

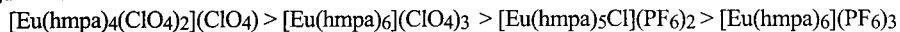
A Spectroscopic Study of Eu^{3+} / Hexamethylphosphoramide (hmpa) with Hexafluorophosphate and Perchlorate anions

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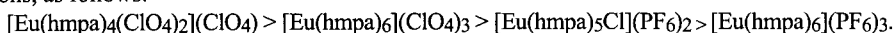
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Hexametilfosforamida (hmpa) é um ligante altamente coordenante às terras raras. Neste trabalho foram estudados os compostos de hmpa com Eu^{3+} , possuindo hexafluorofosfato (PF_6^-) e perclorato (ClO_4^-) como ânions. Os dados de luminescência a 77 e 298 K mostraram que a hipersensitividade da transição $^5\text{D}_0 \rightarrow ^7\text{F}_2$ do Eu^{3+} decresce devido a efeitos de simetria causados pelos ânions, na seguinte ordem:



Os tempos de vida da emissão $^5\text{D}_0 \rightarrow ^7\text{F}_2$ do Eu^{3+} mostraram um decaimento mais rápido para os compostos com ClO_4^- . Foi observada uma diferença estrutural no composto $[\text{Eu}(\text{hmpa})_6](\text{ClO}_4)_3$ quando a temperatura passou de 298 para 77 K. Com o abaixamento de temperatura os ClO_4^- se aproximam do íon Eu^{3+} , modificando a sua simetria e causando um rápido decaimento radiativo. A análise da transição $^7\text{F}_0 \rightarrow ^5\text{D}_2$ do Eu^{3+} , nos espectros de excitação, é útil no estudo das interações entre o íon metálico e seu ambiente nesses compostos.

Hexamethylphosphoramide (hmpa) is a high coordinating ligand for the rare earths. In this work we study the hmpa compounds synthesized with Eu^{3+} , having hexafluorophosphate (PF_6^-) and perchlorate (ClO_4^-) as anions. The luminescence data recorded at 298 and 77 K show a decrease in the hypersensitivity of the $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition due to symmetry effects promoted by the anions, as follows:



The lifetime data of the $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition show a faster radiation decay for the ClO_4^- compounds. In the $[\text{Eu}(\text{hmpa})_6](\text{ClO}_4)_3$ compound a structural change was noticed when the temperature was lowered to 77 K. With the temperature drop the perchlorates approach to the metal ion, modifying its symmetry and promoting a faster decay. The $\text{Eu}^{3+} \ ^7\text{F}_0 \rightarrow ^5\text{D}_2$ transition, in the excitation spectra, is used in order to get useful information about interactions between the metal and the surroundings in these compounds.

Keywords: $\text{Eu}^{3+}/\text{hmpa}/\text{PF}_6^-$ complex, $\text{Eu}^{3+}/\text{hmpa}/\text{ClO}_4^-$ complex, luminescence, lifetime

Introduction

The study of the coordination compounds of rare earths (RE) with hexamethylphosphoramide (hmpa) having perchlorate as an anion¹ revealed that perchlorate could coordinate to the metal ion replacing some hmpa. Therefore, it is interesting to study anions like hexafluorophosphate, tetrafluoroborate, perrenate etc., in order to observe the coordination properties of these ligands in different environments.

The electronic spectroscopy of the RE compounds is mainly the result of the transitions within the 4f configura-

tions. The luminescence lifetime is the time it takes an ion to decay from an excited state to the ground state^{2,3,4}. Changes in the environment can cause only a slight change in the position of the electronic transition lines; however, very different values in the luminescence lifetime have been observed^{5,6}.

The Eu^{3+} has been the most studied among the RE ions since its luminescence spectra possess a relatively small number of transitions. The Eu^{3+} has as the main emitting level the $^5\text{D}_0$ state. The maximum crystal field splitting is $2J + 1$ levels. In this work, the luminescence and lifetime data of the $[\text{Eu}(\text{hmpa})_4(\text{ClO}_4)_2](\text{ClO}_4)$, $[\text{Eu}(\text{hmpa})_6]$

(ClO₄)₃, [Eu(hmpa)₅Cl](PF₆)₂ and [Eu(hmpa)₆](PF₆)₃ at 77 and 298 K were studied with the aim of understanding their coordination and to systematize previous data⁷⁻¹⁰.

