Analysis of the Low Temperature Fluorescence Spectrum of Eu(HMPA)$_4$(ClO$_4$)$_3$ Complex*

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The low temperature fluorescence spectrum of the microcrystalline solid complex Eu(HMPA)$_4$(ClO$_4$)$_3$ has been analyzed under high resolution. The observed splittings of the $^5D_0 \rightarrow {}^7F_{1,2}$ transitions are consistent with a S_4 site symmetry at the Eu(III) site in this complex. Thus the chromophoric group in this complex is the octacoordinated Eu(O)$_8$ unit; the coordinating oxygen atoms being provided by two bidentate perchlorate and four symmetry related P $\rightarrow$ O groups of the HMPA ligands. The infrared, Raman and the conductivity data agree with the formulation [Eu(HMPA)$_4$(ClO$_4$)$_2$](ClO$_4$) for the complex and complement the octacoordinated structure with S_4 symmetry predicted from the splittings of the fluorescent lines. A genuine charge transfer band has been observed at 37.04 kK with a $\delta(-) = 4.8$ kK.

Introduction

Recent interest in the coordination complexes of hexamethylphosphoramide (HMPA = [(CH$_3$)$_2$N]$_3$PO) with the lanthanides and various anions [1–5] has prompted us to examine the fluorescence spectra of these complexes. While it has been concluded [5] that the nitrate groups in lanthanide-tetrakis-hexamethyl-phosphoramide-tris-nitrate [M(HMPA)$_4$(NO$_3$)$_3$] complexes are bidentate with all ligands coordinating (CN = 10), the corresponding perchlorate complexes exhibit infrared frequencies for both coordinated and ionic perchlorate groups [3, 4]. In nitrobenzene solution, the complexes of the type M(HMPA)$_4$(ClO$_4$)$_3$ behave as 1:1 electrolyte [3] showing evidence for coordination of two of the perchlorates [M(HMPA)$_4$-(ClO$_4$)$_2$](ClO$_4$). However, neither the infrared nor the conductivity studies are conclusive on the nature of the coordination of the perchlorate groups. If the coordinated perchlorates are monodentate, this would give an apparent and rather rare coordination number of six for the lanthanides, while the bidentate perchlorates would produce a coordination number of eight for the central lanthanide ions. From the examination of the infrared (nujol mull) and solid state unpolarized Raman spectra of the M(HMPA)$_4$-(ClO$_4$)$_3$ complexes, Scholer and Merbach [4] concluded that the amount of ionic perchlorate diminishes from the lighter to the heavier lanthanides, while bidentate perchlorate is progressively replaced by the monodentate ones, and philosophized this change as due to the decrease in the ionic radii along the lanthanide series. Beside the growing evidence [6] that the heavier lanthanides including Sc(III) and Y(III) could exhibit higher coordination numbers of 8 or 9, conclusions based solely on the change of intensities in the mull spectra should be regarded with serious caution. An obvious comparison of the intensity ratio of the coordinated and ionic perchlorate bands, to establish the nature of change, was not done by these authors [4].

With this background in mind we undertook the study of high resolution fluorescence spectrum of the Eu(HMPA)$_4$(ClO$_4$)$_3$ complex at 77 °K in view to deduce the Eu(III) site symmetry, which would in turn yield information on the nature of the chromophoric groups and coordination number. Eu(III) complexes are particularly amenable to such studies as the fluorescent transitions occurring between low J-values ($^5D_{0,1} \rightarrow {}^7F_{0,1,2,3}$) are very sensitive to the change of metal site symmetry, and group theoretical treatment allows the interpretation of the ligand field splitting and deduction of the metal site symmetry.

