Inorganica Chimica Acta, *142* (1988) 165–168

The Luminescence of Europium Nitrate Hexahydrate, $Eu(NO_3)_3 \cdot 6H_2O$

G. BLASSE, G. J. DIRKSEN and J. P. M. VAN VLIET
Physical Laboratory, University Utrecht, P.O.B. 80.000, 3508 TA Utrecht, The Netherlands

(Received May 21, 1987)

Abstract

Some luminescent properties of single crystals of $Eu(NO_3)_3 \cdot 6H_2O$ are reported at temperatures down to liquid helium. The water molecules are responsible for a considerable amount of quenching of the emission. The Eu^{3+} coordination changes upon lowering the temperature. The number of $^5D_0$–$^7F_2$ lines observed is higher than expected.

Introduction

Recently one of us reported on the emission of the Gd^{3+} ion in a mixed coordination of SO_4^{2-} anions and one water molecule in the host lattice $NaLa(SO_4)_2 \cdot H_2O$ [1]. From the cooperative vibronic emission spectrum, it follows that the electronic transition on the Gd^{3+} ion couples with vibrational transitions on the sulphate and water ligands.

Here we wish to report on observations made for another mixed coordination, *viz.* in $Eu(NO_3)_3 \cdot 6H_2O$. The crystal structure of the lanthanide nitrate hexahydrates is well known. The europium compound has the same structure as $Pr(NO_3)_3 \cdot 6H_2O$, which has been refined by Fuller and Jacobson [2]. Figure 1 shows the coordination around the lanthanide ion. It consists of three bidentate nitrate groups and four water molecules. It is interesting to note that the Pr–O(H_2O) distances are shorter (2.45–2.47 Å) than the Pr–O(NO_3) distances (2.55–2.72 Å). As Fig. 1 shows, the nitrate groups are on one side of the lanthanide ion and the water molecules on the other. The shortest Ln–Ln distance is about 6 Å in this structure.

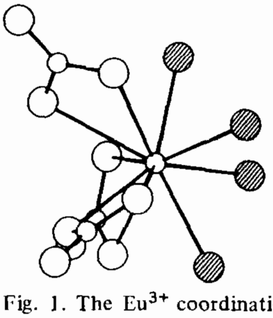

Fig. 1. The Eu^{3+} coordination in $Eu(NO_3)_3 \cdot 6H_2O$. Hatched spheres represent oxygen in water.

The results of this study show that both ligands interact with the Eu^{3+} ion; the implications of this are different.

Experimental

Crystals of $Eu(NO_3)_3 \cdot 6H_2O$ were grown from saturated solutions as described in the literature [3] and checked by X-ray diffraction. They show luminescence of a reasonable intensity under long wavelength ultraviolet excitation. The emission spectrum equals that reported in ref. 3.

The optical set-up has been described elsewhere and consists of a Perkin-Elmer MPF 44 spectrofluorometer equipped with a helium cryostat, and a Molectron DL 200 tunable dye laser pumped with a Molectron OV 14 nitrogen laser [4].

Results and Discussion

Excitation Spectra

The excitation spectrum of the red Eu^{3+} emission shows only the characteristic lines within the $4f^6$ configuration. For wavelengths $\lambda < 300$ nm no luminescence is observed, not even at 4.2 K. The transmission spectrum shows, in addition to these lines, an intense absorption which has its onset at about 320 nm. This is the well-known nitrate-ion absorption. Obviously nitrate-ion excitation results only in rapid non-radiative return to the ground state. This process is so rapid that not only radiative emission but also transfer to Eu^{3+} are not able to compete.