Experimental

Synthesis of [Eu(hmpa)₅Cl](PF₆)₂¹¹

The above compound was obtained by mixing the appropriate amounts of the methanolic solutions of NH₄PF₆ and EuCl₃ with hmpa. The product was recrystallized in acetonitrile and dried at room temperature in vacuo.

Synthesis of [Eu(hmpa)₆](PF₆)₃⁹

The ethanolic solution of Eu(ClO₄)₃ was added to KPF₆ in acetonitrile. After 24 hours at 6 °C the Eu(PF₆)₃ formed was filtered, and the hmpa was added to the solution. The compound which precipitated was separated from the supernatant and dried in dessicator.

Synthesis of [Eu(hmpa)₄(ClO₄)₂](ClO₄)¹²

The ligand hmpa was added to Eu(ClO₄)₃ in acetonitrile. The product was separated from the solution, recrystallized in ethanol and dried.

Synthesis of [Eu(hmpa)₆](ClO₄)₃¹²

The recrystallization of [Eu(hmpa)₄(ClO₄)₂](ClO₄) in acetonitrile (ε = 38) gave rise to [Eu(hmpa)₆](ClO₄)₃. This solvent allows better isolation of the [Eu(hmpa)₆]³⁺ from the counter-ions than ethanol (ε = 24).

Luminescence and lifetime data

The spectroscopic studies were all carried out in the SPEX-FLUOROLOG II spectrofluorometer at 77 K and 298 K. The luminescence data were obtained with a phosphorometer accessory model 1934D at 77 K and 298 K. All samples were sealed in glass capillary tubes (i.d. = 1 mm).

Vibrational data

The infrared spectra were also attained at 298 K on a Perkin Elmer 1430 and a FT IR Nicolet 5ZDX. The Raman spectra at 298 and 77 K kindly provided by Prof. I. Butler from McGill University, Montreal, Canada.

Results and Discussion

The excitation spectra of all the Eu³⁺ compounds are similar, and two strong excitation bands at 391 and 460 nm were observed.

The emission spectra of [Eu(hmpa)₅Cl](PF₆)₂, [Eu(hmpa)₆](PF₆)₃, [Eu(hmpa)₄(ClO₄)₂](ClO₄) at 77 K, and [Eu(hmpa)₆](ClO₄)₃ at 298 and 77 K are presented in Figs. 1, 2, 3, 4 and 5, respectively, at the excitation of 391.5 nm.

The areas of the Eu³⁺ ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F₂ transitions for all the emission spectra were obtained using the SPEX 3.12 software (Figs. 1 to 5). The ⁵D₀ → ⁷F₂ transition occurs through an electric dipole mechanism. It is considered hypersensitive since it changes easily with modifications in the surrounding environment. The ⁵D₀ → ⁷F₁ transition is magnetic dipole and changes very little due to structural alterations. So the ratio of the ⁵D₀ → ⁷F₂ /

