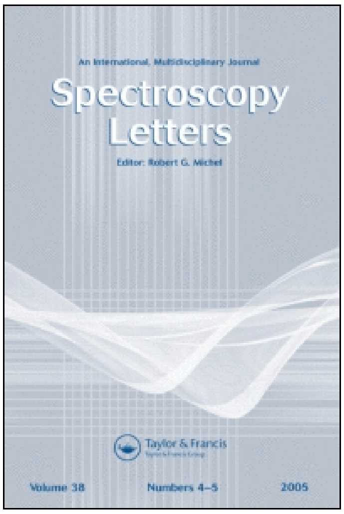

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VARIATION IN THE LUMINESCENCE LIFETIMES OF $EuCl_3 \cdot nH_2O$ (n=0,1,2,3,6)

Key words: Eu^{3+} Ion Luminescence, Luminescence Lifetime, $EuCl_3 \cdot nH_2O$

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ABSTRACT

Eu^{3+} ion emission spectra and luminescence lifetimes were investigated for $EuCl_3 \cdot nH_2O$ (n=0,1,2,3,6). Each compound exhibited a characteristic set of emission bands and a specific luminescence lifetime. The number of water molecules and chloride ions coordinated to the Eu^{3+} ion in these materials was estimated from the observed lifetimes, spectroscopic implications, and expected lanthanide coordination numbers. Approximation of the observed luminescence decay constant for each material was possible through the use of arithmetic terms associated with both the complexed water molecules and the complexed chloride ions which make up the inner-coordination sphere of the Eu^{3+} ion.

INTRODUCTION

There are five established species of $EuCl_3 \cdot nH_2O$ (n=0,1,2,3,6).[1-3] The hexahydrate and anhydrous salt can be readily prepared for desired studies. The other forms have been identified previously only as intermediates in the thermal decomposition processes associated with the formation of EuOCl and $EuCl_3$ from $EuCl_3 \cdot 6H_2O$.[1-3] It was recently observed[4] that the emission spectra from these

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intermediate species could be observed *in situ* by heating the hydrated sample within the spectrometer's sample chamber (i.e. spectral monitoring of the thermal decomposition process). Studies performed in this manner also suggested that several individual hydrates could be prepared and isolated.[4] Following the isolation of these different hydrates, it was then possible to measure and subsequently compare their emission spectra and lifetimes at room temperature.

The Eu^{3+} ion luminescence lifetimes of compounds have been used previously to determine the extent of hydration of the Eu^{3+} ion.[5] This determination is possible because of the large effect water has on the luminescence lifetimes of lanthanide ions. The water molecules appear to provide de-excitation pathways that shorten greatly the emission lifetime, and increases in the number of coordinated water molecules have been correlated to decreases in the lifetime. The specific number of coordinating water molecules can be identified by comparing the luminescence lifetimes of a hydrated species containing normal and deuterated water.[5] In this report, the luminescence lifetimes of the hexa-, tri-, di-, and monohydrate of $EuCl_3$, as well as anhydrous $EuCl_3$, have been determined and are compared and discussed.

EXPERIMENTAL METHODS

Anhydrous $EuCl_3$ was obtained commercially (certified 99.9% Cerac, Inc.). The $EuCl_3 \cdot 6H_2O$ was generated as described previously[4] from the forced precipitation of the solid from an aqueous $EuCl_3$ stock solution prepared from Eu_2O_3 (certified 99.9%, Johnson Matthey) and hydrochloric acid. The tri-, di, and monohydrates were formed successively by thermal decomposition of $EuCl_3 \cdot 6H_2O$.[4] Each sample was heated under a partial vacuum while its emission following laser excitation was monitored continuously. Upon the initial formation of a new hydrate, the sample was equilibrated at temperature for at least an hour, cooled to room temperature, and sealed in the glass tube for further optical studies. The three intermediate hydrates (tri-, di-, and monohydrate) were formed from samples of the hexahydrate at temperatures of approximately 120, 140, and 160 °C, respectively.[4]

Excitation of the samples was accomplished using the 465.8 nm line of a six-Watt argon ion laser (Coherent Radiation, model number: Innova 300). The emitted light, collected at 90° from the incident laser light, was focused onto the entrance slit of a double-meter monochromator (Jobin Yvon/Instruments SA, model number: Ramanor HG.2S spectrophotometer). The dispersed light was analyzed with a cooled photomultiplier tube (Hamamatsu, model number: R636). The signal, following amplification and discrimination, was processed by one of two photon-counting systems. The first system is based on the collection of emission spectra and included a multichannel analyzer (Nicolet, model number; 1170) interfaced with a personal computer using "Spectra Calc" software (Galactic Industries, version 2.12). The second system is based on the collection of luminescence lifetime data and centered around a gated, photon-counting system (Stanford Research Systems, model number; SR400) interfaced with a personal computer using "SR465" software (Stanford Research Systems, version 1.01) for both data collection and determination of the luminescence lifetimes.