Figure 2 shows the excitation spectrum at 200 K in the region of the $^7F_{0,1}$–$^5D_1$ transitions. The broader bands have disappeared at 4.2 K. The sharp lines are due to the $^7F_0$–$^5D_1$ transition which is split into three. Actually the site symmetry of the Eu^{3+} ion is C_1 [2], so that three lines are to be expected. The splitting is, however, very small (~20 cm^{-1}). The thermally excited $^7F_1$–$^5D_1$ transition is much

0020-1693/88/$3.50

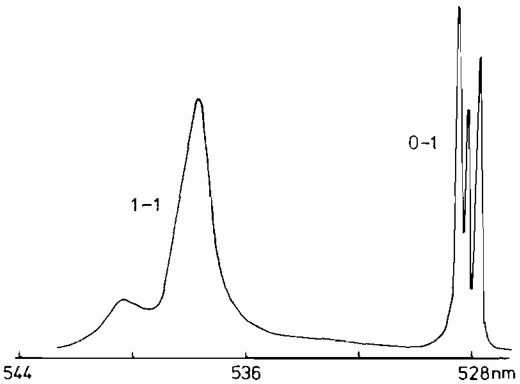

Fig. 2. Excitation spectrum of the Eu^{3+} emission of $Eu(NO_3)_3 \cdot 6H_2O$ at 200 K showing the $^7F_{0,1}$–$^5D_1$ transitions. Measurements on laser set-up. In this and other Figures the notation J–J' stands for a transition ^7F_J–$^5D_{J'}$ (or ^5D_J–$^7F_{J'}$).

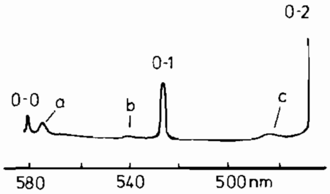

Fig. 3. Excitation spectrum of the Eu^{3+} emission of $Eu(NO_3)_3 \cdot 6H_2O$ at 4.2 K showing the cooperative vibronic transitions in absorption: a, 0–0 + ν(Eu–O); b, 0–0 + $\nu(NO_3)$; c, 0–0 + $\nu(H_2O)$ (see also text). The electronic 0–2 transition is off scale. Spectrofluorometer measurements.

broader. The large width is ascribed to the short lifetime of the $^7F_1$ level which will broaden this level [5]. The splitting observed (~100 cm^{-1}) reflects mainly the $^7F_1$ crystal-field splitting which can, however, be determined more accurately from the emission spectra (see below).

Figure 3 shows the excitation spectrum at 4.2 K in the region of the $^7F_1$–$^5D_{0,1}$ transitions. At 300 K this spectrum is no longer informative due to the presence of transitions from the $^7F_1$ and $^7F_2$ levels. The 0–0 transition is well known for its vibronic components [6]. In the spectrum we observe vibronic lines at 185, ~1300 and ~3400 cm^{-1}. These can be associated with the following vibrations: Eu^{3+}–O^{2-} bending [7], and asymmetric NO_3^- stretching and H_2O stretching, respectively. The coupling with the Eu^{3+}–O^{2-} bending is clearly the stronger, and that with the nitrate the weaker of the three. Since there are three nitrate anions and four H_2O molecules around the Eu^{3+} ion, the numbers cannot explain the difference [1]. It must obviously be assumed that the Eu–O distances, given above, play a role.

Emission Spectra

Figure 4 shows an emission spectrum of $Eu(NO_3)_3 \cdot 6H_2O$ upon excitation into the Eu^{3+} lines at 4.2 K. This spectrum shows several interesting aspects.

(a) The emission from the $^5D_1$ level is still clearly visible. Although its intensity has decreased, it can also be observed at room temperature. Obviously the forbidden character of the $^5D_1$–$^5D_0$ non-radiative transition [8] is so strong, that the available vibrational modes are not able to quench it completely.

(b) The intensity of the $^5D_0$–$^7F_0$ transition is extremely low. At 300 K, however, this line appears clearly in the spectra as a very sharp line (see Fig. 5). This seems to indicate a slight change in coordination in going from 4.2 to 300 K. In layered crystal structures the $^5D_0$–$^5F_0$ emission intensity is known to be critically dependent on the details of the layer packing [9, 10]. Since the coordination has a layered character (nitrate on one side and water on the other), it is conceivable that the temperature variation implies a slight change in the coordination of the Eu^{3+} ion.