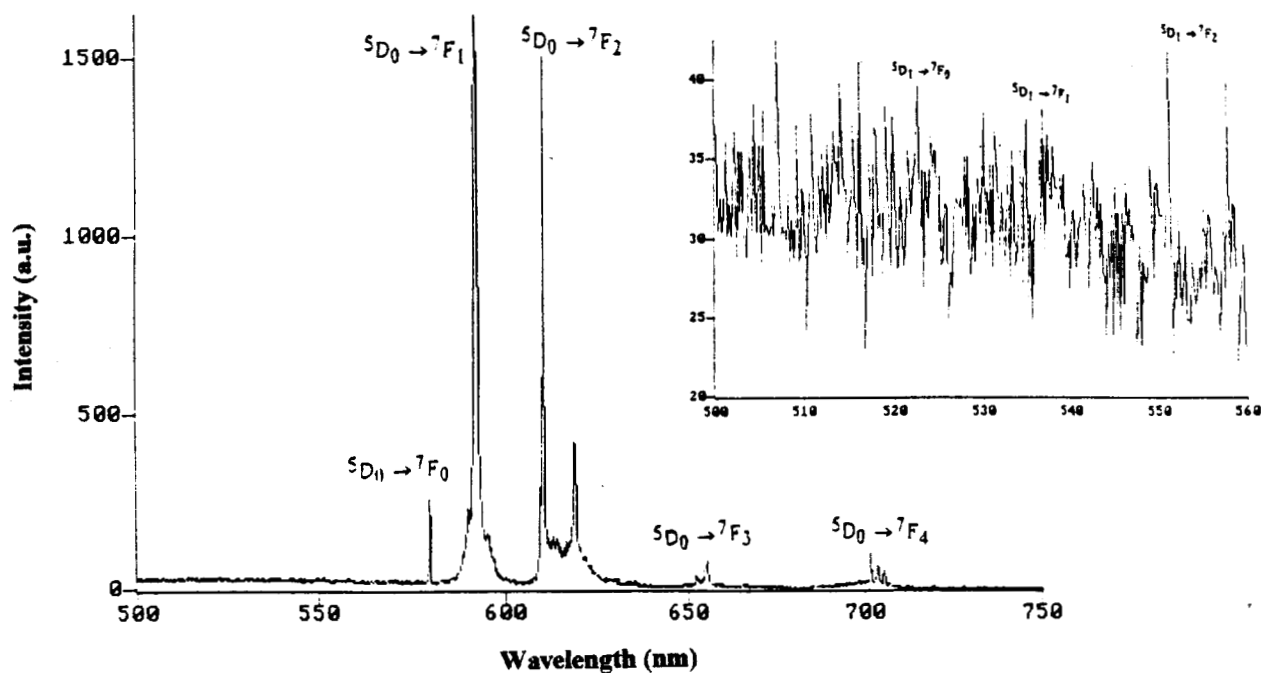


Figure 1. Emission spectrum of Eu³⁺ in the [Eu(hmpa)₅Cl](PF₆)₂ compound, λ_{exc.} = 391.5 nm, T = 77 K.

$^5\text{D}_0 \rightarrow ^7\text{F}_1$ areas gives us the hypersensitivity grade (η_{21})⁹. Table 1 shows η_{21} for the Eu^{3+} compounds at 77 and 298 K, where the variation of η_{21} with the symmetry effects (5 and 6 hmpa < 4 hmpa) can be seen.

The lifetime, τ (ms), of the $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition for the Eu^{3+} compounds, recorded at 77 and 298 K are also

presented in Table 1. ClO_4^- coordinated to Eu^{3+} promotes a shorter decay time due to the coupling of vibrational levels.

A change in the $[\text{Eu}(\text{hmpa})_6](\text{ClO}_4)_3$ structure was noticed. At 298 K ClO_4^- is in the second coordination shell. When the temperature is 77 K, ClO_4^- probably approaches

