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Optical properties of europium compounds of the formulae: $Eu(NCS)_3\cdot 2[N_4(CH_2)_6]\cdot 8H_2O$ and $Eu(NO_3)_3\cdot 2[N_4(CH_2)_6]\cdot 10H_2O$

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Abstract

Optical spectra of two types of europium compounds of the formulae: $Eu(NCS)_3\cdot 2[N_4(CH_2)_6]\cdot 8H_2O$ (1) and $Eu(NO_3)_3\cdot 2[N_4(CH_2)_6]\cdot 10H_2O$ (2) at room and low temperatures are reported. The probabilities of f–f transitions were analysed and their temperature dependencies were explained. Unusually high oscillator strength values were found, particularly for europium thiocyanate. Comparison of the spectroscopic properties of the powder disc sample with the single crystal spectra was made. Absorption and excitation spectra of the title compounds in the region of f–f and C–T transitions in the 4.2–293 K range were studied and the vibronic components were assigned on the basis of IR and Raman data. Temperature dependence of the relative intensities of luminescence lines was examined and luminescence quenching was considered. The decay times for deuterated and non-deuterated samples were measured and the non-radiative processes were analysed.

Keywords: Electronic spectra; Europium thiocyanate urotropine complexes.

1. Introduction

During the last period we have investigated the series of lanthanide nitrates and thiocyanates adducts with hexamethylenetetramine, examined the role of this molecule in modelling the structure of lanthanide complexes and studied the optical properties of these systems. It was found that the structure and composition of the lanthanide nitrates adducts change in whole series, and three groups of single crystals were characterised by X-ray, IR and electron spectroscopy [1–4]. The goal of our present studies is to see if similar relations could be observed in the series of lanthanide thiocyanates. Moreover, the role of hexamethylenetetramine solvent molecules and C–T state on the radiative and nonradiative processes in europium compounds will be analysed. Up to now the optical properties and X-ray data for neodymium representative were reported [2]. The temperature dependences of intensities of f–f transitions will be considered and electron–phonon coupling analysed. Comparison of the spectroscopic properties of europium thiocyanates with that of nitrate analogue will be made, too.

2. Experimental

Single crystals of the title compounds were obtained from aqueous and D_2O solutions according to the method described earlier [1,4].

The X-ray method was used to test the structure of compounds. The europium compound $Eu(NCS)_3\cdot 2[N_4(CH_2)_6]\cdot 8H_2O$ (1) crystallises in the $P2_1/n$ space group: two NCS^- ions are inner-sphere coordinated as it was found from preliminary diffraction studies [5]. Its neodymium analogue is isomorphic with the La one and crystallises in Pnma space group. The compound $Eu(NO_3)_3\cdot 2[N_4(CH_2)_6]\cdot 10H_2O$ (2) crystallises in $P2_1/c$ space group with $Z=4$ and C.N.=9 [6].

The absorption spectra were measured using a Cary-Varian 5 spectrophotometer at 4.2 K and 293 K. The intensities of optical lines were calculated using the TAUS program and transformed to oscillator strength values.

An Amico SPF-500 spectrofluorometer was used for recording the luminescence and excitation spectra at 293 K and 77 K.

