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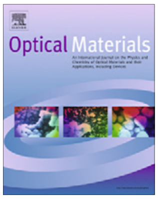

New complexes of europium and gadolinium with 2,4,6-trichlorophenyl acetoacetate as ligand

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ABSTRACT

The synthesis, characterization and photoluminescent properties of new europium complexes with 2,4,6-trichlorophenyl acetoacetate (TCA) and 3-amino-2-carboxypyridine-N-oxide (picNO) ligands have been investigated. Results of the characterization are in agreement with the molecular formula proposed. The emission spectra at 77 K of the $[Eu(TCA)_2(H_2O)_5]OH$ and $[Eu(TCA)_2(picNO)(H_2O)_2]OH$ complexes, excited at 333 nm, display the typical transitions of the europium ion, $^5D_0 \rightarrow {}^7F_J$ (J = 0–4), indicating an efficient luminescence sensitization of this ion by the TCA ligand. The satisfactory agreement between experimental and theoretical absorption spectra of the organic part of the complexes suggests that the geometries optimized by the Sparkle model are correct. These results suggest these complexes as potential candidates as useful markers.

1. Introduction

Complexes of the lanthanides with β-ketoester ligands are little discussed in the literature, despites the fact that these ligands can act as good sensitizers for lanthanide ions [1]. Besides, their similarities with β-diketone ligands suggest that these ligands can lead to promising light-conversion molecular devices. The luminescence in these complexes is particularly efficient as a result of a ligand-to-metal intramolecular energy transfer process. The 4f–4f luminescence efficiency is further improved by replacing water molecules by other ligands in order to avoid highly operative non-radiative decay channels from the emitting level. To this end a special class is represented by N-oxide ligands [2]. Several complexes with different ligands have been synthesized in the last years increasing the number of the applications and the areas where these compounds can be utilized [3–7].

The influence of the chemical environment on the $4f^N$ configurations is of paramount importance when the spectroscopic and magnetic properties of these complexes are investigated. In this context theoretical chemistry has, in recent years, considerably contributed to the design of new lanthanide complexes [8], particularly to the elucidation of the structures of complexes that have not been characterized by X-rays diffraction [4], a point that is crucial in theoretical studies of ligand field and 4f–4f intensities [9].

The energies of chemical bonds in the lanthanide complex are stabilized mainly by the attractive spherical component of the Coulomb interaction between the lanthanide ion and the ligands. Recently a new scale of covalency [10,11] was developed considering the concepts of the overlap polarizability (α^*_{op}) and specific ionic valence in which the degree of covalency can be inferred. This scale proved to be related to the nepheleuxetic effect, defined as the red shift observed in the 4f–4f transitions with respect to the free ion, allowing to estimate the degree of covalency of the bonding in europium complexes.

This paper reports the synthesis, characterization and spectroscopic study of the new europium and gadolinium complexes with the 2,4,6-trichlorophenyl acetoacetate (TCA) and 3-amino-2-carboxypyridine-N-oxide (picNO) ligands. The ground state geometries, the theoretical intensities parameters and absorption spectra of the organic part of the complexes, and the nepheleuxetic effect were investigated.

2. Experimental

The europium chloride was obtained by dissolving its respective oxide in chloride acid followed by drying. The $[Ln(TCA)_2(H_2O)_n]OH$ compounds, Ln = lanthanide, were synthesized by dissolving 1 mmol of europium chloride in triethylorthoformate, then it was dried and dissolved in anhydrous tetrahydrofuran (THF). Subsequently, to the solution was added 2 mmol of ethyl 4,4,4-trifluoroacetoacetate deprotonated previously with the help of strong alkali in dried THF in an inert atmosphere. The compound was dried, neutralized with NH_4Cl, filtered, and washed with water and solvent to eliminate the lanthanide chloride and ligand excesses. The solid compound was dried under vacuum over silica in a

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desiccator. The compounds $[Ln(TCA)_2(picNO)(H_2O)_n]OH$ were obtained by the reaction between the compound $[Ln(TCA)_2(H_2O)_n]OH$ precursors with the picNO ligand in the molar ratio 1:1 of precursor compounds dissolved in ethanol. The compounds were also soluble in methanol and chloroform.

The complexes were characterized by means of chemical analysis, IR vibrational, UV–visible absorption and luminescence spectroscopies. The IR spectra were recorded using a KBr pellet and a spectrophotometer ($4000–400\ cm^{-1}$), BRUKER model IFS 66. The absorption spectra were recorded on a Perkin Elmer LAMBDA 6 UV–visible spectrophotometer.

For the luminescence spectra the samples were excited using a 150 W xenon lamp. The appropriate wavelength was 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 signals detected by a water-cooled RCA C31034-02 photomultiplier and processed by a Jobin Yvon Spectralink system. The excitation spectra were recorded by an EG&G Princeton Applied Research Boxcar, a Gated Integration model 4422 and processed by a model 4402. The excitation spectra of the solid samples were obtained with an ISS K2 multifrequency Cross-Correlation Phase and Modulation fluorometer using a 300 W continuous xenon arc lamp as excitation light source.

3. Theoretical

3.1. Ground-state geometries

It was not possibly to obtain samples in crystalline form, the complexes were dissolved in different solvents and solvent mixtures. After a slow evaporation of the solvent, however, the nucleation process was not favored and the complexes returned to the powder form. Therefore, we calculated the ground state geometries of the europium complexes.