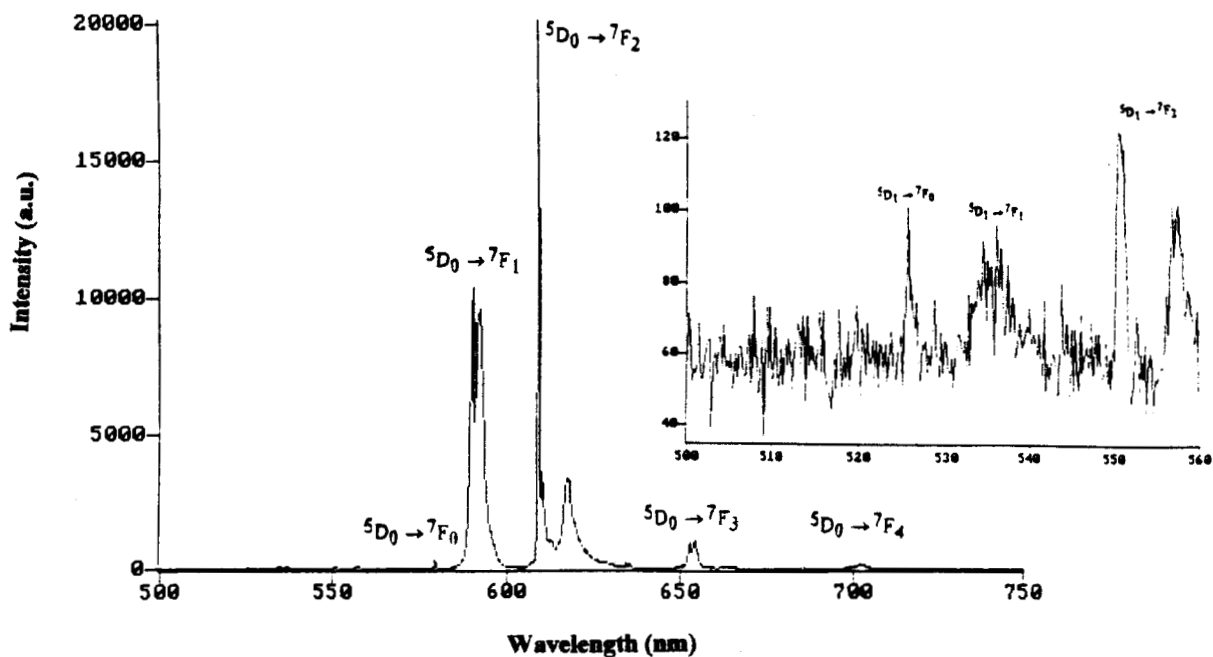


Figure 2. Emission spectrum of Eu^{3+} in the $[\text{Eu}(\text{hmpa})_6](\text{PF}_6)_3$ compound, $\lambda_{\text{exc.}} = 391.5$ nm, $T = 77$ K.

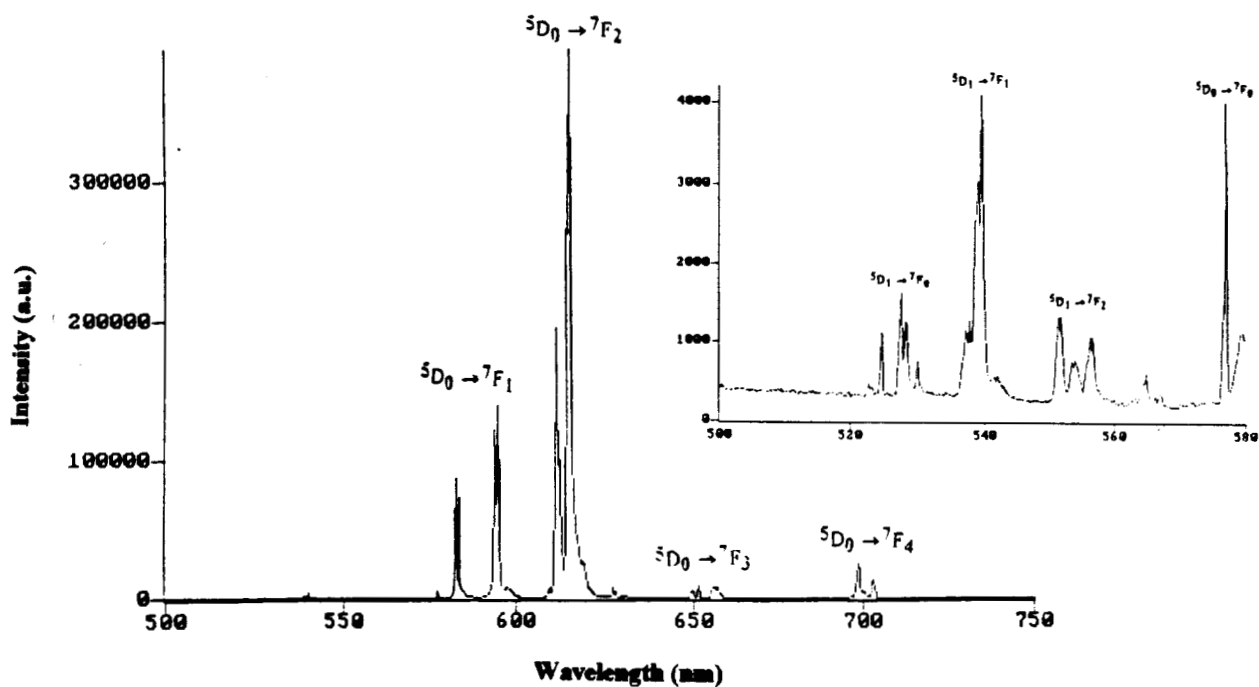


Figure 3. Emission spectrum of Eu^{3+} in the $[\text{Eu}(\text{hmpa})_4(\text{ClO}_4)_2]\text{ClO}_4$ compound, $\lambda_{\text{exc.}} = 391$ nm, $T = 77$ K.

