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# The Solid State Luminescence of the Encapsulation Complex of $Eu^{3+}$ in *p*-t-Butyl-calix[4]arene Tetra-amide

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## Abstract

The luminescence of solid $[Eu \subset l]^{3+}$ ($l = p$-t-butyl-calix[4]arene tetra-amide) has been investigated at 4.2 K. The $Eu^{3+}$–ligand charge-transfer state has been observed in the excitation spectrum. Its role in non-radiative transitions is discussed.

## Introduction

Recently Sabbatini *et al.* have reported on the luminescence properties of the $Eu^{3+}$ ion encapsulated into a *p*-t-butyl-calix[4]arene tetra-amide ligand [1, 2]. Figure 1 gives a schematic representation of this ligand. The $Eu^{3+}$ ion is coordinated by eight oxygen atoms; four of these are of the C=O type and four of the C–O–C type. In view of the importance of encapsulated rare-earth ion complexes [3] it seemed interesting to study the present complex in the solid state down to liquid helium temperature. This type of investigation has been reported before by us [4, 5]. In fact we succeeded in obtaining some new and additional information on the complex, which will be abbreviated here as $[Eu \subset l]^{3+}$.

## Experimental

The preparation of $[Eu \subset l]^{3+}$ has been described before [1, 2]. The way in which the optical measurements were performed has been given in the literature [4, 5].

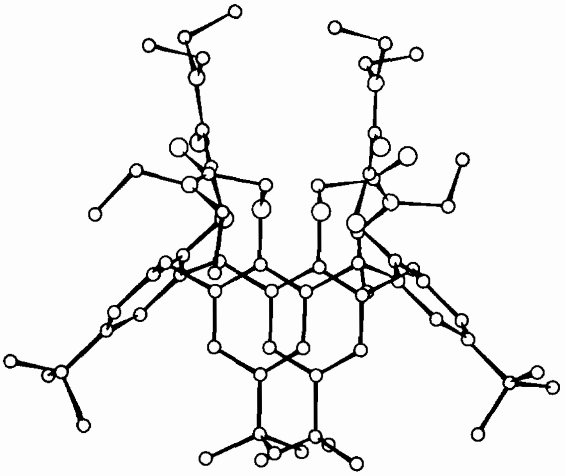

Fig. 1. The *p*-t-butyl-calix[4]arene tetra-amide ligand.

## Results and Discussion

### *The Emission Spectrum*

The $Eu^{3+}$ emission spectrum of the solid is not essentially different from that in solution. Figure 2 gives the emission spectrum at liquid helium temperature. Table 1 summarizes the number of lines observed and to be expected for certain symmetries. It is clear that the exact site symmetry of the $Eu^{3+}$ ion is low, but also that $C_4$ is a good approximation. This is a satisfying observation, since the $Eu^{3+}$ ion is on one side coordinated by a square of C=O oxygen atoms and on the other side by a square of C–O–C oxygen atoms.

### *The Excitation Spectrum*

Whereas the emission spectra of the $[Eu \subset l]^{3+}$ complex in the solid state and in solution are very similar, the excitation spectra are completely differ-

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TABLE 1. Number of emission lines in the spectrum of $[\mathrm{Eu} \subset l]^{3+}$

| | $^5D_0-^7F_0$ | $^5D_0-^7F_1$ | $^5D_0-^7F_2$ | $^5D_0-^7F_4$ |
|---|---|---|---|---|
| Under high resolution at 4.2 K | 1 | 3 | 4–5 | 5 |
| Under lower resolution at 4.2 K | 0 | 2 | 2–3 | 3–4 |
| Expected for $C_2$ | 1 | 3 | 5 | 7 |
| Expected for $C_4$ | 1 | 2 | 2 | 5 |

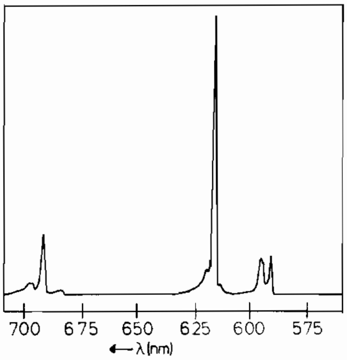

Fig. 2. The emission spectrum of solid $[\mathrm{Eu} \subset l]^{3+}$ at 4.2 K. The excitation wavelength is 395 nm.