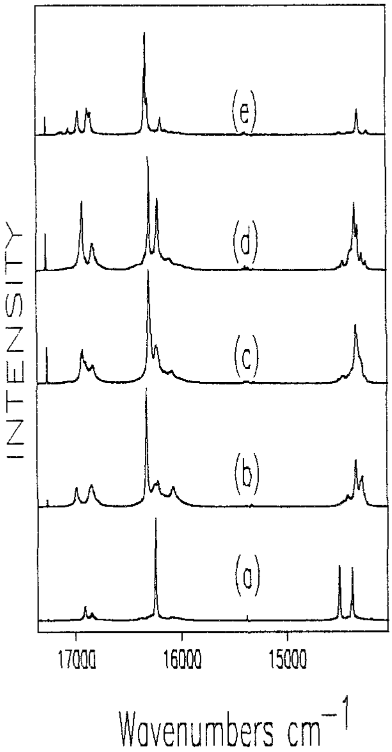

Fig 1. Room Temperature emission spectra from (a) $EuCl_3$, (b) $EuCl_3 \cdot H_2O$, (c) $EuCl_3 \cdot 2H_2O$, (d) $EuCl_3 \cdot 3H_2O$, and (e) $EuCl_3 \cdot 6H_2O$.

RESULTS AND DISCUSSION

Spectroscopic Results

The room-temperature emission spectra from the five $EuCl_3 \cdot nH_2O$ materials are shown in Figure 1 and a compilation of the emission lines is given in Table 1. If these spectra (Figure 1) are compared to those obtained previously at the synthesis temperatures,[4] only slight shifts in appearence and energy, due to the change in temperature are apparent.

Table 1

Major Emission Transition Energies (cm^{-1}) for $EuCl_3 \cdot nH_2O$ (n=0,1,2,3,6)

	n = 6	n = 3	n = 2	n = 1	n = 0
$^5D_0$	14231	14243	14259	14285	14379
to	14315	14280	14295	14341	14393
$^7F_4$	14397	14323	14337	14419	14501
	14485	14350	14383		
		14389	14465		
		14461			
$^5D_0$	15281	15310	15333	15337	15375
to	15373	15355	15369	15388	
$^7F_3$	15386	15380			
		15404			
$^5D_0$	16176	16098	16082	16072	16242[a]
to	16300	16213	16226	16214	
$^7F_2$	16322[a]	16292[a]	16294[a]	16242	
				16320[a]	
$^5D_0$	16820	16826	16834	16846	16850
to	16843	16925	16904	16984	16910
$^7F_1$	16961		16930		
$^5D_0$ to $^7F_0$	17265	17266	17264	17269	------[b]

[a] Transitions at which lifetimes were measured.
[b] Transition forbidden by Laporte selection rules.

Table 2

Luminescence Lifetimes of $EuCl_3 \cdot nH_2O$ (n=0,1,2,3,6)

Compound	Luminescence Lifetime τ (μs)	Decay Constant k (ms^{-1})
$EuCl_3 \cdot 6H_2O$	123	8.13
$EuCl_3 \cdot 3H_2O$	195	5.13
$EuCl_3 \cdot 2H_2O$	158	6.33
$EuCl_3 \cdot H_2O$	171	5.85
$EuCl_3$	205	4.88

The emission spectrum exhibited by the anhydrous $EuCl_3$ matches that previously reported for it.[6] The luminescence lifetimes were measured at energies (16242-16322 cm^{-1}) which correspond to the most intense Eu^{3+} ion transition between the $^5D_0$ excited state and the $^7F_2$ J-state. The luminescence lifetimes of the five compounds, $EuCl_3 \cdot nH_2O$ (n=0,1,2,3,6) are listed in Table 2.

Qualitative Analysis of the Luminescence Lifetimes

It was suggested by Horrocks and Sudnick that as the number of water molecules attached to the Eu^{3+} ion is reduced, the Eu^{3+} ion luminescence lifetime should increase.[5] The lifetimes from our experiments appear at first to contradict this contention, as the dihydrate and monohydrate exhibit shorter luminescence lifetimes than that of the trihydrate. However, upon further consideration of two important points, an interpretation for this difference can be offered.

