the mixture. The red crystals (small needles) were collected by filtration, washed with CH$_3$CN and air-dried. Anal. Calc for C$_{51}$H$_{38}$EuN$_5$S$_6$: C, 57.5;. H, 3.6; N, 6.6. Found: C, 56.8; H, 3.6; N, 7.3. Similarly prepared was the compound [Gd(Ph$_2$NCS$_2$)$_3$phen]. Anal. Calc for C$_{51}$H$_{38}$GdN$_5$S$_6$: C, 57.2; H, 3.6; N, 6.5. Found: C, 55.2; H, 3.1; N, 6.5.

2.3. Spectroscopic Measurements. Steady-state luminescence measurements were performed with a spectrofluorometer (SPEX-Fluorolog 2) with a double grating 0.22 m monochromator (SPEX 1680) and a 450 W xenon lamp as the excitation source. To eliminate the second-order diffraction of the source radiation, a cutoff filter was used in the measurements. All excitation and emission spectra were recorded at room (300 K) and liquid nitrogen (77 K) temperature and collected at an angle of 22.5° (front face) using a detector mode correction. The luminescence decay curves of the emitting levels were recorded at 300 and 77 K, using a phosphorimeter SPEX 1934D accessory coupled to the spectrofluorometer. The signal was detected by a water-cooled Hamamatsu R928 photomultiplier and processed by a DM3000F SPEX system.

3. Theoretical Approach

3.1. Electronic Structure Calculations. To calculate the electronic structure of the free ligands, ab initio (HF/6-31G*) and semiempirical (AM1) molecular orbital calculations were performed. Ab initio calculations were performed using the Gaussian 98 program. The convergence parameters used in these calculations were the defaults of the program. For the semiempirical calculations, MOPAC93r2 was employed. The convergence parameters used in these calculations were GNORM = 0.1 and SCFCRT = 1D-12. The ground-state geometries of the complexes were obtained using the Sparkle/AM1 method.[16] In this chemical model, Eu(III) is represented by a sparkle, which is a point charge +3e in the center of a repulsive potential. This model simulates well the electrostatic interaction between Eu(III) and the ligands.

The energy levels of the organic ligands coordinated to Eu(III) were calculated with the INDO/S-CI model implemented in the ZINDO program.[17] In these calculations Eu(III) was conveniently replaced by a point charge +3e. The lanthanide complexes were thus computed as closed-shell molecules and the CI procedure used included single excitations only, where we employed a CI active space of 13 real and 13 virtual molecular orbitals.

3.2. Energy Transfer Rates. Recently, a theoretical approach for the intramolecular energy transfer process involving the ligand-to-metal charge transfer (LMCT) state in lanthanide compounds was developed by some of us.[14] From this model the energy transfer rate between the excited ligand state and the LMCT state can be calculated by

$$w_{\mathrm{ET}}^{\mathrm{L}} = \frac{2\pi}{\hbar}\frac{e^4}{{R_{\mathrm{L}}}^2}\langle 4\mathrm{f}|\pi^*\rangle^2\langle\phi_0|\pi\rangle^2 F \tag{1}$$

where ϕ_0 is the electron donor orbital in the formation of the LMCT state, π and π^* are ligand molecular orbitals associated with the $\pi \rightarrow \pi^*$ transition and 4f is an atomic orbital. The temperature-dependent factor F contains a sum over Franck−Condon factors and the appropriate energy mismatch conditions.[18] R_{L} is the distance between the donor and the acceptor states in the energy transfer process.[14,19]

According to this model, the energy transfer rate between a 4f state and the LMCT state is given by

$$W_{\mathrm{ET}}^{\mathrm{C}} = \frac{2\pi}{\hbar}\frac{e^2 F}{G(2J+1)}\sum_{\lambda=2,4,6}\omega_\lambda^{\mathrm{CT}}\langle\psi' J'||U^{(\lambda)}||\psi \mathrm{J}\rangle^2 \tag{2}$$

where

$$\omega_\lambda^{\mathrm{CT}} = \langle r^\lambda\rangle^2\langle 3||C^{(\lambda)}||3\rangle^2(1-\sigma_\lambda)^2\left(\frac{(2\lambda+1)e^4(4\mathrm{f}|\phi_0\rangle^2}{(R_{\mathrm{L}}^{\lambda+1})^2} + \frac{(\lambda+1)e^2 S_{\mathrm{CT}}}{(R_{\mathrm{L}}^{\lambda+2})^2}\right) + 2\Omega_\lambda^{\mathrm{ed}}(1-\sigma_1)^2\left(\frac{e^4\langle 4\mathrm{f}|\phi_0\rangle^2}{{R_{\mathrm{L}}}^4} + \frac{e^2 S_{\mathrm{CT}}}{{R_{\mathrm{L}}}^6}\right) \tag{3}$$