The geometries of the complexes were calculated by using the Sparkle/AM1 model [12] implemented in the MOPAC93r2 package [13]. The MOPAC keywords used in all Sparkle/AM1 calculations were: GNORM = 0.25, SCFCRT = 1.D-10 (to increase the SCF convergence criterion) and XYZ (the geometry optimizations were performed in Cartesian coordinates). The results obtained from the geometries were used to calculate the theoretical absorption spectrum using the intermediate neglect of differential overlap/spectroscopic configuration interaction (INDOS/S-CIS) method [14,15] implemented in the ZINDO program [16]. In this calculation the trivalent europium ion is represented by a point charge +3e. The electronic spectra of the organic part of the complexes were determined from the singlet excited state energies and oscillator strengths of each TCA and picNO ligand. Absorption bands were adjusted to a Lorentzian-shaped curve, compatible with the bandwidth experimentally obtained (20 nm).

3.2. Intensities parameters

The intensity parameters, Ω_λ (λ = 2, 4 and 6), in the Judd–Ofelt Theory [17,18] are given by

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

where the $B_{\lambda tp}$ are the intensity parameters for individual transitions between Stark levels and they contain the contributions from both the forced electric dipole (ed) and dynamic coupling (dc) mechanisms:

$$B^{ed}_{\lambda tp} = \theta(t,\lambda)\gamma^t_p \tag{2}$$

and

$$B^{dc}_{\lambda tp} = -\left[\frac{(\lambda+1)(2\lambda+3)}{(2\lambda+1)}\right]^{1/2}\langle 4f|r^\lambda|4f\rangle(1-\sigma_\lambda)\langle f||C^{(\lambda)}||f\rangle\Gamma^t_p\delta_{t,\lambda+1} \tag{3}$$

The quantities γ^t_p (odd-rank ligand field parameters) and Γ^t_p (ligating atom polarizability dependent terms) in Eqs. (2) and (3) contain a sum over the ligating atoms involving a spherical harmonic of rank t (γ^t_p). The nature of the chemical environment and structural aspects in the first coordination sphere of the lanthanide ion are precisely taken into account in this sum. In Eq. (2), the numerical factor $\theta(t,\lambda)$ is a function of the lanthanide ion and in Eq. (3) the quantities $\langle 4f|r^\lambda|4f\rangle$, $(1-\sigma_\lambda)$ and $\left\langle f||C^{(\lambda)}||f\right\rangle$ are a radial integral, a shielding factor and a one electron reduced matrix element, respectively [17,18].

In the theoretical calculations we have used the spherical coordinates obtained from the geometry optimized by Sparkle Model. The isotropic polarizability (α) and the charge factor (g) of the donor atoms were treated within ranges of physical acceptable values assuming three types of oxygen ligating atoms (ketoester, water and picNO oxygen atoms). The calculations allow to obtain the contribution of each mechanism separately.

In order to determine the experimental intensity parameters we have used the following expression [8]:

$$\Omega_\lambda = \frac{3\hbar c^3 A_{0\lambda}}{4e^2\omega^3\chi\left\langle {}^7F_\lambda\left\|U^{(\lambda)}\right\|{}^5D_0\right\rangle^2} \tag{4}$$

where $\left\langle {}^7F_\lambda\left\|U^{(\lambda)}\right\|{}^5D_0\right\rangle^2$ is a squared reduced matrix element whose value is 0.0032 for the ${}^5D_0 \to {}^7F_2$ transition and 0.0023 for the ${}^5D_0 \to {}^7F_4$ one [19], and χ is the Lorentz local field correction term, given by $\chi = \frac{n(n^2+2)^2}{9}$. The index of refraction n has been assumed equal to 1.5.

The spontaneous emission coefficients, $A_{0\lambda}$, were obtained from the Eq. (5) below. The transition ${}^5D_0 \to {}^7F_1$ was used as the reference, once this it is practically insensitive to the chemical environment around the europium ion.

$$A_{0\lambda} = A_{01}\left(\frac{S_{0\lambda}}{S_{01}}\right)\left(\frac{\nu_{01}}{\nu_{0\lambda}}\right) \tag{5}$$

The quantities S_{01} and $S_{0\lambda}$ are the areas under the curves of the ${}^5D_0 \to {}^7F_1$ and ${}^5D_0 \to {}^7F_\lambda$ transitions, with ν_{01} and $\nu_{0\lambda}$ being their energy barycenters, respectively. The coefficient of spontaneous emission, A_{01}, in Eq. (5) is given by the relation $A_{01} = 0.31 \times 10^{-11}\,(n)^3(\nu_{01})^3$, leading to an estimated value around $50\ s^{-1}$ [8].

The emission quantum efficiency (η) of the ${}^5D_0$ level of the europium ion in the complex was determined by using the Equation (6). This quantity is defined as the ratio between the radiative decay rate and the total (radiative + multiphonon non-radiative) decay rate of the emitting level of the Eu^{3+} ion.

$$\eta = \frac{A_{rad}}{A_{rad}+A_{nrad}} \tag{6}$$

The quantity R02 represents the intensity ratio between the ${}^5D_0 \to {}^7F_0$ and ${}^5D_0 \to {}^7F_2$ transitions. This quantity gives information on the J-mixing effect associated with the ${}^5D_0 \to {}^7F_0$ transition.

4. Results and discussion

4.1. Synthesis of the lanthanide complex

The analysis of C, H and N found/calculated for the complexes gave: (%C 29.3/29.3;%H 3.0/2.8) to $[Eu(TCA)_2(H_2O)_5]OH$, (%C 29.0/29.0; 2.6/2.8) to $[Gd(TCA)_2(H_2O)_5]OH$ and (%C 34.2/34.4;%H 3.0/