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# DECAY KINETICS FROM ${}^4I_{9/2}$ STATE OF MIXED 2,6 PYRIDINE DICARBOXYLATE-ACETYLACETONATE COMPLEXES

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The  ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$  luminescence decay curves for a series of complexes  $\text{Er}(\text{pdc})_n(\text{acac})_{3-n}$  (pdc = pyridine-2,6-dicarboxylate, acac = acetylacetonate,  $n = 0, 1, 2, 3$ ) as solids and in dilute aqueous solutions have been investigated. The decays are multiexponential, possible reasons for this and for the short lifetimes observed are discussed.

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## 1. Introduction

Lanthanide ions are widely used as probes of their environment. The most useful ion in this respect is the  $\text{Eu}^{3+}$  cation, because the emission generally occurs between a  $J = 0$  state and the  $J = 0-6$  levels of the ground state. The  $\text{Tb}^{3+}$  cation is also useful but the high spherical degeneracies of the initial and terminal states greatly complicate the interpretation of the spectra. The  ${}^4F_{9/2}$  and  ${}^4I_{9/2}$  states of  $\text{Er}^{3+}$  are conspicuously long lived in high symmetry systems [1]. It was of interest to investigate whether emission from lower symmetry  $\text{Er}^{3+}$  complex ions could be detected and contained useful information.

## 2. Experimental

The complexes  $\text{Er}(\text{pdc})_n(\text{acac})_{3-n}$  (pdc = pyridine-2,6-dicarboxylate, acac = pentane-2,5-dionate) were prepared following a general method [2, 3]. Erbium oxide was dissolved in the minimum amount of aqueous HCl, the pH was adjusted to about 6; the required amount of pdc and acac was dissolved in dilute sodium hydroxide aqueous solution and the pH was adjusted to 9. These two solutions were mixed, and the pH was readjusted to 7. These solutions were allowed to crystallise at room temperature.

Decay curves were measured for the emission of  $12\,200\text{ cm}^{-1}$  (the  ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$  transition), using an excitation wavelength at  $15\,430\text{ cm}^{-1}$  (into the

${}^4I_{15/2} \rightarrow {}^4F_{9/2}$  transition) from a pulsed dye laser as previously described [4], and averaging the decay curves over 5000–8000 pulses. No emission was observed from the  ${}^4F_{9/2}$  state due presumably to the fast relaxation  ${}^4F_{9/2} \rightarrow {}^4I_{9/2}$ . For measurements on the hydrated (deuterated) complexes, the samples were cooled to about 200 K before the cryostat was evacuated to minimise the risk of dehydrating the samples.

### 3. Results and discussion

The 80 K luminescence decay curve of solid  $\text{Na}_3\text{Er}(\text{pdc})_3 \cdot 12\text{H}_2\text{O}$  is multi-exponential. The overall emission intensity is very low but easily detectable. An attempt to fit this decay to a bi-exponential decay gave a poor fit with rate constants of  $1.2 \times 10^5 \text{ s}^{-1}$  and  $1.0 \times 10^4 \text{ s}^{-1}$ . In contrast, the luminescence decay for the corresponding europium complex  $\text{Na}_3\text{Eu}(\text{pdc})_3 \cdot 12\text{H}_2\text{O}$  was exactly single exponential [5]. It is difficult to understand a multi-exponential decay from a single excited state in a stoichiometric complex when there is only one type of ion in the lattice. Whilst we quote decay constants for bi-exponential decays as an approximate descriptor of the data, we emphasize that there is no physical basis for this descriptor, it is not a model. We could equally well fit the data to the sum of three exponentials and the fit would be better (i.e. the descriptor would be nearer to the true descriptor), but have no more physical significance. In an attempt to understand the mechanism of the decay these measurements were repeated on a sample repeatedly recrystallised from  $\text{D}_2\text{O}$ , but there was little change in the decay curve (Fig. 1). The emission from rigorously dehydrated sample is significantly longer

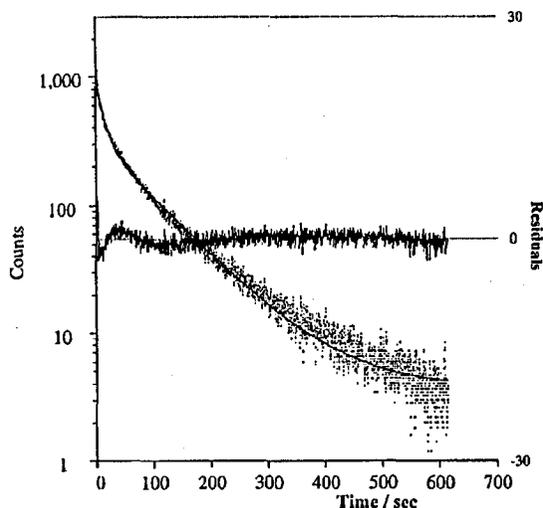


Fig. 1. The time dependence of the  ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$  emission of  $\text{Na}_3\text{Er}(\text{pdc})_3 \cdot 12\text{D}_2\text{O}$  at 80 K with excitation at  $15\,430 \text{ cm}^{-1}$ . The solid line is a least squares fit to the 4000 data points for decay constants of  $8.86 \times 10^4$  and  $1.07 \times 10^4 \text{ s}^{-1}$  and the weighted residuals are shown.

lived but remains multiexponential. The curves may be approximately described by a bi-exponential function with rate constants of  $5.2 \times 10^4$  and  $6.8 \times 10^3 \text{ s}^{-1}$ .

In  $\text{H}_2\text{O}$  solution ( $[\text{Er}] = 0.01 \text{ mol dm}^{-3}$ ) the emission of  $\text{Eu}(\text{pdc})_3^{3-}$  is also multiexponential. A reasonable descriptor of the data corresponds to a bi-exponential function with decay constants  $3.7 \times 10^5$  and  $3.8 \times 10^4 \text{ s}^{-1}$  for a Er:pdc ratio of 1:5. In  $\text{D}_2\text{O}$  at the same concentration these constants decrease slightly as expected. Addition of a large excess of sodium chloride to these solutions results in a slight decrease in the emission intensity and a corresponding increase in the decay constants, the decay remaining multiexponential.

Changing the Er:pdc ratio causes little change in the decay curves until the Er:pdc ratio is below 1:2. At lower ratios the emission becomes very weak and short lived.

Measurement of the 80 K decay constants of the solid mixed complexes,  $\text{Er}(\text{pdc})_n(\text{acac})_{3-n}$ , also gave multiexponential decay curves. For  $n = 0$  the decay constants at 80 K are  $6.9 \times 10^3$  and  $3.7 \times 10^4 \text{ s}^{-1}$  and they increase slightly but monotonically to the values for  $n = 3$ .

We have no simple explanation of the above data. The internal consistency of the data seems to rule out instrumental artefacts and points to the pdc ligand increasing the rate of non-radiative relaxation of the  $^4I_{9/2}$  state presumably by reduction in symmetry.

#### 4. Conclusion

Whilst emission from the  $^4I_{9/2}$  state of complexes of  $\text{Er}^{3+}$  is easily observed, the dominant role of the non-radiative processes in determining the decay kinetics precludes a simple understanding of the observed phenomena.

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