Eu^{3+} supplying the first coordination shell. This is evidenced by the increase in η_{21} and the decrease in τ (ms) of this compound (Table 1). For the other compounds, a small change in the η_{21} was observed, while the lifetime (τ) made almost no change with the decrease in temperature.

Figure 6 presents the infrared spectra of the Eu^{3+} compounds. They confirm that the bond between hmpa and Eu^{3+} ion occurs through the oxygen of the phosphorile ($\nu_{\text{PO}} = 1100 \text{ cm}^{-1}$). This technique was also very helpful in the identification of the PF_6^- and ClO_4^- anions.

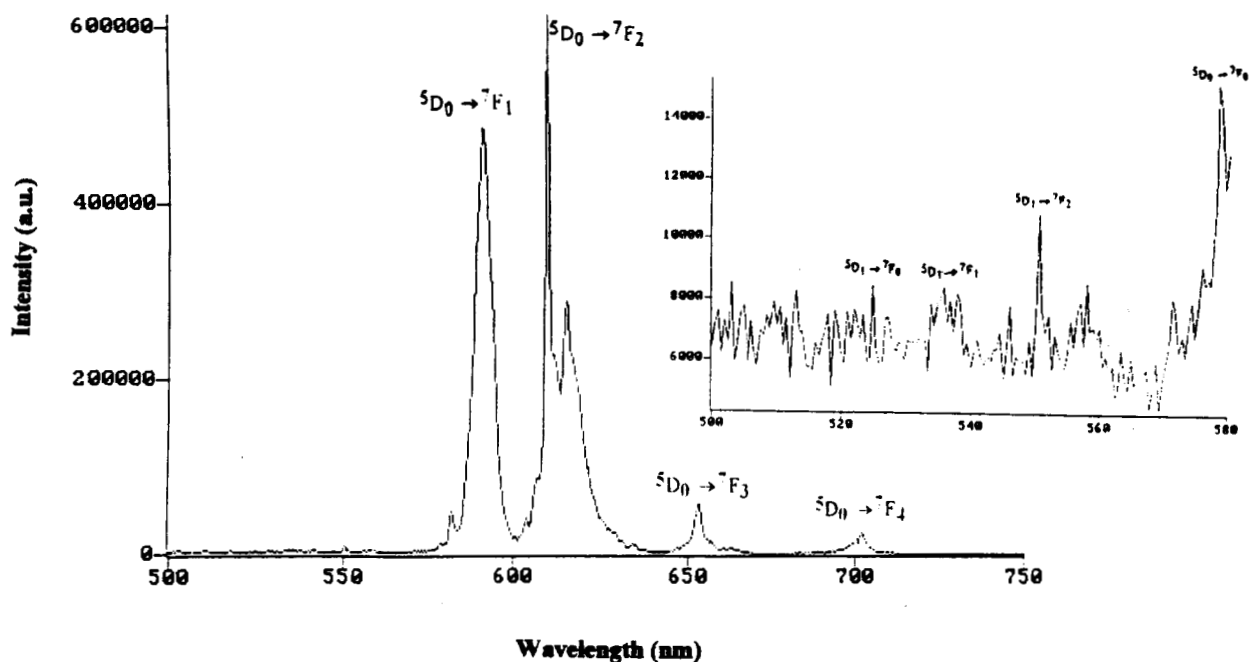


Figure 4. Emission spectrum of Eu^{3+} in the $[\text{Eu}(\text{hmpa})_6](\text{ClO}_4)_3$ compound, $\lambda_{\text{exc.}} = 391 \text{ nm}$, $T = 298 \text{ K}$.

