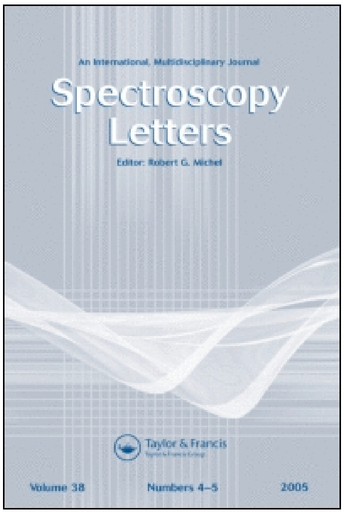

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LUMINESCENT PROPERTIES OF THE HEXAKIS(NITRITO)EUROPATE(III) ION $[Eu(NO_2)_6]^{3-}$

Keywords : europium, luminescence, site symmetry, lifetime, nitrite

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ABSTRACT

The 12-coordinated hexakis(nitrato)europate(III) ion displays a luminescence spectrum compatible with T_h symmetry, with essentially a single emission line at 16 873 cm^{-1} arising from the $^5D_0 \rightarrow {}^7F_1$ transition. At low temperature (4.2 – 170 K), the lifetime of the $^5D_0$ level amounts to 10.9 ms and then sharply decreases because of vibrational de-excitation processes (E_a = 2 250 ± 1 490 cm^{-1}). The forbidden $^5D_0 \rightarrow {}^7F_0$ transition displays an extensive pattern of Stokes and anti Stokes vibrational components and its energy reflects a nephelauxetic parameter for the nitrite ions $\delta_{O(NO_2)}$ equal to -14.4, slightly larger than the one associated to the nitrate ion in $[Eu(NO_3)_6]^{3-}$. The ligand excitation spectrum contains several bands displaying extensive vibrational structure mostly due to the $\delta(NO_2)$ vibrational mode.

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INTRODUCTION

With the exception of hexahalides of the elpasolite type and cubic oxides and sulfides, there are not many lanthanide compounds in which the Ln^{III} cation lies in a site with high symmetry, most of the coordination polyhedra being distorted with respect to the ideal geometry [1]. Hexakis(nitrato)lanthanate(III) ions have been found in many double salts and macrocyclic complexes [2], and their spectroscopic properties have been extensively studied [3-6], contrary to hexakis-(nitrito)lanthanate(III) ions [7] which have drawn far less attention. These anions have been investigated by Roser and Corrucini who have shown by magnetic susceptibility determination that the Ln^{III} cations lie in an unusual tetrahedral site with T_h symmetry and that no phase transition takes place between room temperature and 10 K [8]. In this communication, we present a detailed study of the excitation and emission spectra of $NaCs_2[Eu(NO_2)_6]$ in the temperature range 4.2-295 K, the results of which are consistent with a T_h site symmetry for Eu^{III}.

EXPERIMENTAL

$NaCs_2Eu(NO_2)_6$ was synthesized according to [8] and was characterized by Eu^{III} titration with Titriplex (Merck) and IR spectroscopy. A 2% Eu-doped Gd sample was also prepared. Excitation and emission spectra were recorded on a home-assembled high-resolution laser spectrofluorimeter previously described [9]. The emission spectra are corrected for the instrumental function, but not the excitation spectra. IR spectra were recorded on a Bruker IFS-113v Fourier transform spectrometer on polyethylene pellets (5%; lower limit : 25 cm^{-1}). Raman spectra were measured on a Ramalog-4 spectrometer from Spex industries on bulk samples placed in a capillary (lower limit 75 cm^{-1}).