First, the Eu^{3+} ion luminescence lifetimes are dependent on the number of water molecules occupying positions in the inner coordination sphere of the Eu^{3+} ion, not the total number of hydrating waters per formula unit. Water molecules can bridge between metal ions. They can also occupy sites that are not coordinated to the metal ion. If either bridging or uncoordinated waters are present, the number of waters in the inner coordination sphere of the emitting atom can not be approximated by the number of waters of hydration.

Secondly, the luminescence lifetime-hydration number correlation considers only the effect of water on the luminescence lifetime.[5] Although complexing agents like the Cl^- ion do not have as large an effect on the luminescence lifetime as does water, compounds containing coordinated chloride ions also exhibit luminescence lifetimes much shorter than the intrinsic lifetime of Eu^{3+} ion's emission (e.g., Cl^- ions can also influence Eu^{3+} luminescence lifetimes).

In the series of compounds studied here, the hexahydrate is known to be eight coordinate (complexed by six water molecules and two chloride ions),[7] and exhibits a luminescence lifetime of about 123 μs. This value is consistent with the lifetime previously reported for this compound.[5] After formation of the trihydrate, the luminescence lifetime rose to 195 μs, in accord with an increase in the lifetime correlating with the loss of three waters of hydration. With this change, the coordination number of the Eu^{3+} ion has now appeared to drop to five, a relatively low value for a lanthanide ion. It is probable that the third chloride ion now occupies a position in the first coordination sphere, resulting in a coordination number of six for the Eu^{3+} ion.

$EuCl_3 \cdot 2H_2O$ has a luminescence lifetime of about 158 μs (compared to 195 μs for the trihydrate), an apparent contradiction to the increased lifetime expected with the loss of hydrated water. However, this decrease in the luminescence lifetime can be explained if the two remaining water molecules form bridges to the nearby Eu^{3+} ions. Thus, instead of the simple loss of a water molecule resulting in an increased lifetime (coordination number of five), we propose that a total of four bridging water molecules are coordinated to each Eu^{3+} ion along with the three chloride ions; this would be consistent with the shorter luminescence lifetime and provide a coordination number of seven for the Eu^{3+} ion.

The monohydrate's lifetime of about 175 μs (compared to 158 μs for the dihydrate) now exhibits the expected increase in luminescence lifetime, reflecting the loss of half of the bridging water molecules, which decreases the Eu^{3+} ion's coordination number to five. It is believed that chloride ions may bridge to neighboring Eu^{3+} ions at this point, increasing the coordination number to a value more consistent with that normally associated with a lanthanide ion. The similarities between the emission spectra of the hexahydrate and the monohydrate suggest that the inner coordination spheres of the two species may be similar. Due to this similarity, it is proposed that the three chloride ions bridge to adjacent Eu^{3+} ions with the addition of three other bridging chloride ions from neighboring $EuCl_3$ units. This would then result in a coordination number of eight for the Eu^{3+} ion in the monohydrate, like that of the hexahydrate. The inner coordination sphere of the Eu^{3+} ion in the monohydrate would consist of six chloride ions and two water molecules, as opposed to six water molecules and two chloride ions in the hexahydrate.

This inner coordination sphere for the monohydrate is also supported by the red shift observed in the Eu^{3+} ion emission feature associated with the transition between the $^5D_0$ and $^7F_0$ levels (see Table 1). The crystal field imposed upon the emitting Eu^{3+} ion is strongly effected by its coordination. An expansion or contraction of a metal ion's coordination sphere is normally reflected by a shift in energy (expansion, shift to higher energy; contraction, shift to lower energy). In the cases of the hexa-, tri-, and dihydrates of $EuCl_3$, the shifts are less than a wavenumber at approximately 17265 cm^{-1} (see Table 1), indicating little expansion or contraction of the coordination sphere. In the case of the monohydrate, the shift is about four wavenumbers toward higher energy. Thus, this observed shift to higher energy supports the suggested expansion of the Eu^{3+} ion's coordination sphere to accommodate a coordination number of eight.

It is well known that the Eu^{3+} ion in anhydrous $EuCl_3$ is coordinated to nine chloride ions.[8] Each chloride ion bridges between two adjacent Eu^{3+} ions. The luminescence lifetime of the Eu^{3+} ion in $EuCl_3$ was about 205 μs, consistent with that reported in the literature.[9] This lifetime, while longer than that of the monohydrate (as expected), is only slightly longer than that of the trihydrate. This implies the additional chloride ions attached to the Eu^{3+} ion in the anhydrous compound also influence the Eu^{3+} ion's luminescence lifetime.