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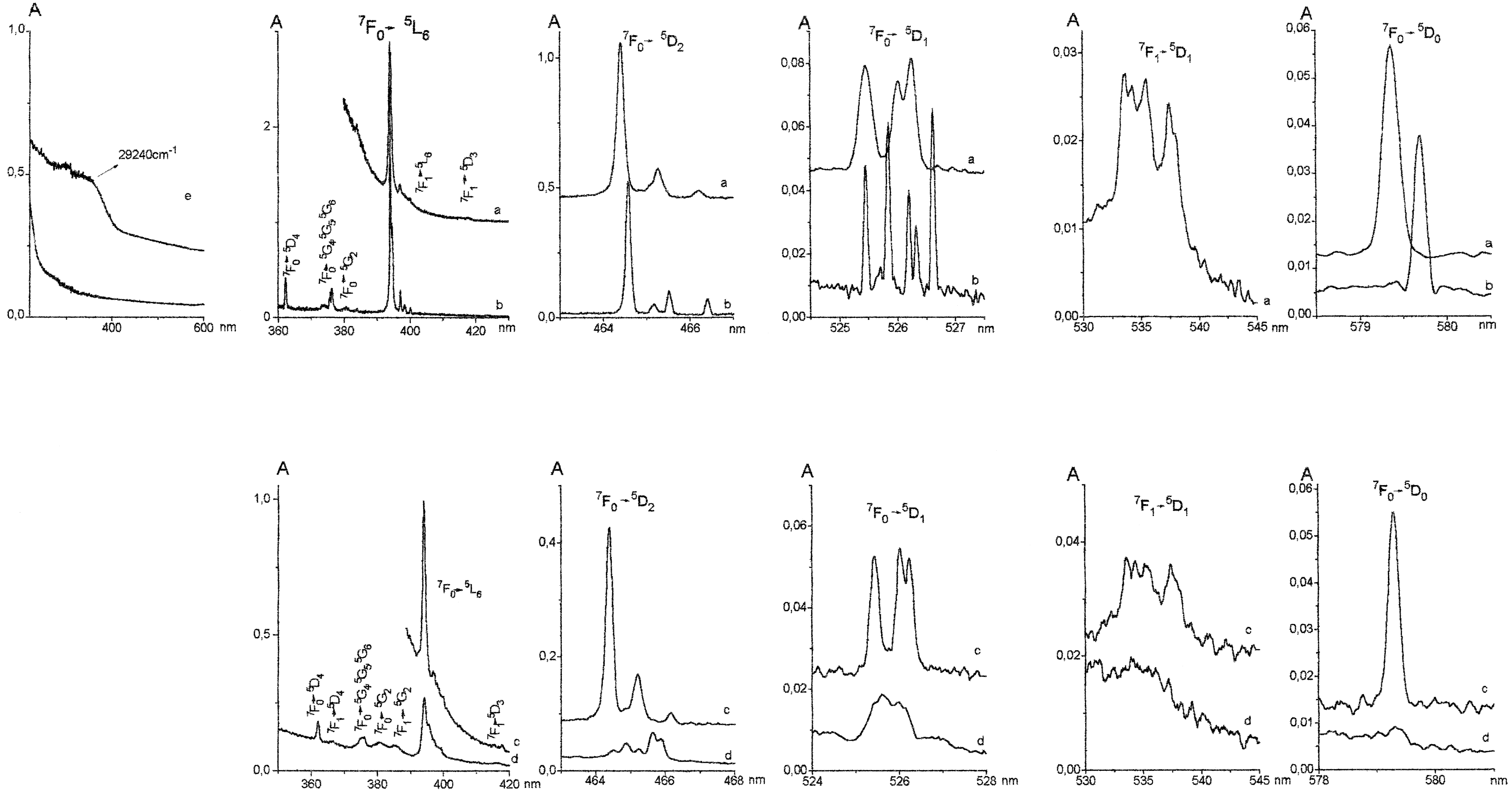

Fig. 1. The absorption spectra for $Eu(NCS)_3 \cdot 2[N_4(CH_2)_6] \cdot 8H_2O$: single crystal at 293 K ($d=0.113$ cm) (**a**), at 4.2 K ($d=0.066$ cm) (**b**), powder sample at 293 K (**c**) and for $Eu(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot 10H_2O$ in powder sample at 293 K (**d**); (**e**) the C–T band for $Eu(NCS)_3 \cdot 2[N_4(CH_2)_6] \cdot 8H_2O$ in paraffin oil compared to the ligand spectra.

Lifetimes were obtained using a Jobin Yvon THR 1000 spectrophotometer, a Hamamatsu R928 photomultiplier as a detector and a digital oscilloscope Tektronix TDS 380 for data collection. Decay curves deconvolution was done with a PSIPLOT software.

Raman spectra were measured at 293 K and 4.2 K in the 40–3000 cm^{-1} region with a Joel S1 spectrometer equipped with argon laser (C. Zeiss Jena).