RESULTS AND DISCUSSION

Under excitation at 425 nm (through the NO_2^- levels, *vide infra*), the emission spectrum of a solid sample of $NaCs_2[Eu(NO_2)_6]$ at 77 K is dominated by the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition which displays one sharp and symmetrical component at 16 873 cm^{-1}(full width at half height : 10 cm^{-1}), as expected for a Eu^{III} ion lying in a site with T_h symmetry (electric dipole transitions are forbidden). The remaining bands arise (i) from vibronic transitions, recognizable to their intensity increase upon increasing the temperature from 4.2 K to 295 K, and (ii) from weak magnetic dipole contributions to the electronic transitions to ^7F_J (J =0, 2-6). No emission band from the other excited states, $^5D_1$, $^5D_2$, $^5D_3$ or $^5D_4$, could be identified and similar spectra are obtained under excitation through the $^5D_0 \leftarrow {}^7F_1$ transition and for the Eu-doped Gd sample. The presence of numerous vibronic transitions prevented a precise analysis of these electronic components, although the spectral intensity could be integrated to determine the contribution of each transition to the total emission intensity. At 77 K, the relative intensity of the $^5D_0 \rightarrow {}^7F_J$ transitions amounts to 1.00, 0.21, 0.01, 0.04, 0.02, and 0.12 for J = 1, 2, 3, 4, 5, and 6, respectively. If vibronic transitions are also integrated, the combined intensity of these transitions and of the electronic transitions to ^7F_J with J = 0, 2-6 amounts to 44% of the total emission intensity.

The lifetime of the $Eu(^5D_0)$ level is long, 10.9 ms at 4.2 K, and temperature independent between 4.2 K and 170 K. The observed radiative rate constant k_{obs} = 92 s^{-1} contains three contributions : $k_{obs} = k_r + k_{nr} + k_{vibr}$. The radiative rate constant k_r may be estimated taking the proposed generic value of 50 s^{-1} for the radiative rate of the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ [10] : $k_r = 1.4x50 = 70$ s^{-1} since the contribution of $^5D_0 \rightarrow {}^7F_1$ to the total luminescence intensity (without vibronic contributions) is 1/1.4. If vibronic transitions are taken into account, we get $k_r + k_{vibr} = 88$ s^{-1}. The difference between the latter value and k_{obs} represents the contribution of the non-radiative processes other than vibrational de-excitation, k_{nr} = 4 s^{-1}. The decay of the $^5D_0$ excited state is therefore due for 76% to the radiative process, for 4 % to non-radiative processes and for 20% to de-excitation through vibronic contributions. This explains why the $Eu(^5D_0)$ lifetime decreases dramatically for temperatures higher than 170 K, reaching 0.28 ms at 295 K. This interpretation is substantiated by the lifetime of the Eu-doped Gd sample, where

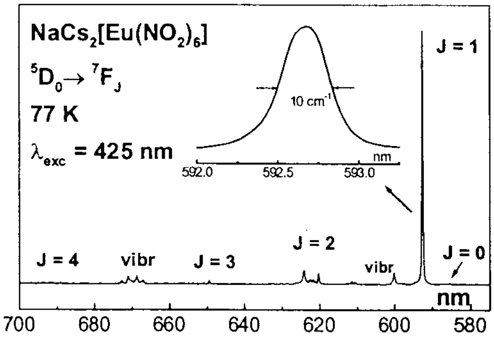

FIG. 1. Emission spectrum of $NaCs_2[Eu(NO_2)_6]$ at 77 K.

Eu^{III} ions are sufficiently isolated to avoid non-radiative processes, which amounts to 11.6 ms, corresponding to k_{obs} = 86 s^1 ≈ $k_r + k_{vibr}$ (Eu sample). Analysis of the temperature dependence of k_{obs} between 170 and 295 K according to the Arrhenius equation [11], $\ln(k\text{-}k_0) = \ln A - E_a/RT$ (k_0 is the rate constant at 4.2 K) yields $E_a = 2\ 250 \pm 140$ cm^{-1} (Fig. 2). This relatively large value indicates that several high energy vibrational modes from the nitrite ions are involved, for instance the ν_s, ν_{as}, δ_s, and δ_{as} vibrations. The IR and Raman spectra of $NaCs_2[Eu(NO_2)_6]$ are reported in Table 1, which clearly shows the complementary nature of the two set of data, expected for T_h symmetry : strong IR bands have weak or no Raman counterparts, and vice-versa.