if $|J - J'| \leq \lambda \leq J + J'$ ($J = J' = 0$ excluded and $\lambda = 2$, 4 and 6), or

$$W_{\mathrm{ET}}^{\mathrm{ex}} = \frac{8\pi}{3\hbar}\frac{e^4}{{R_{\mathrm{L}}}^4}\frac{(1-\sigma_0)^2}{(2J+1)}F\langle\psi' J'||S||\psi J\rangle^2\sum_m \times \langle\Psi_{N-1}4\mathrm{f}|\sum_k r_k C_0^{(1)} s_{-m}(k)|\Psi_{N-1}\phi_0\rangle^2 \tag{4}$$

if $J - J' = 0, \pm 1$ ($J = J' = 0$ excluded), where S is the total spin operator of the lanthanide ion, σ_λ is a shielding factor, $\langle r^\lambda\rangle$ is a radial expectation value and S_{CT} is the dipole strength

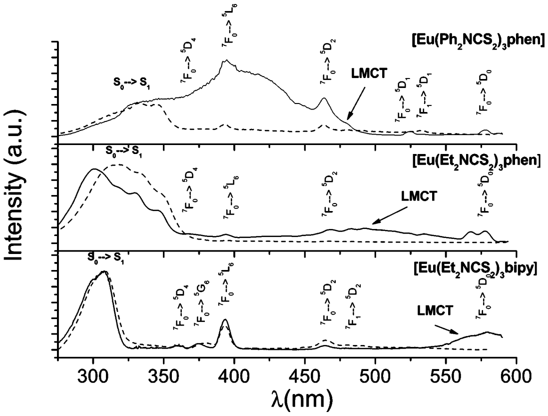

Figure 1. Excitation spectra of the Eu(III) complexes with dithiocarbamate ligands at room temperature (dash) and at 77 K (solid). The $^5D_0 \rightarrow {}^7F_2$ emission near 612 nm was monitored.

associated with the LMCT transition. The quantities Ω_λ^{ed} are the intensity parameters given by the Judd–Ofelt theory considering only the forced electric dipole contribution.[20] These quantities depend both on geometrical parameters of the coordination polyhedron and on the ligand field model considered. In this work the simple overlap model (SOM) has been adopted.[21]

For the case of the energy transfer between ligand-centered states and 4f states the formalism developed by Malta et al., described in several earlier works, has been used.[22]

4. Results

4.1. Experimental Results. For the new synthesized complex [Eu(Ph$_2$NCS$_2$)$_3$phen] as well as for the other two dithiocarbamates complexes, [Eu(Et$_2$NCS$_2$)$_3$bpy] and [Eu(Et$_2$NCS$_2$)$_3$phen], investigated in this work, a moderately weak photoluminescence from the Eu(III) ion was detected at both 77 and 300 K. To the best of our knowledge, this is the first time that a photoluminescence from a Eu(III) dithiocarbamate complex is detected at room temperature. The difficulty lies in the fact that low lying LMCT states generally promote efficient luminescence quenching. Figure 1 shows the excitation spectra for the Eu(III) ion in the investigated complexes, by monitoring the $^5D_0 \rightarrow {}^7F_2$ emission to guarantee that only absorbances that populate the $^5D_0$, the main emission level in this ion, are observed.

Many features of the excitation spectra correspond to intraconfigurational 4f–4f transitions. At room temperature, the first excited level of Eu(III), the $^7F_1$ level, is 30% populated—according to our estimate based on the Boltzman distribution—leading to some observable transitions originated from this level. An efficient ligand-to-metal energy transfer process is indicated, because the most intense feature in the spectrum of each compound is a broad band corresponding to ligand-centered electronic transitions. The broad band observed for the complex [Eu(Ph$_2$NCS$_2$)$_3$phen] in the spectral region between approximately 270 and 370 nm is very similar to the one observed for the complex [Eu(Et$_2$NCS$_2$)$_3$phen], indicating that in both cases the corresponding excited state, a singlet state, is localized in the 1,10-phenanthroline ligand. In the same region, a similar band, presumably localized in the 2,2′-bipyridine ligand, is observed for the [Eu(Et$_2$NCS$_2$)$_3$bpy] complex.