3. Results and discussion

X-ray data of neodymium single crystals show asymmetric arrangement of water molecules and NCS^- ions in the first coordination sphere of the adduct with hexamethylenetetramine. Only two thiocyanate ions are inner-sphere coordinated, water molecules bring C.N. to 9 [7]. It looks similar to the europium adducts, where however C.N. is equal to 8 [5]. Thus, essential differences were found in two types of urotropine adducts of lanthanide nitrates and thiocyanates. This arrangement reflects in relatively high intensities of f–f transitions of this crystal [2].

Fig. 1 shows the absorption spectra of europium thiocyanate single crystal and powder sample in the range of f–f and charge–transfer (C–T) bands. The latter are located at a relatively low energy (29 240 cm^{-1}), comparable with C–T transition for simple europium thiocyanate in alcohol solution (28 900 cm^{-1}) [8]. In the spectra of aqueous solution of the Eu^{3+} ion, the charge–transfer band was observed too, but at higher energy (34 200 cm^{-1}) [8].

The f–f transitions were recorded from $^7F_0$ and $^7F_1$ levels to ^5D_J and $^5L_6$, ^5G_J ones at room temperature. The relatively strong $^7F_0 \rightarrow {}^5D_0$ transition points to a low symmetry of the system investigated. Splitting of the other bands confirms this kind of the symmetry, too. It is also well manifested in high intensities of electronic transitions, which are compiled in Table 1. A drastically high intensity for the hypersensitive one was observed, being almost four times higher than those reported by us for europium nitrate adduct [3]. Besides low symmetry, the observed changes of intensities could be the result of the differences in polarizability and anisotropy of the system under investigation (Eu–O;N bonds). ΔR for respective bonds in urotropine adduct of neodymium thiocyanate is 0.045. Similar changes in intensities were reported for the single crystal spectra of their neodymium analogues but those differences were not so significant [2].

Two opposite effects participate in the intensities of electronic transitions with lowering temperature in the europium spectra. A decrease of temperature leads to depopulation of $^7F_1$ level; as a result intensities of all transition from $^7F_0$ ground term increase. On the other hand, a decrease of temperature leads to decrease of intensities created by electron–phonon coupling and are involved in intensities of the bands integrated during the calculation procedure. The final effect of calculated intensities depends on these two aspects (see Table 1). In our spectra the former effect predominates.

Absorption spectra at 4.2 K are presented in Fig. 1 (bottom traces). 0–0 line is sharp (4 cm^{-1} half band width) pointing at one metal centre in the structure. On the other hand the $^7F_0 \rightarrow {}^5D_1$ transition (magnetic dipole origin) is composed of five sharp strong components. The number of components exceeds that expected for one metal centre in the structure. In an earlier report [3] we suggested the existence of two groups of the metal centre in the urotropine adduct of europium nitrate with a $P2_1/c$ space group and $Z=4$ at low temperature. However, in absorption spectra of this single crystal all bands are complex and composed of more components than expected for one site (see Fig. 2 in [3]). In now presented spectra the rest bands are not as complex as the $^7F_0 \rightarrow {}^5D_1$ one. The $^7F_0 \rightarrow {}^5D_2$

Table 1
The oscillator strength values of f–f transitions $P \cdot 10^{-8}$ for the $Eu(NCS)_3 \cdot 2[N_4(CH_2)_6] \cdot 8H_2O$ crystal at different temperature and for the powder samples of the title compounds[a]

$P \cdot 10^8$	$Eu(NCS)_3 \cdot 2[N_4(CH_2)_6] \cdot 8H_2O$			$Eu(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot 10H_2O$	
	Crystal		Powder	Crystal [3]	Powder
	293 K	4.2 K	293 K	293 K	293 K
$^7F_0 \rightarrow {}^5D_0$	0.60	0.67	5.98	0.09	0.78
$^7F_1 \rightarrow {}^5D_1$	7.68		39.36	1.24	21.30
$^7F_0 \rightarrow {}^5D_1$	1.82	2.47	13.71	1.41	10.90
$^7F_0 \rightarrow {}^5D_2$	17.00	18.95	92.46	4.90	57.51
$^7F_1 \rightarrow {}^5D_3$	4.70		24.72	4.83	32.55
$^7F_1 \rightarrow {}^5L_6$	6.85		44.05	6.81	40.82
$^7F_0 \rightarrow {}^5L_6$	197.06	430.27	704.51	197.29	969.62
$^7F_1 \rightarrow {}^5G_2$				34.70	195.38
$^7F_0 \rightarrow {}^5G_2$		27.92		35.81	242.93
$^7F_0 \rightarrow {}^5G_4, {}^5G_5, {}^5G_6$		90.48		37.40	228.95
$^7F_1 \rightarrow {}^5D_4$				4.56	34.77
$^7F_0 \rightarrow {}^5D_4$		73.06		24.20	202.28

[a] The lifetimes for non-deuterated and deuterated europium thiocyanate adducts with hexamethylenetetramine are 195.2 μs and 1840 μs, respectively.