The highly forbidden $^5D_0 \rightarrow {}^7F_0$ transition could be located at 17 235 cm^{-1} (77 K) by comparing the emission spectrum in the region 17 000-17 500 cm^{-1} with the excitation spectrum recorded upon monitoring the luminescence from $^5D_0 \rightarrow {}^7F_1$. The transition is accompanied by an extensive pattern of Stokes and anti-Stokes vibronic transitions. We note from Fig. 3 that the intensities of the vibronic transitions are larger in the excitation spectrum than in the emission spectrum, as often observed for Eu^{III} [12]. The analysis of the vibrational pattern is given in Table 2. Frey and Horrocks have recently proposed a correlation between the

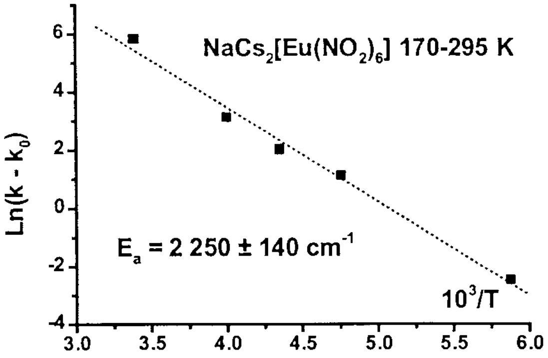

FIG. 2. Temperature dependence of the observed radiative rate constant.

TABLE 1

Identified Vibrations (200 – 2600 cm^{-1}) for $NaCs_2[Eu(NO_2)_6]$ along with their Assignment in T_h Symmetry.[a]

IR		Raman		Assignment [7]	
222	s			$\delta(NO_2)r$	T_u
		238	w		
248	w				
321	w	321	w		
838	s	839	w	$\delta(NO_2)sym$	T_u
		845	m	$\delta(NO_2)as$	E_g+A_g
1163	w				
1239	m			} $\nu(NO_2)sym$	T_u
1245, 1270sh	s	1255	w		
1332	w	1335	s	$\nu(NO_2)as$	E_g+A_g
1384	w				
		1866, 1961, 2353	b,w	combinations	
2560	w	2552	m	$2\nu(NO_2)$	

a) Key : as asymmetric, m medium, r rocking, s strong, sym symmetric, b broad, sh shoulder, w weak

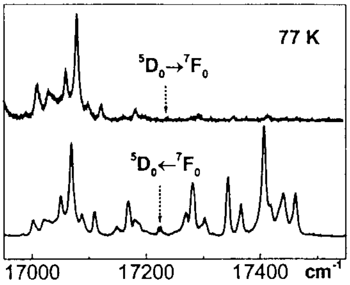

FIG. 3. Vibronic transitions associated to $^5D_0 \rightarrow {}^7F_0$ (top) and $^5D_0 \leftarrow {}^7F_0$ (bottom).

TABLE 2

Vibronic Transitions (cm^{-1} from the 0-0 transition, + = anti-Stokes, - = Stokes) in Spectra of $NaCs_2[Eu(NO_2)_6]$ at 77 K and Vibrational Transitions (295 K).

Excitation		Emission		IR	Raman
8	-4				
27	-25			26	
44	-44	45	-45	44	
55	-54	56	-56	54	
75	-74	77	-77	69w	77
116	-117	117	-116		116
137	-140	139		140w	137
		-140		162w	159
177	-178	177	-179	179	
210	-208	208	-209	222	
230	-229	228	-230		238
256	-248		-250	248	

energy of the 0-0 transition, that is the position of the $^5D_0$ level, and parameters describing the ability δ of coordinating atoms to produce a nephelauxetic effect :

