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# Fluorescence Spectra and Lifetime Measurements of a Formato Complex of Europium(III) in HCOOH–HCOONa Buffer Solution*

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## Abstract

The photophysical properties of the $Eu^{3+}$ ion in HCOOH–HCOONa buffer solution were studied. The high resolution emission spectrum is consistent with the presence of only one $Eu^{3+}$ containing species of $C_{2v}$ symmetry. The emission quantum yield in $D_2O$ solution is 0.17 upon excitation at 394 nm in the $^5L_6$ absorption band.

Luminescence decay measurements in $H_2O$ ($\tau$ = 140 ns) and $D_2O$ ($\tau$ = 2.50 ms) solutions show that the formato complex contains seven water molecules in the first coordination sphere. The most likely formulation of the formato complex ion in solution is $Eu(HCOO)_2(H_2O)_7{}^+$, where the formate ion plays the role of a monodentate ligand.

## Introduction

Several experimental techniques can be employed to determine the composition and structure of rare earth complexes in aqueous solution. As far as the $Eu^{3+}$ complexes are concerned, high resolution emission spectra and luminescence decay measurements can be very useful to establish the symmetry of the coordination site and the number of water molecules in the first coordination sphere [1, 2]. For these reasons, $Eu^{3+}$ is also widely employed as a luminescent probe in determining the structure of biomolecular systems [2].

Except for the study by Kropp and Windsor [3], the aliphatic monocarboxylato $Eu^{3+}$ complexes have not been investigated from a photophysical point of view. In this paper we report the results of an investigation carried out on the bis-formato europium(III) complex ion with the aim of elucidating its composition and structure in aqueous solution.

## Experimental

Anhydrous europium(III) formate was synthesized from $Eu_2O_3$ following a literature method [4]. The solutions to be studied were prepared by dissolving the anhydrous complex (5 mM) into a buffer solution (pH 3.5) containing 0.381 M HCOOH and 0.205 M HCOONa. Under such conditions, 95.4% of the $Eu^{3+}$ ion was present as bis-formato complex, as indicated by the previously reported stability constant [5]. $D_2O$ was 99.9% in purity and all the other chemicals used were of reagent grade. Since the total H/D ratio in the deuterated solution was less than 1%, deuterated formate and formic acid were not used (see also ref. [3a]).

Absorption spectra were recorded with a Cary 219 spectrophotometer, and low resolution emission spectra with a Perkin-Elmer 650-40 spectrofluorimeter. High resolution emission spectra were obtained by a Jasco R 300 Raman spectrometer using a Spectra-Physics Ar laser for excitation at 465.8 nm. Emission lifetimes were measured by a JK System 2000 Neodymium Yag DPLY 4 laser, exciting with the second harmonic at 532 nm and following the emission at 620 ± 10 nm. The scattering in the lifetime values so obtained was <5%. The emission quantum yield was evaluated by the method given by Haas and Stein [6] using $Eu(ClO_4)_3$ as a standard ($\phi_{em}$ = 0.20 in $D_2O$ for 394 nm excitation). The experimental uncertainty on the quantum yield value was ~10%.

All measurements were carried out at room temperature (~22 °C).

## Results and Discussion

All the experiments were carried out at pH = 3.5, a little lower than the $pK_a$ of formic acid. At higher pH, Eu(III) formate is almost insoluble. Furthermore, because of its lower solubility, sample solutions in which more than 99% of the $Eu^{3+}$ ion is present as a bis-formato complex cannot be used.

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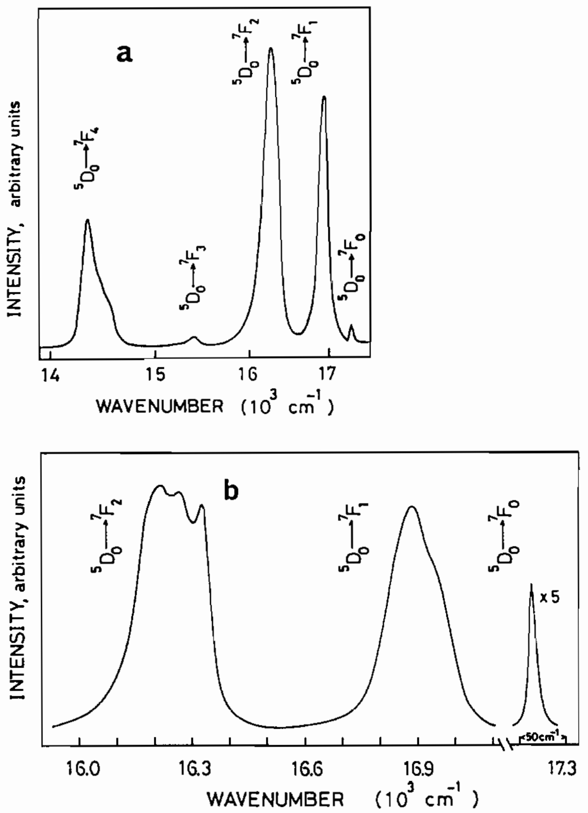

Fig. 1. Fluorescence spectra of $Eu(HCOO)_2^+$ ion of $5 \times 10^{-3}$ M in HCOOH–HCOONa buffer deuterated aqueous solution at pH 3.5 under low (a) and high (b) resolution conditions.