At 77 K broad excitation bands appear, whereas they are not observed at 300 K. We attribute these bands to LMCT states. In general, the main mechanism of the luminescence sensitization of lanthanide ions via the "antenna effect" involves the energy transfer from a ligand-centered triplet state to 4f states of the Ln(III) ion. For this reason, it is expected that the excitation spectrum of the triplet state in a Gd(III) complex may be very similar to the excitation spectrum of the $^5D_0$ level of the corresponding Eu(III) complex. However, if quenching channels that do not exist in the Gd(III) complex are operative in the Eu(III) complex, as LMCT bands, the two spectra may be very different. The excitation spectra of the Gd(III) complexes are presented in Figure 2.

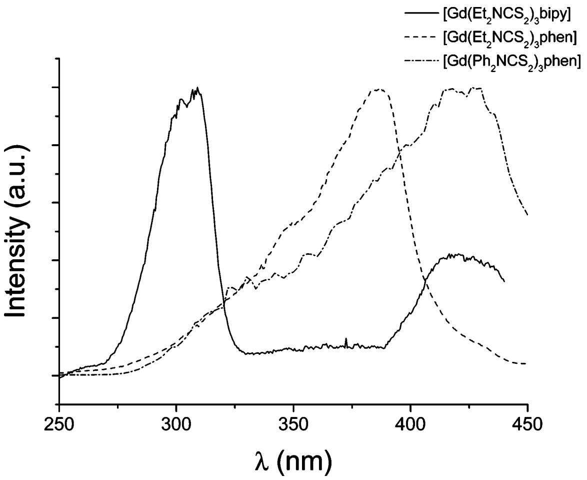

Figure 2. Excitation espectra of the complexes [Gd(Et$_2$NCS$_2$)$_3$bpy], [Gd(Et$_2$NCS$_2$)$_3$phen], and [Gd(Ph$_2$NCS$_2$)$_3$phen] at 77 K, with emissions fixed at 473, 510, and 550 nm, respectivelly.

In the excitation spectra of all of the Gd(III) complexes, there are bands that do not arise in the corresponding Eu(III) complexes. We attribute these bands to singlet states localized in the dithiocarbamate ligands. The populations of these singlet states are being quenched by the LMCT state and, therefore, do not relax through the triplet donor level. In the case of the complex [Eu(Ph$_2$NCS$_2$)$_3$phen], the quenching occurs at 300 K but not at 77 K. In this way, at room temperature, the 4f state is depopulated by the LMCT band close to but slightly above it and, therefore, does not relax through the $^5D_0$ level. For this reason, some 4f–4f absorbances around the region where the LMCT bands appear, and which cannot be observed at 300 K, can be detected at 77 K (Figure 1).

For each of the Gd(III) complexes, we observed two emission bands in their emission spectra: the first one, of higher energy, appears when the complexes are excited at the energy corresponding to the singlet state of the heterobiaryl ligands, and corresponds to the triplet state of these ligands, T_L. The second one, of lower energy, appears when the complexes are excited at the energy corresponding to the singlet state of the dithiocarbamate ligands, and corresponds to the triplet state of the these ligands, T_{dt}.

Figure 3 shows the $^5D_0 \rightarrow {}^7F_J$ ($J = 0-4$) emission spectra of the Eu(III) dithiocarbamate complexes at room temperature. In each of these cases, the excitation is at the maximum on the left side shown in Figure 1, corresponding to levels centered into the heterobiaryl ligands.

All peaks in the emission spectra originate from the $^5D_0$ level. The presence of the $^5D_0 \rightarrow {}^7F_0$ transition, which appears only in low symmetries as C_{nv}, C_n and C_s, indicates that all the complexes present a low symmetry coordination geometry. In agreement with this observation is the fact that the $^5D_0 \rightarrow {}^7F_1$ transition presents three peaks, indicating that the degeneracy of the $^7F_1$ level is completely removed.

From the emission and excitation spectra of all studied complexes, it is possible to construct the relevant electronic level structures for the Eu(III) complexes. The results are presented

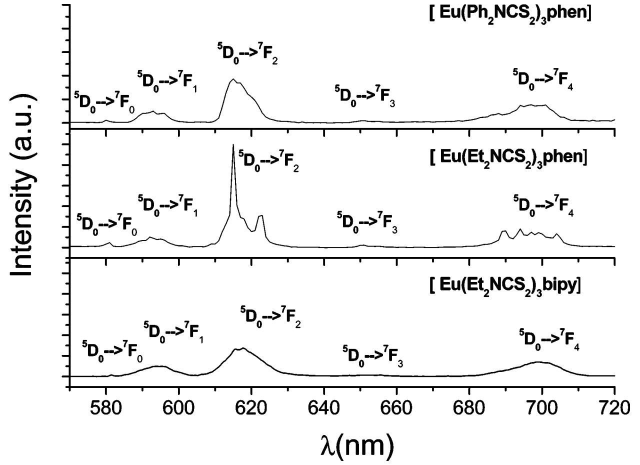

Figure 3. Emission spectra of the Eu(III) complexes with dithiocarbamate ligands at 77 K.