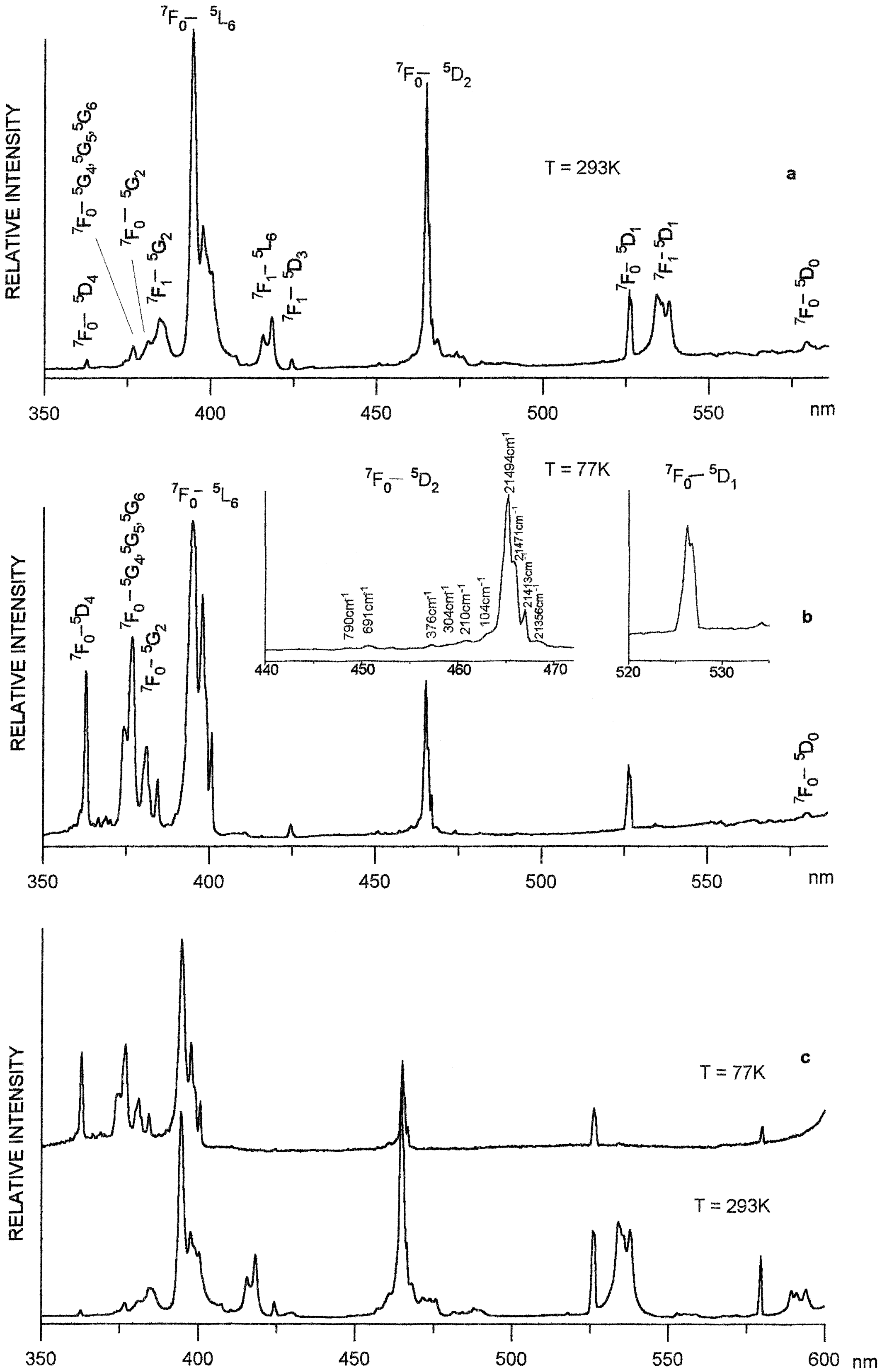

Fig. 2. The excitation spectra for $Eu(NCS)_3 \cdot 2[N_4(CH_2)_6] \cdot 8H_2O$ single crystal at 293 K (**a**) at 77 K (**b**) and in powder sample at 293 K; 77 K (c).