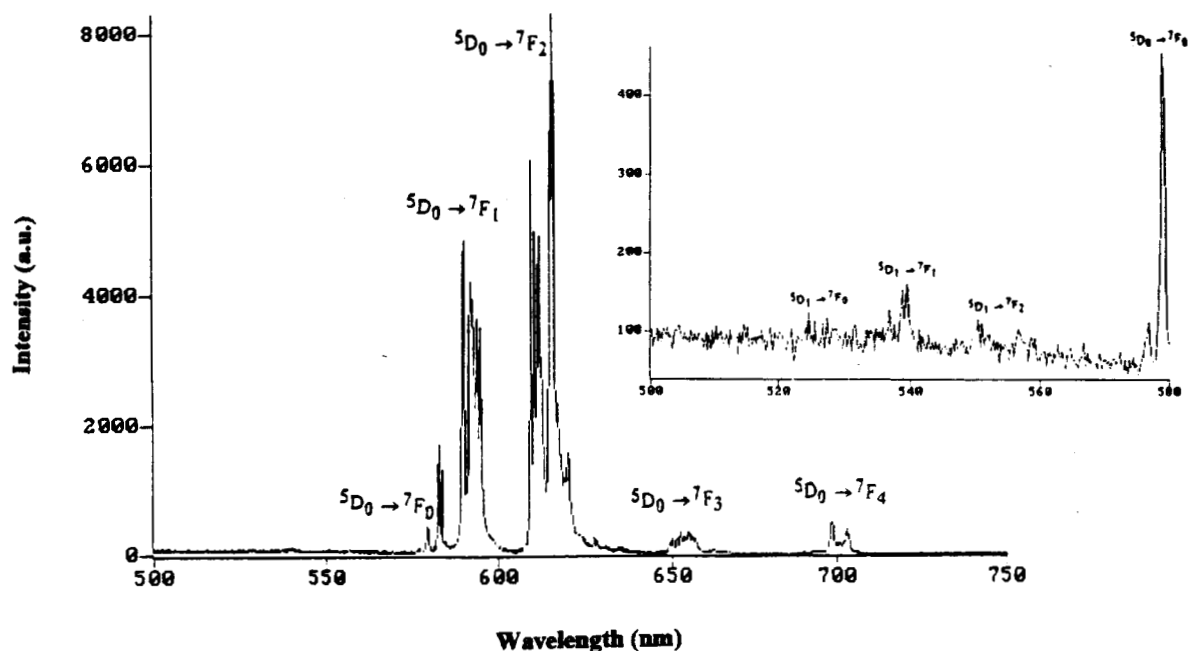


Figure 5. Emission spectrum of Eu^{3+} in the $[\text{Eu}(\text{hmpa})_6](\text{ClO}_4)_3$ compound, $\lambda_{\text{exc.}} = 391 \text{ nm}$, $T = 77 \text{ K}$.

Table 1. Relative area of the $^5\text{D}_0 \rightarrow ^7\text{F}_2 / ^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition (η_{21}) and the lifetimes (τ , ms) of the $\text{Eu}^{3+} ^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition for the Eu^{3+} compounds, recorded at 298 and 77 K.

Compounds	298 K		77 K	
	η_{21}	τ (ms)	η_{21}	τ (ms)
$[\text{Eu}(\text{hmpa})_5\text{Cl}](\text{PF}_6)_2$	1.1	4.4	0.8	4.5
$[\text{Eu}(\text{hmpa})_6](\text{PF}_6)_3$	1.1	4.4	0.9	4.6
$[\text{Eu}(\text{hmpa})_6](\text{ClO}_4)_3$	1.2	4.0	1.7	2.6
$[\text{Eu}(\text{hmpa})_4(\text{ClO}_4)_2]\text{ClO}_4$	3.2	2.4	2.8	2.3

Table 2 shows the infrared and Raman frequencies (cm^{-1}) for ClO_4^- vibrations¹².

The presence of only one band at 908 cm^{-1} and the band at 620 cm^{-1} split in three (Table 2 and Fig. 6) for $[\text{Eu}(\text{hmpa})_4(\text{ClO}_4)_2](\text{ClO}_4)$, suggests that there is a ClO_4^- bidentate resulting in a C_{2v} symmetry or a ClO_4^- unidentate resulting a C_{3v} symmetry. These attributions are in agreement with the data in the literature¹³⁻¹⁷.

$[\text{Eu}(\text{hmpa})_6](\text{ClO}_4)_3$ does not present bands at 930 cm^{-1} , and the band at 630 cm^{-1} does not split (Fig. 6). This is consistent with Td symmetry for ClO_4^- ions.