Results and Discussion

The room temperature absorption spectrum of the solid complex, Eu(HMPA)$_4$(ClO$_4$)$_3$, exhibits a strong and broad absorption band at 270 nm (37037 cm^{-1}) having a half-width (δ–) of ~4.8 kK (1 kK = 1000
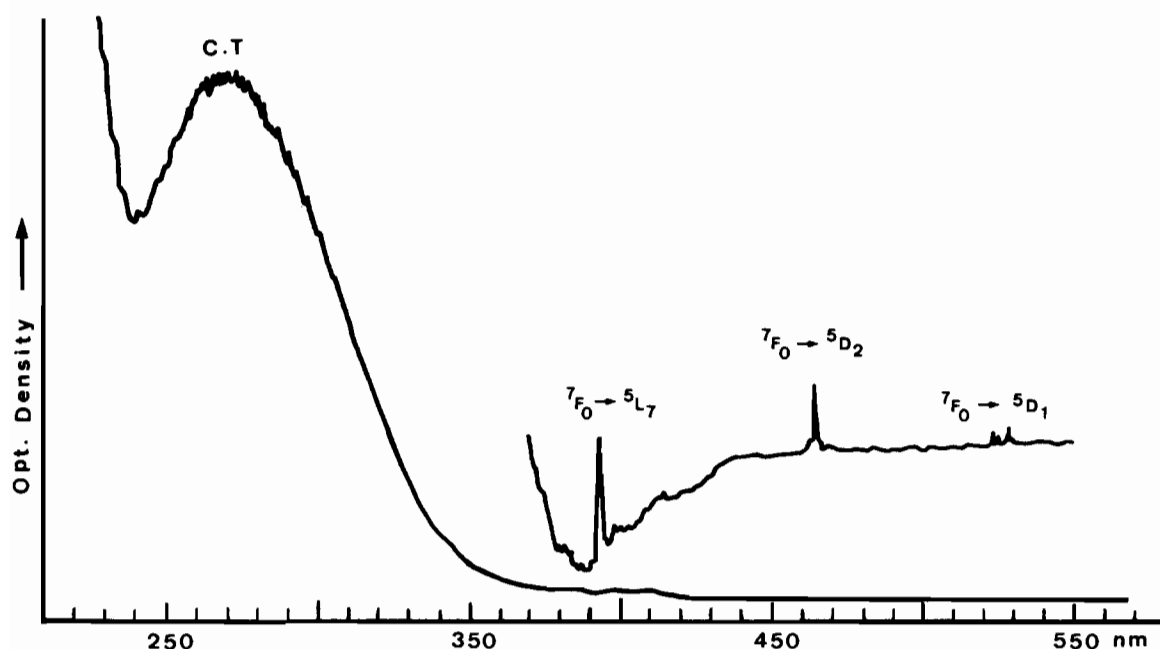

Fig. 1. Room temperature solid state spectrum of Eu(HMPA)$_4$(ClO$_4$)$_3$ in the ultraviolet and visible region.

cm^{-1}) towards the small wavenumber side (Fig. 1). This band is due to the genuine charge transfer from the highest filled M.O. of the ligands to the partly filled 4f shell of Eu(III). In comparison to the similar band of Eu(III) in ethanol (44.1 kK) [7], a red shift of some 7 kK for this charge transfer band is noted. The present value of 4.8 kK for (δ—) agrees well with that of Eu(III) in ethanol (4.5 kK), and that predicted by Jørgensen [7] for the genuine charge transfer bands in the lanthanide complexes. Beside this broad electron transfer band, we are able to locate the sharp f → f electronic transitions of Eu(III) in the visible region for this complex, e.g., $^7F_0 \rightarrow ^5L_7$ at 25445 cm^{-1}, and $^7F_0 \rightarrow ^5D_2$ at 21645, 21552, 21368 cm^{-1}. The $^7F_0 \rightarrow ^5D_1$ transition of very weak intensity was found to occur at 19098, 19048 and 18921 cm^{-1} (Fig. 1).

The relevant details of the fluorescence spectrum of the microcrystalline Eu(HMPA)$_4$(ClO$_4$)$_3$ complex at 77 °K are collected in Table I and a part of the spectrum showing the ligand field splitting of the $^5D_0 \rightarrow ^7F_{0,1,2}$ transitions is reproduced in Fig. 2. As the nephelauxetic effect in the lanthanide complexes is rather small and the ligand field splitting only spreads the lines within about 200 cm^{-1}, no great errors in the assignments of the f → f transitions are usually encountered, when the selection is made on the basis of consistency with the known energy level scheme of Eu(III) and ligand field classification [8, 9].