TABLE 1: Experimental Energy Levels Obtained for the Investigated Complexes (cm^{-1})

	$[Eu(Et_2NCS_2)_3bpy]$	$[Eu(Et_2NCS_2)_3phen]$	$[Eu(Ph_2NCS_2)_3phen]$
S_L	32787	27548	27624
S_{dt}	23641	25907	23577
T_L	23148	21645	21978
T_{dt}	19120	20012	20877
$^5D_4$	27762	27322	27308
$^5G_6$	26709		26245
$^5L_6$	25394	25381	25342
$^5D_3$	24329		
$^5D_2$	21533	21368	21570
$^5D_1$	18954	18692	19062
$^5D_0$	17271	17212	17277
$^7F_2$	1086	953	1057
$^7F_1$	372	336	389
LMCT	17527	19080	19960

in Table 1. The energy of each 4f level was considered as the center of the respective narrow band of excitation. The energies of the singlets and LMCT states were considered as the energy corresponding to the half-height in the smaller energy side of the best-adjusted Gaussian band shape. In the case of the LMCT band, the Gaussian was obtained via Gaussian deconvolution. All adjustment procedures presented $r^2 > 0.99$ and $\chi^2 < 10^{-4}$. The energies of the triplet levels were obtained from the onset of the emission spectra, considering the spectral region of higher energy, which corresponds to the zero-phonon transitions.

The lifetimes of the $^5D_0$ level in the $[Eu(Et_2NCS_2)_3bpy]$, $[Eu(Et_2NCS_2)_3phen]$, and $[Eu(Ph_2NCS_2)_3phen]$ complexes, are respectively 50 ± 3, 224 ± 10, and 261 ± 21 μs at 77 K, and <50, 90 ± 15, and 75 ± 6 μs at room temperature. These lifetimes are very low in comparison with those of many lanthanide compounds with O-donor ligands, which indicate that the quenching process is caused by the LMCT bands. The strong dependence of the lifetimes on the temperature agrees with this assignment. However, the values obtained for the $[Eu(Et_2NCS_2)_3phen]$ and $[Eu(Ph_2NCS_2)_3phen]$ complexes at 77 K are higher than those obtained by Kobayashi et al. for the $Na[Eu(S_2CN(CH_3)_2]\cdot 3.5H_2O$ complex at 4.2 K, indicating a better quantum efficiency for these compounds.[12]

Covalency in coordination compounds can be described both via theoretical parameters, as the α_{OP} parameter recently introduced by Malta et al,[23] and by empirical parameters, such as the *nephelauxetic* parameter (β), Sinha's parameter (δ) or Choppin's bonding parameter ($b^{1/2}$) that can be considered as spectroscopic covalency parameters of the metal−ligand bond.[24] For our purposes, we have considered only the empirical parameters and have assumed the energy levels of the Eu(III) ions incorporated in the LaF_3 matrix to be the same as the free ion energy levels. Table 2 shows some of these spectroscopic parameters obtained from the experimental data presented above.

TABLE 2: Spectroscopic Parameters Obtained for the Eu(III) Investigated Complexes

	$[Eu(Et_2NCS_2)_3bpy]$	$[Eu(Et_2NCS_2)_3phen]$	$[Eu(Ph_2NCS_2)_3phen]$
β	0.9987	0.9953	0.9991
δ	0.1265	0.4723	0.0919
$b^{1/2}$	0.0251	0.0485	0.0214
N_v (cm^{-1})	848	940	533
$10^{20}\Omega_2$ (cm^2)	5.5 ± 0.3	8.0 ± 0.4	6.7 ± 0.3
$10^{20}\Omega_4$ (cm^2)	8.4 ± 0.4	11.5 ± 0.6	13.8 ± 0.7
A_{rad} (s^{-1})	338 ± 17	468 ± 23	458 ± 23
τ_{300K} (μs)	< 50	90 ± 15	75 ± 6
τ_{77K} (μs)	50 ± 3	224 ± 10	261 ± 21
η_{300K} (%)		4.2 ± 0.9	3.4 ± 0.4
η_{77K} (%)	1.7 ± 0.2	10.5 ± 1.0	12.0 ± 1.6

The results indicate that the interaction between the Eu(III) ion and $R_2NCS_2^-$ is less covalent for R = Ph than for R = Et. In this last case, the covalency depends on the second ligand L, being higher for L = 1,10-phenanthroline than for 2,2′-bipyridine. This is in agreement with the results obtained by Su et al. for the complexes in chloroformic solutions, via f−f absorption spectra.[25]