transition is split into four components shifted by ~7 cm^{-1} from respective components observed at 293 K. Thus, the nature of these additional levels needs future investigation of selective excitation spectra. They could belong either to traces of other lanthanide ions in crystals investigated (which was excluded by ICP AES analysis) or are the result of dynamics in solids with creation of high symmetry site. In this case 0–0 and 0–2 transitions are very weak or even not observable; the remaining components of higher levels are less split and unresolved in conditions of measurement.

Moreover, C–T transition is shifted drastically, at a low temperature to higher energy; thus, it well explains the role of this state in the Eu^{3+} emission quenching.

The absorption spectra of powder specimens of the same compositions as of the title compounds were measured in disc samples (see Fig. 1). The aim of that was to study the effect of crystal anisotropy with asymmetric arrangement of ligands. The structure of bands confirms well the same structure of compounds, but unexpectedly high intensities were obtained for all the transitions; corresponding oscillator strengths values are collected in Table 1. This increase of intensities of f–f transition in comparison to the single crystal spectra was observed by us in few cases [9,10], a similar phenomenon was reported by Solomon [11].

Let us analyse the excitation spectra for $Eu(NCS)_3 \cdot 2[N_4(CH_2)_6] \cdot 8H_2O$ at 293 K and 77 K (see Fig. 2.). The room temperature measurements show bands from the lowest ground state $^7F_0$ and from $^7F_1$ one, too. Therefore, the $^7F_0 \rightarrow {}^5D_1$ transition is assisted by very strong components $^7F_1 \rightarrow {}^5D_1$ transition, which is not observed at 77 K. It points to a relatively low ΔE between $^7F_0$ and $^7F_1$ levels, which leads to population of the first excited state at room temperature.

Inspection of the temperature dependence of electronic transitions probabilities in excitation and emission spectra suggests the role of C–T transition in the emission processes. An unexpected effect of lowering 0–0 transition intensities was found (see Fig. 3a at 77 K). A decrease of relative intensities $^5D_0 \rightarrow {}^7F_0 / {}^5D_0 \rightarrow {}^7F_1$ was also seen. It can be caused by some transformation of the crystal structure when lowering temperature. Moreover, complex structure of $^5D_0 \rightarrow {}^7F_1$ and $^7F_2$ bands in emission spectra indicates the resonance effect of vibrational modes with C–F Stark components of electronic levels. Confrontation of respective transitions to the levels with the same J in emission and excitation spectra seems to confirm such a