It will be seen from the Table and Fig. 2 that the threefold degeneracy of the $^7F_1$ level and the five-fold degeneracy of the $^7F_2$ level are not completely

removed. This, together with the extremely low intensity (∼ 1.3 percent of the strongest $^5D_0 \rightarrow ^7F_2$ transition) of the $^5D_0 \rightarrow ^7F_0$ transition at 17240 cm^{-1} (taken to be forbidden), clearly indicates a higher site symmetry for Eu(III) than C_{1h}, C_n and $C_{n'v}$ in this complex. The very small splittings (20 cm^{-1}) of the $^5D_0 \rightarrow ^7F_2$ (16235, 16255 cm^{-1}) and the $^5D_0 \rightarrow ^7F_1$ (16800, 16820 cm^{-1}) transitions into two almost equal intensity components (Fig. 2) indicate that these lines could only originate from an E-component. The site symmetries that generate an E-component for the magnetic dipole allowed $^5D_0 \rightarrow ^7F_1$ transition are D_6, D_{6h}, S_6, D_4, D_{4h}, S_4, D_3, D_{3d}, D_{3h} and D_{2d}. We would further note that E is the only component that is experimentally observed for the $^5D_0 \rightarrow ^7F_1$ transition in this complex (Fig. 2). This still further reduces the site symmetries in question to D_{2d} and S_4

We will now consider the splittings of the electric dipole allowed $^5D_0 \rightarrow ^7F_2$ transition. Besides the E-components mentioned earlier, we are able to observe a split peak at 16320 and 16340 cm^{-1} for this transition (Fig. 2). These are the B-components. A D_{2d} symmetry allows only the electric dipole transition $^5D_0(A_1) \rightarrow ^7F_2(B_2)$, whereas, under S_4 site symmetry transitions to both of the B-components $^5D_0 \rightarrow ^7F_2(2B)$ are allowed. Thus the splittings of the $^5D_0(A) \rightarrow ^7F_2(2B, E)$ transition are consistent with a S_4 site symmetry at Eu(III) site in Eu(HMPA)$_4$(ClO$_4$)$_3$ complex. The splitting of the $^5D_0 \rightarrow ^7F_3$ transition into 2E and one B components (Table I) is also in good agreement with the postulated S_4 site symmetry for this complex.

TABLE 1. Details of the Observed Fluorescence Transitions of $Eu(HMPA)_4(ClO_4)_3$ Complex.[a]

Obs. Transition $\bar{\nu}$ (cm^{-1})	Calc. $\bar{\nu}$ (cm^{-1})	Halfwidth $\Delta\bar{\nu}$ (cm^{-1})	Relative Intensity	Assignment
15221 15245				$^5D_0(A) \rightarrow {}^7F_3(E)$
15347				$^5D_0(A) \rightarrow {}^7F_3(B)$
15382 15395				$^5D_0(A) \rightarrow {}^7F_3(E)$
16235 16255		50	65	$^5D_0(A) \rightarrow {}^7F_2(E)$
16320 16340		50	35	$^5D_0(A) \rightarrow {}^7F_2(B)$
16800 16820		25	57	$^5D_0(A) \rightarrow {}^7F_1(E)$
17075 17100 17125 17150 17170		11 15	30	see text
17240		18	1.3	$^5D_0(A) \rightarrow {}^7F_0(A)$
17300 17310			0.4	$^5D_1 \rightarrow {}^7F_3$
17890 17934 17944 17970	17885 17935			$^5D_1(E) \rightarrow {}^7F_2(E)$
18000	17970 17990 18000 18015		1.6	$^5D_1(E) \rightarrow {}^7F_2(2B)$
18020 18030	18020 18035			$^5D_1(B) \rightarrow {}^7F_2(E)$
18075 18100	18100 18120			$^5D_1(B) \rightarrow {}^7F_2(2B)$
18450	18450			$^5D_1(E) \rightarrow {}^7F_1(E)$
18500 18530	18500 18530		2.2	$^5D_1(E) \rightarrow {}^7F_1(B)$
18575 18595	18580 18600			$^5D_1(B) \rightarrow {}^7F_1(E)$
18890 18920			0.9	$^5D_1(E) \rightarrow {}^7F_0(A)$
19020				$^5D_1(B) \rightarrow {}^7F_0(A)$

[a]The intensities are calculated as percentage of the total intensity of the $^5D_0 \rightarrow {}^7F_2$ transition. The integrated intensity ratio $\eta(^5D_0 \rightarrow {}^7F_2)/(^5D_0 \rightarrow {}^7F_1) = 1.75$.