The Auzel parameter (N_V) is a measure of the ligand field strength.[26] In this work this parameter was calculated by considering the maximum Stark splitting of the $^7F_1$ level. The results show that the ligand field strength in the dithiocarbamate complexes increases with the bond covalency. This behavior is in qualitative agreement with ligand field models that consider covalency effects, as the angular overlap model,[27] the covalo-electrostatic model[28] and the simple overlap model.[21]

The Judd−Ofelt intensiy parameters Ω_2 and Ω_4 (the Ω_6 parameter was not determined because the $^5D_0 \rightarrow {}^7F_6$ transition could not be detected), determined from the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively, by taking the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ as the reference,[26] did not present significant changes by changing the ligands. However, Ω_2, as expected, increases with covalency.[29] The intensity parameters were used to determine the radiative rates, via the Judd−Ofelt theory, assuming a refraction index of 1.5 in the Lorentz's local field correction.

The quantum efficiencies, η, for the dithiocarbamate complexes were determined from the ratio between the radiative decay rate and the total decay rate (the inverse of the measured lifetime). The Eu(III) dithiocarbamate complexes presented very low efficiencies highly dependent on the temperature.

The rationalization of the experimental data, presented in this section, in terms of correlations between spectroscopic parameters and electronic structure of the complexes will be described in the following section.

4.2. Theoretical Results and Discussion. As indicated in Figure 4, the special feature of the dithiocarbamate ligand is an additional π-electron flow from the nitrogen atom to the sulfur atoms via a planar delocalized π-orbital system. As a result of this heuristic description for the dithiocarbamate molecule, a strong electron donation capacity is expected, resulting in a high electron density on the Eu(III) neighborhood. The covalency of the ligand−Ln(III) bond and, consequently, the LMCT states may depend on this fact. In this way, if the R group bonded to the nitrogen atom is an electron donor, the resonance form **2** will be stabilized and, consequently, a higher covalency is expected. On the other hand, if R is an electron acceptor, form **1** will be stabilized and a lower covalency is expected.

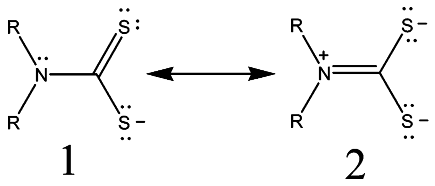

Figure 4. Resonance structures for a generic dithiocarbamate ligand.

TABLE 3: Caulculated Atomic Charges, Bond Distances and Orbital Energies for the Dithiocarbamate Ligands

		$Et_2NCS_2^-$	$Ph_2NCS_2^-$
charge in the S atoms (a.u)	AM1	−0.52	−0.44
	HF/6-31G*	−0.51	−0.47
charge in the N atom (a.u)	AM1	−0.30	−0.23
	HF/6-31G*	−0.57	−0.74
distance bond of C−S (Å)	AM1	1.65	1.63
	HF/6-31G*	1.72	1.70
distance bond of $N-CS_2$ (Å)	AM1	1.40	1.42
	HF/6-31G*	1.36	1.38
energy of HOMO (eV)	AM1	−3.3	−3.7
	HF/6-31G*	−3.0	−3.1
energy of LUMO (eV)	AM1	4.7	3.1
	HF/6-31G*	8.2	6.3

The ethyl group, as well as other alkyl groups, acts predominantly as a weak donor for a π-system, via hyperconjugation.[30] On the contrary, the phenyl group acts as an electron acceptor, attracting the electronic pair of the nitrogen into the aromatic ring. To check the validity of this reasoning, molecular orbital calculations at both semiempirical and ab initio levels for the $Et_2NCS_2^-$ and $Ph_2NCS_2^-$ ligands were performed. Some relevant properties obtained from these calculations are shown in Table 3.

The molecular orbital calculations indicate, through the bond lengths C−S and $N-CS_2$ and through the atomic charges on the N and S atoms, that the stabilization of the form **2** and, consequently, of the electron donation, is increased when the Ph ligand is substituted by Et. This fact is in agreement with the relative energy position of the LMCT band as well as with the covalency, ligand field strength and intensity parameters obtained for the complexes [$Eu(Et_2NCS_2)_3$phen] and [$Eu(Ph_2NCS_2)_3$phen].

High level ab initio molecular orbital calculations cannot be easily performed for large lanthanide coordination compounds. However, a semiempirical scheme that combines the Sparkle/AM1[16] and the INDO/S-CI[17] models has been used with considerable success in the calculation of the geometries and the electronic structures of the coordinated ligands of many lanthanide complexes.[31] This scheme was utilized in this work and the coordinates of the lanthanide first coordination sphere obtained via the Sparkle/AM1 are shown in Table 4.