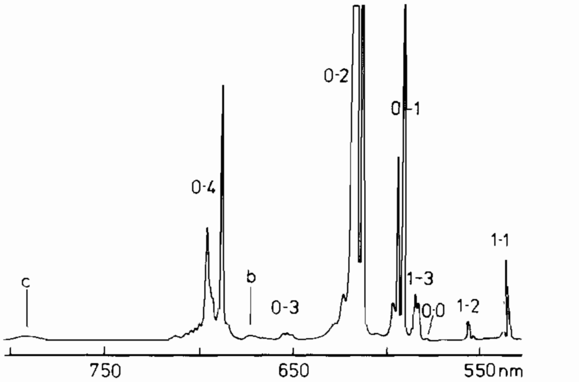

Fig. 4. Emission spectrum of the Eu^{3+} luminescence of $Eu(NO_3)_3 \cdot 6H_2O$ at 4.2 K. Spectrofluorometer measurements. The arrows indicate the cooperative vibronic transitions: b, 0–2 – $\nu(NO_3)$; c, 0–2 – $\nu(H_2O)$.

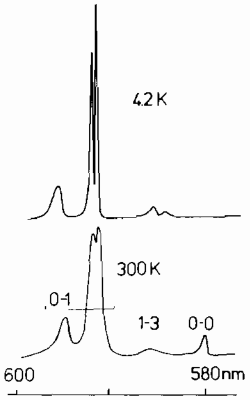

Fig. 5. Emission spectra of the Eu^{3+} luminescence of $Eu(NO_3)_3 \cdot 6H_2O$ at 4.2 and 300 K. Measurements with laser set-up. Note the change in 0–0 emission intensity.

(c) The $^5D_0$–$^7F_1$ emission (Fig. 5) is split into three lines, yielding a total $^7F_1$ crystal-field splitting of about 130 cm^{-1}. This is well in line with the value obtained from the excitation spectra. This value must be considered as a weak crystal-field splitting [7]. The broadness of the longer wavelength component, especially notable at 4.2 K (Fig. 5), is due to the shorter lifetime of the final level which can easily relax to the lower $^7F_1$ components (see above and ref. 5). The splitting into three lines reflects the absence of symmetry elements at the Eu^{3+} site.

(d) The $^5D_0$–$^7F_2$ transition shows clearly too many lines (seven, see Table I). In view of the five-fold degeneracy of the $^7F_2$ level, the number to be expected is five. Such a deviation has been discussed by Caro in terms of phonon interference [5, 11]. The present data suggest an interference with the symmetric nitrate vibration ($\nu_1 \sim 1050$ cm^{-1}). Its frequency equals the energy difference between the higher $^7F_2$ components and the $^7F_0$ ground state (see Table I).

TABLE I. Peak Positions of the Seven $^5D_0$–$^7F_2$ Emission Transitions for Eu^{3+} in Eu(NO$_3$)$_3$·6H$_2$O at 4.2 K Relative to the Position of the $^5D_0$–$^7F_0$ Transition

Transition	Position (cm^{-1})	Peak intensity
1	943	10
2	1031	5
3	1045	8
4	1058	2.5
5	1069	0.5
6	1082	2
7	1092	3.5

(e) When looking for cooperative vibronic emission, we found in the spectra two weak and broad features which might well be due to such transitions. One is at 672 nm, the other at about 790 nm. The former lies at about 1400 cm^{-1} and the latter at about 3500 cm^{-1} lower energy than the most intense $^5D_0$–$^7F_2$ emission. They might well be due to cooperative vibronic transitions. In emission the vibronic line involving the nitrate group is more intense than that involving the water molecule. This is contradictory to what was found in the excitation spectra. However, the electronic transition is different in the two cases. It should also be realised that the intensities are so low that their accuracy cannot be high.

It is interesting to note that Bünzli and Pradervand [12] report transitions in the emission spectra of [Eu(NO$_3$)$_2$(18-6)]$_3$[Eu(NO$_3$)$_6$] (where (18-6) stands for the 18-crown-6-ether) and Eu$_2$Mg$_3$(NO$_3$)$_{12}$·24H$_2$O which are situated near to 672 nm. They are ascribed to vibronic transitions in general, but we assume that they are of the same type as proposed by us, *viz.* cooperative vibronic transitions on the Eu^{3+} ion and the NO$_3^-$ ion (ν_3).