Within the spectral range investigated, we are able to observe the $^5D_1 \rightarrow {}^7F_{0,1,2,3}$ transitions. These transitions are in general very weak, except for the two lines at 17125 and 17150 cm^{-1}. The high intensity of these two lines could not be accounted for a transition involving $^5D_1 \rightarrow {}^7F_3$. Examination of the Raman spectrum of this complex reveals two strong peaks at 17170 and 17340 cm^{-1} (Raman shifts of 2260 and 2090 cm^{-1} respectively), which are not due to the ligand vibrations. A possible explanation for the occurrence of the peaks in this region could be that these bands originate from some form of electronic Raman effect. Further investigation on the origin of these bands is in progress. Incidentally, the
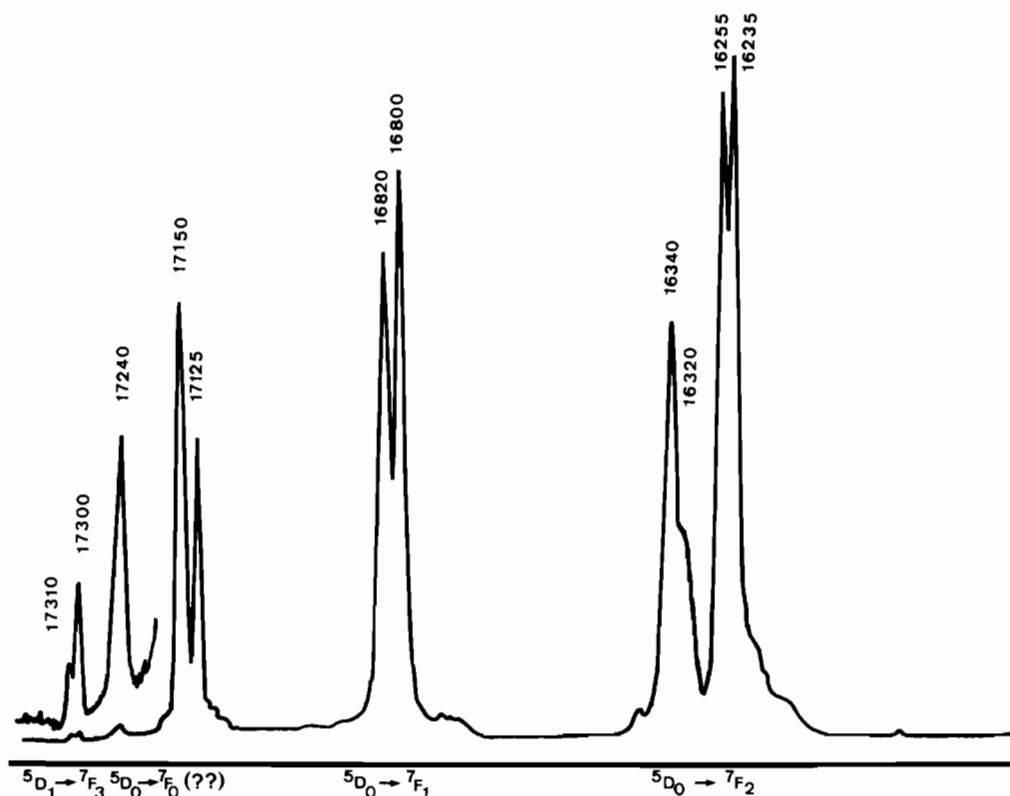
Fig. 2. A part of the fluorescence spectrum of Eu(HMPA)$_4$(ClO$_4$)$_3$ at 77 °K.

complex Eu(HMPA)$_4$(NO$_3$)$_3$ also shows a doublet, shifted to lower wavenumber side (16940 and 16906 cm^{-1}) around this region.