In all cases, Eu(III) is octacoordinated and has a distorted antiprismatic geometry, as determined experimentally for the diethyldithiocarbamate complexes.[25] The average errors in the prediction of distances were 15% for the Eu−S distances and only 1% for the Eu−N distances. The larger error in the prediction of the S coordinated bond is probably due to covalency effects not included in Sparkle/AM1.[16] However, this error is not higher than those observed in DFT calculations for some lanthanide complexes.[32]

From the polyhedrons presented in Table 4 we were able to proceed with a theoretical calculation of the quantities Ω_λ^{ed} that were used in the calculations of the energy transfer rates. These quantities depend on the so-called charge factors g_j appearing in the simple overlap model for the ligand field and cannot be directly compared with the experimental Ω_λ parameters, once these latter contain additional contributions from the dynamic coupling mechanism.[22] In view of the complexity of the ligand field effects in the studied complexes, in the calculations of the Ω_λ^{ed} quantities the g_j's were taken as freely varying parameters, with values selected from the best theoretical results obtained for the N_V parameters in comparison with the experimental ones. The obtained best theoretical values are shown in Table 5.

TABLE 4: Spherical Atomic Coordinates for the Coordination Polyhedra Calculated from the Sparkle Model for the Investigated Complexes

	atoms	R (Å)	θ (deg)	ϕ (deg)
$Eu(Et_2NCS_2)_3$bpy	S1	2.377	97.5	14.8
	S2	2.397	81.6	75.2
	S3	2.370	136.7	281.1
	S4	2.401	149.5	163.9
	S5	2.407	96.3	132.0
	S6	2.379	64.9	187.9
	N8	2.535	63.1	291.9
	N9	2.541	9.5	33.6
$Eu(Et_2NCS_2)_3$phen	S1	2.370	86.9	358.0
	S2	2.401	97.1	59.3
	S3	2.377	13.0	268.4
	S4	2.397	55.8	152.6
	S5	2.379	162.1	161.0
	S6	2.407	104.6	118.6
	N8	2.535	100.6	284.8
	N9	2.541	96.9	218.4
$Eu(Ph_2NCS_2)_3$phen	S1	2.368	90.0	0.0
	S2	2.402	90.0	61.8
	S3	2.377	18.9	283.3
	S4	2.394	49.5	158.0
	S5	2.377	155.7	148.4
	S6	2.405	96.6	120.2
	N8	2.533	111.9	287.3
	N9	2.538	97.8	220.4

TABLE 5: Intensity Parameters (Eq 1, in Units of 10^{-20} cm^2) and Ligand Field Parameters (Eq 2, in cm^{-1}) Calculated for the Eu(III) Dithiocarbamate Complexes (ed = Eletric Dipole Contribution Only)

	[$Eu(Et_2NCS_2)_3$bpy]	[$Eu(Et_2NCS_2)_3$phen]	[$Eu(Ph_2NCS_2)_3$phen]
g_S	2.2	2.2	2.0
g_N	1.7	0.3	0.3
Ω_2^{ed}	6.0	12.4	10.1
Ω_4^{ed}	0.4	0.4	0.3
Ω_6^{ed}	0.4	0.3	0.2
N_v	839	942	532

TABLE 6: Calculated Singlets and Triplets Levels of the Ligands for the Investigated Complexes

	[$Eu(Et_2NCS_2)_3$bpy]	[$Eu(Et_2NCS_2)_3$phen]	[$Eu(Ph_2NCS_2)_3$phen]
S1	26337	26313	26120
S2	26433	26396	26902
S3	26746	26738	27035
S4	30629	30309	29337
T1	18697	20112	23118
T2	24460	22550	23787
T3	24644	24187	24272
T4	25440	25466	26162

The obtained values for N_V are in good agreement with the experimental ones. Furthermore, the relative order of the best g_j values for the ligands Et_2NCS_2 and Ph_2NCS_2 is consistent with the expected donation capacities of these ligands, as discussed above. These facts indicate that the selected g_j values can be considered as reliable for our purposes. Table 6 presents the energies of the first four singlet and triplet excited states of the coordinated ligands, obtained via the INDO/S-CI, as described earlier.

In accordance with the experimental results presented in the previous section, the INDO/S-CI calculations show two distinct sets of singlet and triplet states, one at lower energy (the first three singlets and triplets) located in the dithiocarbamate ligands and another one (the forth singlet and triplet) at higher energy located predominantly on the heterobiaryl ligands. The INDO/S-CI results place the first singlet and triplet excited levels within 9% and 16% with respect to the experimental ones, respectively, and are thus of enough accuracy to be useful to confirm our previous spectroscopic assignments. However, for the specific case of our quantitative analysis of the photoluminescence process, we suspect that this accuracy is not sufficient and, for this reason, we have preferred to use the experimental values of the energy levels.