$$\tilde{\nu} - \tilde{\nu}_0 = C_{CN}\sum_i n_i\delta_i$$

where C_{CN} is a coefficient depending upon the Eu^{III} coordination number (1.0 for CN = 9), n_i the number of atoms of type i, and $\tilde{\nu}_0$ = 17'374 cm^{-1} at 295 K [13]. We have checked the validity of this equation for $Mg_3Eu_2(NO_3)_{12}{\cdot}24H_2O$ the $^5D_0{\rightarrow}^7F_0$ transition of which occurs at 17 247 cm^{-1} [4], which translates to 17 256 cm^{-1} at 295 K ($\tilde{\nu}$ increases by approximately 1 cm^{-1} per 24 K). With C_{CN} = 0.75 for 12-coordination (the six nitrate ions are bidentate), and $\delta_{O(NO_3)}$ = -13,3 [13], we predict $\tilde{\nu}$ = 17 254 cm^{-1}, in very good agreement with the experimental value. For the hexanitrite, $\tilde{\nu}$(295 K) = 17 244 cm^{-1}, which leads, for 12-coordinate Eu^{III}, to $\delta_{O(NO_2)}$ = -14.4, a value only slightly larger than the one found for nitrate, but which points to a somewhat larger charge delocalization, that is a larger covalent contribution to the Ln-ONO bonding than in hexanitrates.

Finally, we have examined the excitation spectrum of $NaCs_2[Eu(NO_2)_6]$ in the range 300-550 nm (Fig. 4). It displays a sharp band at 18 897 cm^{-1} attributed to $^5D_1{\leftarrow}^7F_0$, a very weak $^5D_1{\leftarrow}^7F_1$ transition at 18 519 cm^{-1}, and two highly structured and broad bands in the ranges 480-360 and 360-300 nm (the cutoff at 300 nm is due to the excitation lamp used). Transitions of the nitrite ion alone (C_{2v} symmetry) originate from the $^1A_1$ level and end to the $^3B_1$ (22 500 cm^{-1}), $^1B_1$ (27 000 cm^{-1}), $^1A_2$ (34 000 cm^{-1}), and $^1B_1$ (46 000 cm^{-1}) levels [7]. For $[Ln(NO_2)_6]$ (T_h symmetry), the a_1 and b_1 orbitals of the nitrite ions give rise each to several levels (a_g + e_g + t_u), so that spectra with more transitions are expected. This is seen in the vibrational fine structure of the lower energy band which contains several vibrational progressions having different origins, pointing to the presence of several electronic transitions. The two more prominent series have approximately the same $\tilde{\nu}$(639 and 636 cm^{-1}) arising from the $\delta(NO_2)$ mode (838 cm^{-1} in the ground state, 632 cm^{-1} in the absorption spectrum of $NaNO_2$ [14]). The higher energy band also contains more than one vibrational progression, the principal one having $\tilde{\nu} \approx 560$ cm^{-1}.

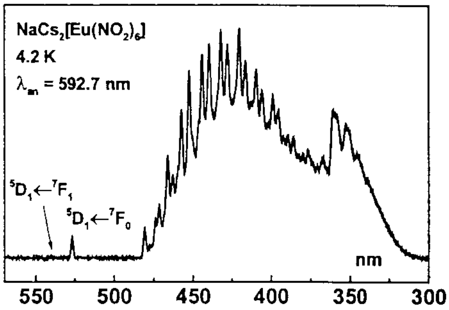

FIG. 4. Excitation spectrum of $NaCs_2[Eu(NO_2)_6]$ at 4.2 K (λ_{an} = 592.7 nm).

CONCLUSION

This photophysical and vibrational investigation of $[Eu(NO_2)_6]^{3-}$ has confirmed that the anion possesses a cubic T_h symmetry and that distortion of the skeleton through NO_2 vibrations is not large since the forbidden $^5D_0 \rightarrow {}^7F_J$ (J = 0, 2-6) transitions do not pick intensity. Moreover, the only allowed transition, $^5D_0 \rightarrow {}^7F_1$ has a weak intensity compatible with its magnetic dipole character and displays only a single, narrow band at all temperatures. The nephelauxetic parameter calculated for NO_2^- (-14.4) points to a 12-cordinated Eu^{III} ion with Ln-NO_2 bond slightly more covalent than the Ln-NO_3 one.

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