In the region where the $^5D_1 \rightarrow {}^7F_0$ transition is expected to occur, we have observed three lines, one singlet of very weak intensity at 19020 cm^{-1} and a doublet at 18890 and 18920 cm^{-1}, having twice the intensity of the singlet. The S_4 site symmetry allows only the $^5D_1(E) \rightarrow {}^7F_0(A)$ magnetic dipole transition and the observed doublet is assigned to this transition. The low intensity singlet is probably due to the forbidden $^5D_1(B) \rightarrow {}^7F_0(A)$ transition. Support for this assignment came from the observed doublet at 18595 and 18575 cm^{-1} of the $^5D_1 \rightarrow {}^7F_1$ transition (Table I). This doublet is assigned to the $^5D_1(B) \rightarrow {}^7F_1(E)$ transition, which places the $^5D_1(B)$ component at 1775 cm^{-1} higher than the $^5D_0$ level. Thus the calculated value for the $^5D_1(B)$ component is 19015 cm^{-1}, in very good agreement with the observed position at 19020 cm^{-1}, The occurrence of this line is probably due to partial breakdown of the S_4 selection rule.

Some difficulty is encountered in assigning the electric dipole allowed $^5D_1(E) \rightarrow {}^7F_1(B)$ transition, as the $^7F_1(B)$ component was not experimentally observed due to strict S_4 selection rule for the $^5D_0 \rightarrow {}^7F_1$ transition. However, the doublet at 18500 and 18530 cm^{-1} (Table I) could be assigned to the $^5D_1(E) \rightarrow {}^7F_1(B)$ transition. The calculated position for the $^5D_0 \rightarrow {}^7F_1(B)$ transition is 16850 cm^{-1}, placing the $^7F_1(B)$ component 390 cm^{-1} above the $^7F_0(A)$. Other calculated positions for the $^5D_1(E) \rightarrow {}^7F_1(E)$ transition agree very well with the observed positions (Table I).

The observed and the calculated positions of the components for the symmetry allowed $^5D_1 \rightarrow {}^7F_2$ transitions agree extremely well (Table I). However, no definite assignment for the $^5D_1(E) \rightarrow {}^7F_2(A)$ transition could be made, as the $^7F_2(A)$ component was not observed. Similarly, the comparison between the observed and the calculated positions of the $^5D_1 \rightarrow {}^7F_3$ transition is undesirable due to the unavailability of all ligand field components of $^7F_3$ level.

From the absorption and fluorescence data it is possible to construct a part of the low-lying energy level scheme for the Eu(HMPA)$_4$(ClO$_4$)$_3$ complex with the following center of gravity (in cm^{-1}):

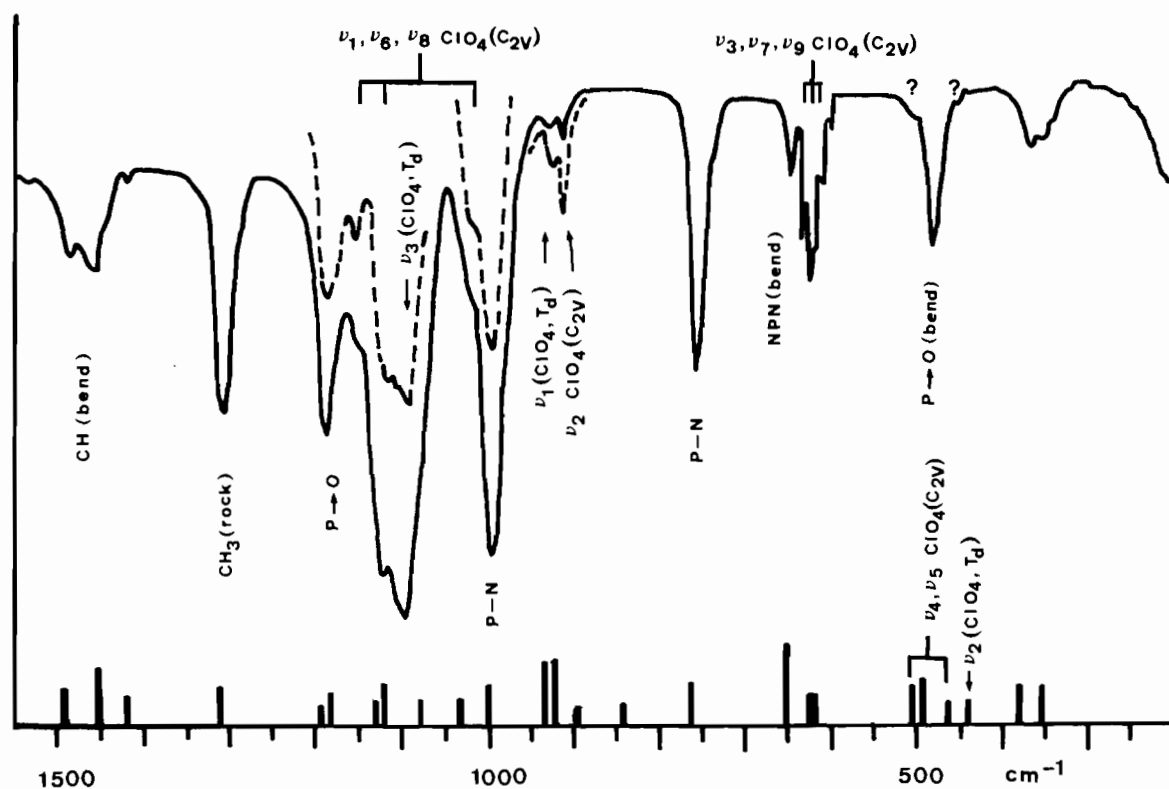| $^7F_0$	$^7F_1$	$^7F_2$	$^7F_3$	$^5D_0$	$^5D_1$	$^5D_2$
Eu(HMPA)$_4$(ClO$_4$)$_3$						
0	403	952.5	1942	17240	18943	21522
Eu-ethylsulphate						
0	370	1058	1906	17257	19016	21495