To determine the mechanism involved in the photoluminescence process in the studied complexes, we have computed both transfer and back transfer rates between the ligand centered, 4f and LMCT states, as well as the photoluminescence quantum yield q, according to the equations previously described in refs 14 and 31. This quantity is defined as the ratio between the number of photons emitted by the Eu(III) ion and the number of photons absorbed by the ligand and should not be confused with the quantum efficiency η, described above.[33,34] In these calculations we have used typical values for $\hbar\gamma_L$ equal to 3000 cm^{-1}, for both the ligand centered and LMCT states,[14,31] and R_L equal to 2 and 3.5 Å, for the ligand and LMCT state, respectively, which have been estimated from the geometry given by the sparkle model and electronic densities given by the INDO/S-CI.[14,19] The values of the transition rates (radiative and nonradiative) involved were chosen according to typical values that have been used in several specific cases.[22,31] The values of decay rates considered in the ligands were 10^8 s^{-1} for the intersystem crossing singlet → triplet, and 10^6 s^{-1} for the intersystem crossing triplet → singlet and for the internal conversion singlet → singlet. Nonradiative decay rates in the lanthanide ion were also taken as 10^6 s^{-1}, except for the $^5D_0$ level, for which the inverse of the lifetime at 77 K was taken due to the large energy gap between this level and the ^7F_J manifolds.[14,22,31] Except for the $^5D_0 \rightarrow {}^7F_J$ transitions, in which the experimental total radiative rate A_{rad} was used, all radiative decays were neglected. According to our knowledge, decay rates from LMCT states in Eu(III) complexes have not been determined, because fluorescence from these states in general cannot be experimentally detected. However, indirect evidences indicate that their values are higher than 10^7 s^{-1}.[10] In view of the complexity to determine these rates, they were treated as freely varying parameters, with values selected to describe the experimental ratios between the quantum efficiencies at 77 and 300 K, obtained for the complexes [Eu(Et_2NCS_2)$_3$phen] and [Eu(Ph_2NCS_2)$_3$phen]. The estimated values were 5×10^7 and 4×10^{11} s^{-1} for $Et_2NCS_2^-$ and $Ph_2NCS_2^-$, respectively. The relevant energy transfer rates as well as the calculated quantum yields are shown in Table 7.

TABLE 7: Calculated Energy Transfer Rates (W_{ET}), Back-Transfer Rates (W_{bET}) and Quantum Yields (q) for the Investigated Complexes

		[Eu(Et_2NCS_2)$_3$bpy]				[Eu(Et_2NCS_2)$_3$phen]				[Eu(Ph_2NCS_2)$_3$phen]			
		300 K		77 K		300 K		77 K		300 K		77 K	
		log(W_{ET})	log(W_{bET})	log(W_{ET})	log(W_{bET})	log(W_{ET})	log(W_{bET})	log(W_{ET})	log(W_{bET})	log(W_{ET})	log(W_{bET})	log(W_{ET})	log(W_{bET})
heterobiaryl	S → $^5D_4$	7.4	−3.2	7.4	<−15	8.5	7.7	8.5	6.3	8.5	7.5	8.5	5.5
	S → $^5D_3$	8.9	−8.7	8.8	<−15	10.9	4.3	10.9	<−15	10.9	4.1	10.8	<−15
	S → $^5D_2$	8.7	11.1	1.6	11.1	5.3	10.9	−11.0	10.9	6.0	11.0	−8.3	11.0
	T → $^5D_2$	3.0	−0.3	3.0	−10.1	3.1	2.5	3.1	0.9	3.1	2.3	3.1	−0.2
	T → $^5D_1$	11.1	2.4	11.1	<−15	11.4	5.3	11.4	−12.6	11.4	5.3	11.4	−12.3
	T → $^5D_0$	10.7	−1.5	8.6	<−15	11.2	2.0	9.4	<−15	11.1	1.3	8.9	<−15
$R_2NCS_2^-$	S → $^5D_3$	9.8	11.2	5.6	11.2	11.2	7.9	11.1	−1.5	9.6	11.2	4.9	11.2
	S → $^5D_2$	9.5	5.1	9.5	−7.6	8.9	−0.5	8.9	<−15	9.5	5.3	9.5	−6.8
	S → $^5D_1$	11.4	1.7	11.4	<−15	10.4	−4.6	10.4	<−15	11.5	2.1	11.5	<−15
	S → $^5D_0$	11.0	−2.3	9.1	<−15	9.9	−8.3	8.1	<−15	11.0	−2.1	9.0	<−15
	T → $^5D_3$	−0.6	10.3	<−15	10.3	1.5	10.6	<−15	10.6	3.5	10.8	<−15	10.8
	T → $^5D_2$	−2.1	2.9	<−15	2.9	0.2	3.1	−8.0	3.1	1.7	3.1	−2.5	3.1
	T → $^5D_1$	11.7	11.3	11.7	10.3	11.6	8.9	11.6	1.0	11.6	7.8	11.6	−3.1
	T → $^5D_0$	11.7	7.9	9.7	−5.3	11.6	5.8	9.8	−12.8	11.4	3.9	9.2	<−15
LMCT	S → LMCT	10.4	−2.3	10.4	<−15	10.3	−4.0	10.3	<−15	10.9	5.3	10.9	−11.0
	T → LMCT	11.0	7.7	11.0	−1.9	11.0	9.1	11.0	3.6	11.0	11.0	11.0	11.0
	$^5D_4$ → LMCT	4.8	<−15	4.8	<−15	6.0	−11.1	6.0	<−15	6.9	−6.5	6.9	<−15
	$^5D_3$ → LMCT	9.2	−5.0	8.6	<−15	10.3	−0.6	10.2	<−15	10.8	3.6	10.8	<−15
	$^5D_2$ → LMCT	8.8	0.4	8.8	<−15	9.1	4.4	9.1	−9.4	9.3	7.8	9.3	3.6
	$^5D_1$ → LMCT	10.6	7.6	10.6	−1.0	10.9	11.7	8.5	11.7	7.8	11.6	−3.1	11.6
	$^5D_0$ → LMCT	11.3	11.8	7.9	10.0	7.9	11.8	−5.1	10.1	3.9	11.4	<−15	9.5
q (%)		0.0		0.1		10.4		4.3		10.5		3.0	