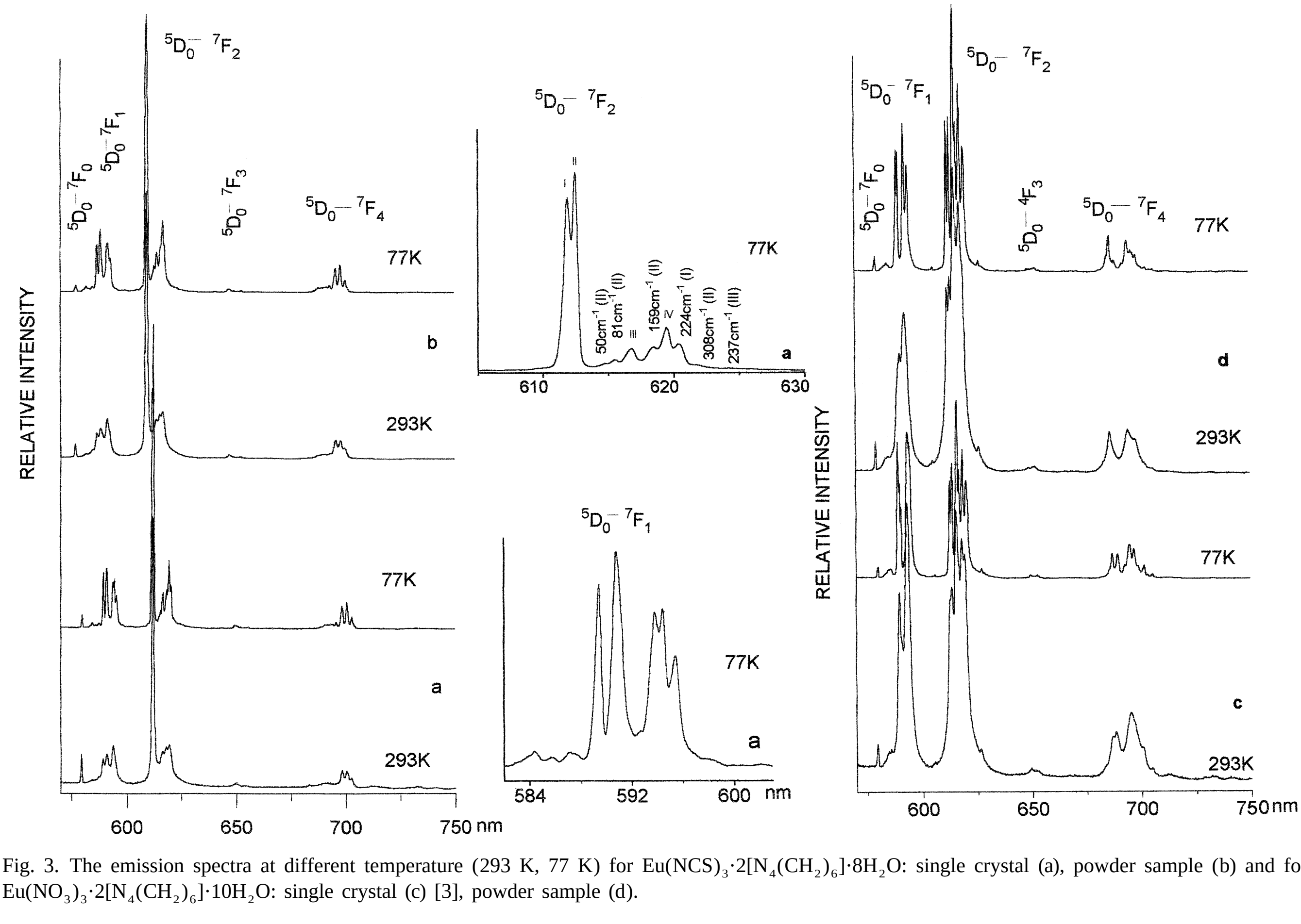

Fig. 3. The emission spectra at different temperature (293 K, 77 K) for $Eu(NCS)_3 \cdot 2[N_4(CH_2)_6] \cdot 8H_2O$: single crystal (a), powder sample (b) and for $Eu(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot 10H_2O$: single crystal (c) [3], powder sample (d).

phenomenon. Note that in excitation spectra the electronic transitions are less split, which is given by the lower resolution of the measurement. Note also the stronger vibronic components at the high energy range of electronic transitions than in the emission one, which is typical of this type of spectrum and indicates the role of C–T state in the electron–phonon coupling mechanism.

Again comparison of the above emission spectra with those for relevant nitrate adduct establishes drastic differences in their structures (see Fig. 3c and d).

Low temperature spectra permit the assignation of the vibronic components, both in the excitation and emission spectra on the basis of IR and Raman data (see Table 2). Some vibronic components can indicate the electron–phonon coupling with mode of urotropine molecules located in the outer sphere of metal ions. Analysis of vibronic components were also made in excitation spectra of urotropine analogue of europium nitrate (see Table 2) [12].