The symmetry attributions of all of these compounds have already been made in previous studies¹⁴⁻¹⁷ and are in agreement with $[\text{Eu}(\text{hmpa})_4(\text{ClO}_4)_2](\text{ClO}_4)$: D_{2d} or S_4 ; $[\text{Eu}(\text{hmpa})_6](\text{ClO}_4)_3$: distorted O_h or C_{4v} ; $[\text{Eu}(\text{hmpa})_5\text{Cl}](\text{PF}_6)_2$: C_{4v} and $[\text{Eu}(\text{hmpa})_6](\text{PF}_6)_3$: distorted O_h . For the latter this attribution is only valid at 298 K.

Table 2. Infrared and Raman frequencies (cm^{-1}) for the normal vibrations of ClO_4^- observed in RE compounds, by Scholer and Merbach¹².

Td ionic ClO_4^-	C_{3v} unidentate -*O-ClO ₃	C_{2v} bidentate -*O > ClO ₂ -*O <
sym. def. $\text{A}_1(\text{R})$ $\sim 930 \text{ cm}^{-1}$	ClO stret. $\text{A}_1(\text{R, IV})$ $\sim 930 \text{ cm}^{-1}$	ClO_2^* sym.stret. $\text{A}_1(\text{R, IV})$ $\sim 930 \text{ cm}^{-1}$
sym. def. $\text{E}(\text{R})$ $\sim 460 \text{ cm}^{-1}$	rocking $\text{E}(\text{R, IV})$ $\sim 460 \text{ cm}^{-1}$	ClO_2^* sym.def. $\text{A}_1(\text{R, IV})$ $\sim 475 \text{ cm}^{-1}$
asym. stret $\text{T}_2(\text{R, IV})$ $\sim 1100 \text{ cm}^{-1}$	sym. stret. $\text{A}_1(\text{R, IV})$ $\sim 1030 \text{ cm}^{-1}$	asym. stret. $\text{B}_1(\text{R, IV})$ $\sim 1130 \text{ cm}^{-1}$
asym. def. $\text{T}_2(\text{R, IV})$ $\sim 625 \text{ cm}^{-1}$	asym. def. $\text{E}(\text{R, IV})$ $\sim 1150 \text{ cm}^{-1}$	asym. stret. $\text{B}_2(\text{R, IV})$ $\sim 1180 \text{ cm}^{-1}$
	sym. def. $\text{A}_1(\text{R, IV})$ $\sim 645 \text{ cm}^{-1}$	rocking $\text{B}_1(\text{R, IV})$ ~ 615 and 620 cm^{-1}
	asym. def. $\text{E}(\text{R, IV})$ $\sim 620 \text{ cm}^{-1}$	rocking $\text{B}_2(\text{R, IV})$

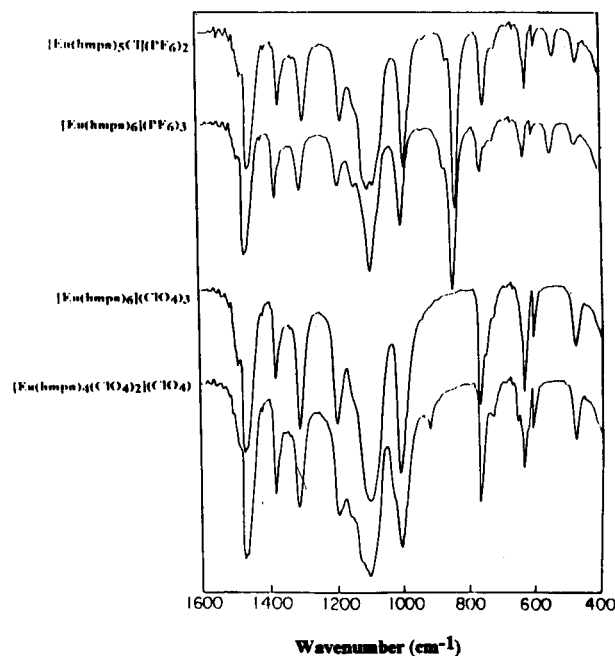


Figure 6. Infrared spectra of the Eu^{3+} compounds, carried out in a KBr cell at 298 K.

Figure 7 shows the Raman spectra of the $[\text{Eu}(\text{hmpa})_6](\text{ClO}_4)_3$ compound recorded at 80 and 298 K. The band at 928 cm^{-1} appears alone at 298 K and in two peaks at 80 K. The band at 622 cm^{-1} is also split in two peaks: 621 and 642 cm^{-1} . These data are in agreement with two kinds of ClO_4^- ions, and confirm the structural change when the temperature is lowered.