Our results indicate that in all cases an efficient energy transfer process ligand → Eu(III) occurs, as observed in many complexes with high luminescence quantum yield.[19,22,31] On the other hand, in the present case, an efficient energy transfer process from both 4f states and ligand-centered states to the LMCT states takes place. As the LMCT states for the complexes [Eu(Et_2NCS_2)$_3$phen] and [Eu(Ph_2NCS_2)$_3$phen] are slightly above the $^5D_1$ and $^5D_0$ levels, the strong dependence of the photoluminescence on the temperature is governed mainly by the channels $^5D_{1,0}$ → LMCT, as can be observed from the corresponding energy transfer rates calculated at 300 and 77 K. The complex [Eu(Et_2NCS_2)$_3$bpy] presents, in comparison with the other two complexes, a lower luminescence efficiency and a weaker dependence on the temperature, because the LMCT state in this complex lies below both $^5D_1$ and $^5D_0$ levels. In this case, according to our theoretical model, the temperature dependence is associated with the thermal population of the $^7F_1$, for which the selection rules on the J quantum number allow an energy transfer process through the exchange mechanism.[14]

The energy transfer process involving 4f and LMCT states has been described in several papers,[9,10] in contrast to the case ligand → LMCT energy transfer process. As shown theoretically in ref 14, this latter process constitutes an efficient luminescence quenching channel.

The theoretical description of both luminescence sensitization via the "antenna effect" and the quenching produced by the LMCT state is in agreement with the experimental results previously described. The emission quantum yield q is approximately equal to the emission efficiency η when an efficientenergy transfer process in the complex takes place, which is usually the case for lanthanide complexes. In this context, the relative value of the quantum efficiency for the Eu(III) dithiocarbamate complexes as well as its dependence with the temperature could be satisfactorily modeled by our theoretical approach.

5. Conclusions

For the first time, photoluminescence in Eu(III) dithiocarbamate complexes could be detected at room temperature. For the complexes [Eu(Et_2NCS_2)$_3$phen], [Eu(Et_2NCS_2)$_3$bpy] and [Eu(Ph_2NCS_2)$_3$phen] investigated in the present work, correlations between the electronic structure of the dithiocarbamates ligands and covalency, intensity and ligand field spectroscopic parameters could be observed. The relative values of the emission quantum efficiencies obtained for these complexes, as well as their dependence with temperature, could be satisfactorily described by the theoretical methodology recently developed.[14]

The present work might be useful as a starting point for future works involving this methodology for systems in which the LMCT states may act as an efficient luminescence quenching channel. Furthermore, it might serve as a starting point for other research involving photoluminescence in the uncommon lanthanide sulfur-coordinated complexes, thus contributing to a better knowledge of the chemical bond and, consequently, of the chemical properties of these complexes.

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