Fig. 3. Infrared spectrum (solid line: CsBr pellet; broken line: as nujol mull) of Eu(HMPA)$_4$(ClO$_4$)$_3$. The Raman lines are shown at the bottom of the figure. Other low frequency Raman lines were observed at 120 and 80 cm^{-1}.

When these values are compared with those of Eu(III)-aquo ion in Eu(III)-ethylsulphate [10], the values of the nephelauxetic parameter $\beta = 1.001$ and Sinha's covalency parameter [11] $\delta \approx -0.001$ percent are obtained. This negative covalency effect is compatible with the same observed for other lanthanide-HMPA-perchlorate complexes [5], and some ternary Eu(III) complexes [12].

In summarizing we conclude that the chromophoric group in Eu(HMPA)$_4$(ClO$_4$)$_3$ complex is Eu(O)$_8$ with two bidentate perchlorates related by a S$_4$ symmetry operation, and contributing four oxygen atoms for coordination. The four P $\rightarrow$ O groups from four coordinated HMPA molecules complete the octacoordination around Eu(III), [Eu(HMPA)$_4$-(O$_2$ClO$_2$)$_2$](ClO$_4$). This formulation is in accord with the conductivity [3], the infrared and the Raman data. Assignments of the infrared and the Raman bands (Fig. 3) on the basis of the presence of both bidentate and ionic perchlorate groups agree very well with the observed spectra. The assignments are given on the figure.

Experimental

Partially dehydrated europium perchlorate was dissolved in absolute ethanol containing an excess of triethylorthoformate as dehydrating agent. To this solution was added a slight excess over four times the molar proportion of distilled HMPA. The precipitate formed was collected on a filter, washed several times with absolute ethanol, and then dried in a vacuum desiccator for several weeks. *Anal.* Calcd for Eu(C$_6$H$_{18}$N$_3$PO)(ClO$_4$)$_3$: C 24.69, H 6.22, N 14.39, P 10.61, Cl 9.11; found C 24.54, H 6.1, N 14.28, P 11.1, Cl 9.10%. The absence of water peak in the infrared showed the samples to be anhydrous. Handling of the sample in air did not change the characteristic or the infrared spectrum. Other features of the infrared spectrum agreed well with a sample provided by Merbach.

The solid state absorption spectrum was measured as thinly dispersed nujol mull in a QS 81 sandwich type quartz cell, placed in the secondary position of a Unicam SP 1700 spectrophotometer. The fluorescence spectrum at 77 °K was obtained for the microcrystalline sample in an apparatus (Spectrograph ISP 67) described previously [13]. The resolution was better than 5 cm^{-1} below 20 kK and 10 cm^{-1} above it. The exciting wavelength was 3650 Å. The infrared spectrum was measured in CsBr pellet and as nujol mull with a PE 283 instrument, and the solid state Raman spectrum with a Cary 82 laser spectrometer.

Acknowledgment

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