Figure 1a shows the low resolution emission spectrum of the complex in aqueous solution, and Fig. 1b shows part of the same spectrum under high resolution conditions. The assignment of the various bands is indicated in the figure for identification purposes. Comparison with the emission spectrum of the $Eu^{3+}$ ion [7] shows that the intensities of the $^5D_0 \rightarrow {}^7F_0$ and of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ bands are enhanced upon complexation. Note that, as is usually the case [1], no emission can be seen from the $^5D_1$ excited state because of the fast radiationless decay of $^5D_1$ to $^5D_0$ [8].

Since the $^7F_0$ and $^5D_0$ levels of the $Eu^{3+}$ ion can never be split by ligand field, the number of peaks in the region of the $^5D_0 \rightarrow {}^7F_0$ transition corresponds to the number of $Eu^{3+}$ containing species which are present in solution (n.b. in some cases the observation of distinct peaks could be prevented by resolution and/or intensity reasons). As one can see from the high resolution spectrum of Fig. 1b, only one narrow and symmetric peak is present in the $^5D_0 \rightarrow {}^7F_0$ region which is consistent with the presence of only one $Eu^{3+}$ containing species, as expected on the basis of the experimental conditions used (*i.e.*, strong excess of HCOOH and HCOONa compared with $Eu^{3+}$) and of the known [5] stability constant of the $Eu(HCOO)_2^+$ species.

The gaussian analysis of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ bands obtained under high resolution conditions (Fig. 1b) shows that three and, respectively, at least four components are present. This shows that the $Eu^{3+}$ containing species exhibits a low symmetry. The number of components of the observed bands is consistent with a $C_{2v}$ symmetry, which is the highest possible symmetry for $Eu(HCOO)_2^+$ as well as for $Eu(HCOO)_2(H_2O)_n^+$ (see below).

The emission quantum yield was 0.17 in $D_2O$ solution, as compared with the quantum yield 0.20 observed for the $Eu_{aq}^{3+}$ in $D_2O$ [6]. The lifetime of the luminescence decay was 140 ns in $H_2O$ and 2.50 ms in $D_2O$. The corresponding values for $Eu_{aq}^{3+}$ are 110 ns and 3.57 ms [9].

According to Horrocks *et al.* [2a], the number $q$ of water molecules coordinated to $Eu^{3+}$ in Eu(III) complexes can be evaluated, with an estimated uncertainty of 0.5, from the following equation:

$$q = 1.05(1/\tau_{H_2O} - 1/\tau_{D_2O}) \qquad (1)$$

where $\tau_{H_2O}$ and $\tau_{D_2O}$ are the luminescence decay lifetimes (in ms) measured in $H_2O$ and $D_2O$ solutions. Using the lifetime values obtained in this work (see above), eqn. 1 yields $q = 7.2$ which means that in solution the formulation of the bis-formato complex ion is $Eu(HCOO)_2(H_2O)_7^+$. The same method shows that the $Eu_{aq}^{3+}$ ion can be formulated $Eu(H_2O)_9^{3+}$ [9]. If, as it seems likely, $Eu^{3+}$ maintains the coordination number 9 also in the bis-formato complex, it follows that $HCOO^-$ must play the role of a monodentate ligand. Bidentate formate would in fact occupy too much volume in the first coordination sphere of $Eu^{3+}$ to allow the coordination of 7 water molecules.

Finally, it is worthwhile noting that in $H_2O$ solution the lifetime of the formato complex is longer than that of the $Eu^{3+}$ ion, whereas the opposite is true in $D_2O$ solutions. This behavior can be rationalized on the basis of the vibronic coupling mechanism [10] which governs the non-radiative deactivation of the $^5D_0$ emitting state. The efficiency of such a mechanism is related to the number and energy of high frequency vibrations which can couple with $Eu^{3+}$ so as to accept the 12,300 $cm^{-1}$ excess electronic energy of $^5D_0$ compared with $^7F_6$ [11, 12]. In $H_2O$ solution the most important role is played by the O–H vibrations of the coordinated water molecules, whose number is higher in the $Eu_{aq}^{3+}$ ion than in the formato complex. Thus, the latter species is longer lived. In $D_2O$ solution, however, the coordinated solvent can only supply relatively low energy O–D oscillators which are much less effective than O–H oscillators, as shown by the increased lifetime. Under such conditions, the presence of relatively higher energy vibrations (like C–H) in the formato complex could offer a slightly more efficient path.

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