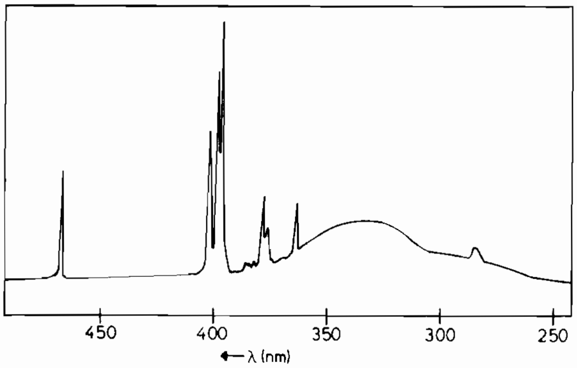

Fig. 3. The excitation spectrum of the $Eu^{3+}$ emission of solid $[\mathrm{Eu} \subset l]^{3+}$ at 4.2 K.

ent. Figure 3 shows the solid state excitation spectrum at liquid helium temperature. Whereas the solution excitation spectrum is dominated by a strong excitation band corresponding to ligand absorption and subsequent energy transfer to the encapsulated $Eu^{3+}$ ion, the solid state spectrum lacks this excitation band completely. It shows a broad excitation band extending from 400 to 300 nm. Excitation into this spectral region results in $Eu^{3+}$ emission only. If one considers the solution spectrum carefully, it becomes clear that the 300–400 nm band is also present in this spectrum.

Our interpretation of these phenomena is as follows. The ligand absorption band is assumed to be mainly due to absorption in the phenyl group ($\epsilon_{max} \sim 10^3$ $M^{-1}$ $cm^{-1}$ [1, 2]). In solution the transfer rate is larger than the phenyl radiative rate, resulting in $Eu^{3+}$ emission. There is no reason why these rates should be strikingly different in the solid state. Therefore, the absence of the phenyl excitation band may indicate that the excited phenyl state is transferred from complex to complex, migrating in this way to quenching centres. This transfer rate is then larger than the rate of transfer to $Eu^{3+}$. This type of migration over ligands of an encapsulating complex in the solid state has been observed by us before [4, 5]. It cannot take place for the complex in the (diluted) solution. However, it cannot be excluded that the absence of the ligand absorption band is (also) due to the strong absorption of the solid, like in the bpy cryptates [4, 5].

The broad and weaker band at longer wavelengths is ascribed to a charge-transfer (CT) transition between the C=O groups and the central $Eu^{3+}$ ion. Its $\epsilon$ value is lower than that of the ligand as is to be expected [3]. This type of CT has also been observed for similar coordinations, viz. $Eu(FOD)_3$ (~360 nm, FOD = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione [6]) and $Eu(AP)_6(ClO_4)_3$ (~370 nm, AP = antipyrine [7]).

Such a low-lying CT band was observed also for the $[\mathrm{Eu} \subset 2.2.1]^{3+}$ cryptate [4]. Excitation into this CT band yields only very weak emission. This was ascribed to the low position of the CT band [4, 8]. However, the present complex shows a reasonable, although not high quantum efficiency, for CT excitation. Therefore the efficiencies for CT excitation of $[\mathrm{Eu} \subset l]^{3+}$ and $[\mathrm{Eu} \subset 2.2.1]^{3+}$ present a problem.

In view of a consideration of a simple configurational coordinate diagram [8–10], our observations indicate that the CT offset is larger in $[\mathrm{Eu} \subset 2.2.1]^{3+}$ than in $[\mathrm{Eu} \subset l]^{3+}$. Encapsulated complexes are very suitable for promoting the small offset necessary for efficient luminescence [11]. In $[\mathrm{Eu} \subset l]^{3+}$ there is a close coordination around the $Eu^{3+}$ ion which does not permit a large offset. However, in $[\mathrm{Eu} \subset 2.2.1]^{3+}$ the situation is different. Most probably this cryptate has a configuration which is on one side open [11] due to the too small radius of the $Eu^{3+}$ ion. This configuration has been observed by an X-ray diffraction study on $[\mathrm{Ln} \subset 2.2.1](ClO_4)_3 \cdot 2CH_3CN$ (Ln = $Pr^{3+}$ or $Er^{3+}$) [12].