Quantitative Aspects of Luminescence Lifetimes

The observed decay constant ($k_{obs.}$) of the luminescence lifetime can be expressed as the sum of the intrinsic constant of the emitting species ($k_{int.}$) and the constant associated with nonradiative pathways of de-excitation ($k_{nonrad.}$). Thus,

$$k_{obs.} = k_{int.} + k_{nonrad.} \tag{1}$$

The $k_{int.}$ is often very small in comparison to $k_{nonrad.}$. If this is the case, then Eqn. (1) can be simplified to

$$k_{obs.} \cong k_{nonrad.} \tag{2}$$

If the largest contributor to the non-radiative decay depends on processes involving species within the inner coordination sphere of the Eu^{3+} ion (water molecules and/or chloride ions), then Eqn. (2) can be expanded to Eqn. (3), where "n" is the number of water molecules attached to the Eu^{3+} ion, and "m" is the number of chloride ions attached.

$$k_{obs.} \cong m * k_{chloride} + n * k_{water} \tag{3}$$

Using the lifetimes observed for the compounds with known coordination (the anhydrous salt and $EuCl_3 \cdot 6H_2O$), the values of k_{water} and $k_{chloride}$ can be determined. In anhydrous $EuCl_3$, nine chloride ions are attached to each Eu^{3+} ion.[8] Using "n" = 0, "m" = 9, and $k_{obs.}$ = 4.88 ms^{-1} (Table 2) for Eqn. (3), $k_{chloride}$ has a value of 0.542 ms^{-1}/Cl^-. The Eu^{3+} ion in the hexahydrate compound is coordinated by six water molecules and two chloride ions.[7] Inserting the values of "n" = 6, "m" = 2, $k_{obs.}$ = 8.13 ms^{-1} (Table 2) , and $k_{chloride}$ = 0.542 ms^{-1}/Cl^- in Eqn. (3), a value of 1.17 ms^{-1}/H_2O is calculated for k_{water}.

These k_{water} and $k_{chloride}$ values can now be used to predict the luminescence lifetimes associated with the suggested coordination spheres of the Eu^{3+} ion in the other hydrate compounds. The trihydrate was assigned a coordination number of six; having three waters and three chloride ions. Substituting these values of "n" and "m" into Eqn. (3) provides a $k_{obs.}$ of 5.14 ms^{-1} and a corresponding lifetime of 195 μs, identical to that observed experimentally. The dihydrate was assigned a coordination number of seven; having three chloride ions and four bridging water molecules. Substituting "n" = 4 and "m" = 3 into Eqn. (3) yields a $k_{obs.}$ of 6.31 ms^{-1}, which corresponds to a lifetime of 158 μs. This predicted value is also identical to that observed experimentally from the $EuCl_3 \cdot 2H_2O$ sample. The coordination of the Eu^{3+} ion in the monohydrate compound was believed to consist of six chloride ions and two water molecules. Using Eqn. (3) with these values yields a $k_{obs.}$ of 5.59 ms^{-1} and a corresponding luminescence lifetime of 179 μs. The experimental value of 171 μs is in excellent agreement, considering experimental errors and the expansion of the coordination sphere implied by the shift in the spectral features. The consistent agreement between the calculated and measured lifetimes implies that a model based on the inner sphere coordination of the emitting Eu^{3+} ion appears to be valid and would be useful in predicting luminescence lifetimes.

CONCLUSIONS

The results of our investigations suggest that the coordination number of the Eu^{3+} ion in $EuCl_3 \cdot 3H_2O$ is six, which includes three water molecules and three chloride ions. In $EuCl_3 \cdot 2H_2O$, the Eu^{3+} ions have a coordination number of seven; three chloride ions and four bridging water molecules. Similarly, a coordination number of eight is suggested for the Eu^{3+} ion in $EuCl_3 \cdot H_2O$, where there are six bridging chloride ions and two bridging water molecules.

The values measured for the luminescence lifetimes of the five $EuCl_3 \cdot nH_2O$ (n=0,1,2,3,6) compounds can be calculated by summing the effects associated with the complexing ligands within the inner coordination sphere of the emitting Eu^{3+} ion. This summation includes terms associated with both complexed water molecules and complexed chloride ions. From our results, it has been determined that for each water molecule that occupies a Eu^{3+} ion's inner sphere coordination site, the $k_{obs.}$ is increased by a factor of 1.17 ms^{-1}/H_2O. Similarly, a chloride ion occupying an inner sphere coordination site increases the $k_{obs.}$ by a factor of 0.542 ms^{-1}/Cl^{-}. Although the effect of a chloride ion on the luminescence lifetime of the Eu^{3+} ion is less than half of that associated with a water molecule, the chloride ion plays an important and predictable role in the observed lifetimes of these five Eu^{3+} compounds. Whether this approach is limited to the $EuCl_3 \cdot nH_2O$ system, or can be extended to other systems, will be the object of future studies.

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