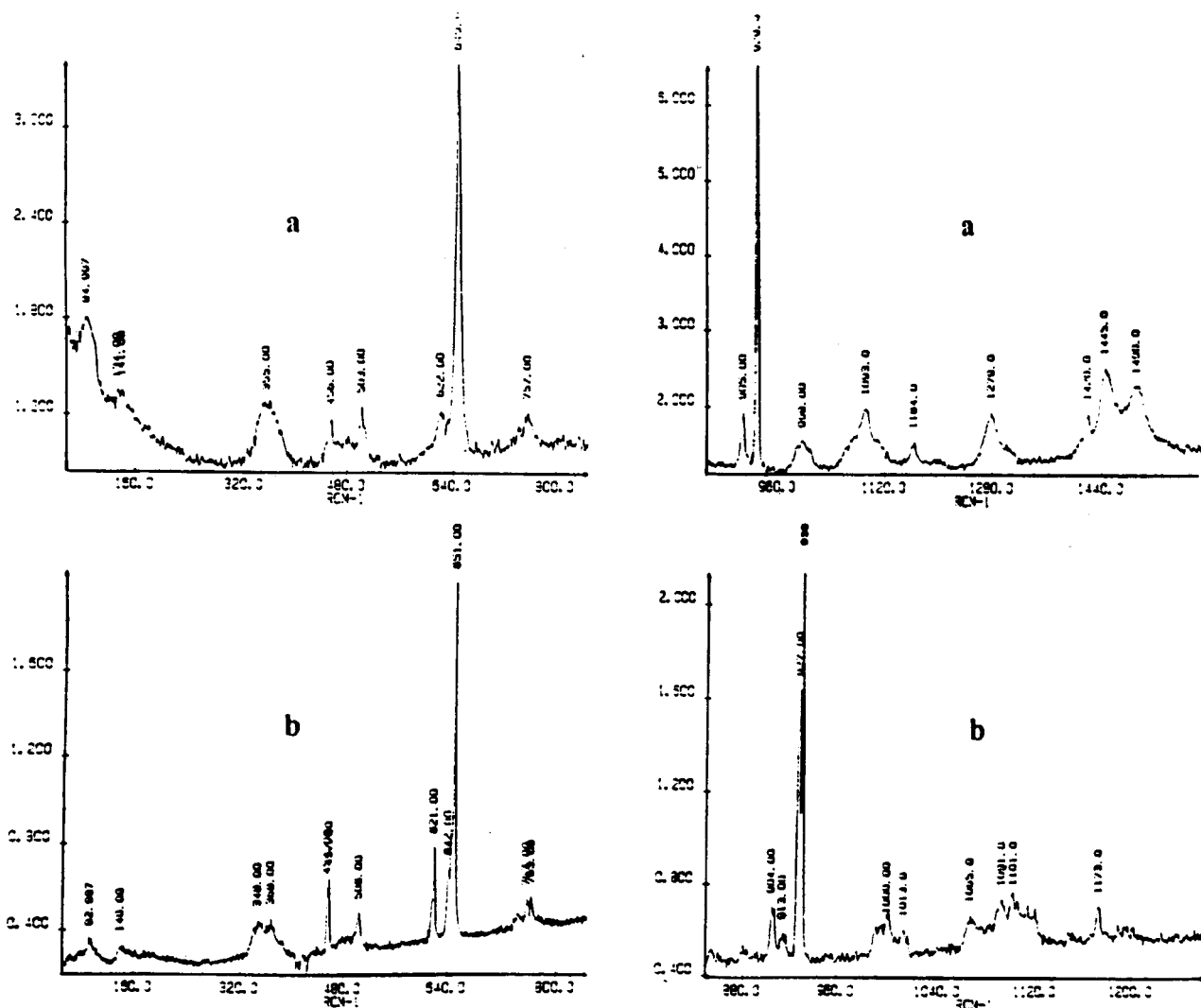


Figure 7. Raman spectra of the $[\text{Eu}(\text{hmpa})_6](\text{ClO}_4)_3$ compound at (a) 298 K and (b) 80 K.

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