Our observations indicate, therefore, that the CT state of $[\mathrm{Eu} \subset 2.2.1]^{3+}$ is not only at low energy, but also at large offset. This has to be ascribed to the configuration of the cryptate.

### *Decay Times*

The decay curve of solid $[\mathrm{Eu} \subset l]^{3+}$ at liquid helium temperature is biexponential. The relevant decay times are $\tau_f = 0.5$ ms and $\tau_s = 1.3$ ms, corresponding to decay rates $P_f = 2000$ $\mathrm{s}^{-1}$ and $P_s = 770$ $\mathrm{s}^{-1}$.

These data can be analysed as follows. About 1/7 of the emission spectrum consists of magnetic-dipole emission ($^5D_0-^7F_1$). Since the rate for $^5D_0-^7F_1$ magnetic-dipole emission is ~43 $\mathrm{s}^{-1}$ [13], the total radiative rate of $\mathrm{Eu}^{3+}$ in $[\mathrm{Eu} \subset l]^{3+}$ is ~300 $\mathrm{s}^{-1}$. This is slower than the rates observed in solution, viz. 525 $\mathrm{s}^{-1}$ in heavy water and 1540 $\mathrm{s}^{-1}$ in water [1, 2]. The difference between these two latter values is due to a non-radiative transition involving the O–H vibration of water [8]. They indicate that in solution the $\mathrm{Eu}^{3+}$ ion in $[\mathrm{Eu} \subset l]^{3+}$ is bonded to one $H_2O$ molecule [1, 2]. This non-radiative rate ($P_{nr}(H_2O)$) equals 1015 $\mathrm{s}^{-1}$, where we assume that in $D_2O$ its value vanishes.

The non-radiative process which remains, occurs via the CT state [8] and is called here $P_{nr}(\mathrm{CT})$. Its rate is given by $P_{nr}(\mathrm{CT}) = P(D_2O) - P_r = 525 - 300 = 225$ $\mathrm{s}^{-1}$.

These data can now be applied to the results for the solid. The value of $P_s$ is ascribed to a complex without a water molecule, i.e. $P_s = 770$ $\mathrm{s}^{-1}$, $P_r = 300$ $\mathrm{s}^{-1}$, so that $P_{nr}(\mathrm{CT}) = 470$ $\mathrm{s}^{-1}$. The value of $P_f$ is ascribed to a complex with one water molecule, i.e. $P_f = 2000$ $\mathrm{s}^{-1}$, $P_r = 300$ $\mathrm{s}^{-1}$, $P_{nr}(\mathrm{CT}) = 470$ $\mathrm{s}^{-1}$, so that $P_{nr}(H_2O) = 1230$ $\mathrm{s}^{-1}$. In fact this value agrees well with $P_{nr}(H_2O)$ derived above in a completely different way (1015 $\mathrm{s}^{-1}$). The analysis shows that the quenching process via the charge-transfer state is more rapid in the solid than in solution. This is ascribed to a slightly different offset of the CT state in the two phases [4].

### *X-ray Excitation*

Under X-ray excitation the solid $[\mathrm{Eu} \subset l]^{3+}$ complex shows a red emission of reasonable intensity. The emission spectrum is not different from those mentioned above. Also $[\mathrm{Eu} \subset 2.2.1]^{3+}$ was reasonably efficient under X-ray excitation [14]. The 2.2.1 cryptate shows a considerable amount of $\mathrm{Eu}^{2+}$ emission under X-ray excitation. For $[\mathrm{Eu} \subset l]^{3+}$ we did not observe any $\mathrm{Eu}^{2+}$ emission under X-ray excitation. This may indicate that the complex is very stable.

In conclusion we have unraveled the charge-transfer transition of the $[\mathrm{Eu} \subset l]^{3+}$ complex and the role of the charge-transfer state in the non-radiative processes.

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