Table 2
The electronic and vibronic components in excitation and emission spectra of $Eu(NCS)_3 \cdot 2[N_4(CH_2)_6] \cdot 8H_2O$ and $Eu(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot 10H_2O$ [3] crystals at 77 K

	Energy [cm^{-1}]	ΔEnergy (from 0–phonon line) [cm^{-1}]	
	$Eu(NCS)_3 \cdot 2[N_4(CH_2)_6] \cdot 8H_2O$		
$^7F_0 \rightarrow {}^5D_0$	17 241		
$^7F_0 \rightarrow {}^5D_1$	18 984		
	19 002		
$^7F_0 \rightarrow {}^5D_2$	21 356		
	21 413		
	21 471		
	21 494		
	21 598	104	lattice mode
	21 704	210	γ (Eu–OH$_2$)
	21 798	304	γ (Eu–NCS)
	21 870	376	Δ CN$_{HMTA}$
	22 185	691	Δ CN$_{HMTA}$
	22 284	790	Δ CN$_{HMTA}$
$^5D_0 \rightarrow {}^7F_2$	16 343 I		
	16 328 II		
	16 276	52 (II)	lattice mode
	16 247	81 (II)	lattice mode
	16 213 III		
	16 169	159 (II)	δ (O–Eu–O)
	16 143 IV		
	16 119	224 (I)	ν (Eu–OH$_2$)
	16 084	259 (I)	ν (Eu–NCS)
	16 020	308 (II)	ν (Eu–NCS)
	15 976	237 (III)	ν (Eu–OH$_2$)
	$Eu(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot 10H_2O$		
$^7F_0 \rightarrow {}^5D_0$	17 241		
$^7F_0 \rightarrow {}^5D_1$	18 993		
	19 002		
$^7F_0 \rightarrow {}^5D_2$	21 322		
	21 379		
	21 448		
	21 471		
	21 657	186	δ (O–Eu–O)
	22 198	727	ν_3 (NO$_3^-$)
	22 485	1014	ν_2(NO$_3^-$); τ (CH$_2$)$_{HMTA}$
	22 766	1295	ν_1(NO$_3^-$); ω CH$_{HMTA}$

Let us return to the excitation spectra of europium thiocyanate at UV region and compare them with the absorption and powder spectra. Comparison of both the excitation spectra (at 293 K and 77 K) points to drastic differences in intensities of $^5D_2$ and $^5L_6$ levels. There are strong components in the 350–390 nm region at 77 K. It allows us to suppose about the role of the C–T band in the deexcitation process and emission quenching.

Judging from X-ray data one can expect strong quenching of Eu^{3+} emission by high energy OH vibration mode and by relatively high ν_{CN} modes. From this point of view some unexpected effects could be caused by hexamethylenetetramine molecules, which are involved in hydrogen bonds with OH_2, which leads to leakiness of this former mode in the quenching process; besides, it implies vibronic coupling also with urotropine modes.

From the decay rate measurement for deuterated and normal europium hydrate adduct the number of water molecules (four) was evaluated but without consideration of the multiphonon relaxation promoted by the C–N mode. Thus coordination number determined on this basis is to low and will be the subject of our further studies.

4. Summary

1. The oscillator strength values for $Eu(NCS)_3 \cdot 2[N_4(CH_2)_6] \cdot 8H_2O$ are higher than those for $Eu(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot 10H_2O$ crystal, especially for the hypersensitive transition $^7F_0 \rightarrow {}^5D_2$, pointing to lower symmetry and a lower anisotropy effect. Similar behaviour was observed for respective neodymium compounds.
2. Both for (1) and (2) europium compounds, significant increase in oscillator strength values was observed for powder samples in comparison to those for the single crystals.
3. Analysis of the absorption and excitation spectra of the two types of compounds indicates the role of charge–transfer (C–T) states in the quenching of europium emission.
4. Differences in the splitting pattern of the transition in absorption and emission spectra of europium compounds for the level with the same J allow us to consider the role of resonance effect in vibronic coupling.
5. The charge–transfer band of $Eu(NCS)_3 \cdot 2[N_4(CH_2)_6] \cdot 8H_2O$ crystal at 29 240 cm^{-1} was observed, similar to that of europium thiocyanate in aqueous (34 200 cm^{-1}) and non-aqueous (28 900 cm^{-1}) solutions.
6. The unexpectedly complex structure of $^7F_0 \rightarrow {}^2D_1$ and $^5D_0 \rightarrow {}^7F_1$ bands was observed at 4.2 K, being the result of dynamics in solids.

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