Finally, we note in this connection that we also observed for Tb(NO$_3$)$_3$·6H$_2$O crystals weak cooperative vibronic transitions which are very similar to those reported by Stavola *et al.* [13]. At about 735 nm there is a weak emission transition ascribed to $^5D_4$–$^7F_4$ in cooperation with a 3500 cm^{-1} vibration of the water molecule. The others, and those coupled with the nitrate vibration, coincide with pure electronic transitions on Tb^{3+}, or are too weak to be observed.

Decay times

The decay curves of the Eu^{3+} emission of Eu(NO$_3$)$_3$·6H$_2$O are all exponential. The corresponding decay time amounts to 180 μs in the temperature range 4.2–300 K. This is a too short a decay time for a purely radiative transition on the Eu^{3+} ion.

Since the shortest Eu–Eu distance in the crystal structure of europium nitrate hexahydrate is about 6 Å and the decay time is temperature independent, we can neglect any non-radiative loss due to energy migration to killers [14, 15]. Quenching via the Eu^{3+}–O^{2-} charge-transfer state [7] can also be excluded, since this state must be situated at 300 nm or shorter wavelengths (overlapped by the nitrate absorption band). Therefore the non-radiative loss is ascribed to multiphonon emission.

An estimation of the pure radiative decay time was made as follows. The radiative transition probability of the $^5D_0$–$^7F_1$ transition is to a good approximation independent of the Eu^{3+} coordination, since it is a magnetic-dipole transition and is forbidden as a forced electric-dipole transition. Therefore the ratio of the $^5D_0$–$^7F_1$ magnetic-dipole emission intensity and the emission intensities of all other emission transitions is a measure of the total radiative decay time [16]. Using data in the literature, this yields an estimated radiative decay time for Eu^{3+} in Eu(NO$_3$)$_3$·6H$_2$O of about 1000 μs. Therefore, the quantum efficiency of our sample amounts to about 18%, independent of temperature.

The only vibration which is able to quench the Eu^{3+} emission of our sample is that of the water molecule. The energy gap involved is some 12 000 cm^{-1}. A nitrate vibration of 1400 cm^{-1} cannot contribute to an effective non-radiative decay rate, since more than 8 vibrations have to be excited simultaneously. For the water molecule (3500 cm^{-1}), however, only 3 to 4 vibrations need to be excited. Usually this yields a sizeable decay rate. Actually, if we use the well-known Horrocks' relation [17] with τ(D$_2$O) = 1000 μs and τ(H$_2$O) = 180 μs, we arrive at a number of 4.5 water molecules around the Eu^{3+} ion, which is very near to the crystallographically determined number of 4. The quenching is, therefore, ascribed to the water molecules which coordinate the Eu^{3+} ion.

Conclusions

We have shown that the ligands of the Eu^{3+} ion in $Eu(NO_3)_3 \cdot 6H_2O$ influence the luminescence properties. The water molecules are responsible for a considerable non-radiative loss; the presence of water molecules and nitrate anions leads to cooperative vibronic emission. The emission spectrum shows that it is dangerous to use Eu^{3+} as a probe of local site symmetry because of phonon interference. Finally, the emission spectra indicate a small change in coordination upon lowering the temperature.

References

1 G. Blasse, *Inorg. Chim. Acta, 132,* 273 (1987).
2 C. C. Fuller and R. A. Jacobson, *Cryst. Struct. Commun., 5,* 349 (1976).
3 B. Piriou and D. Svoronos, *J. Less-Common Met., 112,* 275 (1985).
4 P. A. M. Berdowski and G. Blasse, *J. Luminescence, 29,* 243 (1984).
5 P. Caro, O. K. Moune, E. Antic-Fidancev and M. Lemaitre-Blaise, *J. Less-Common Met., 112,* 153 (1985).
6 See e.g. N. Yamada, S. Shionoya and T. Kushida, *J. Phys. Soc. Jpn., 32,* 1577 (1972).
7 G. Blasse, M. Buijs and N. Sabbatini, *Chem. Phys. Lett., 124,* 538 (1986).
8 J. M. F. van Dijk and M. F. H. Schuurmans, *J. Chem. Phys., 78,* 5317 (1983).
9 G. Blasse and A. Bril, *J. Chem. Phys., 46,* 2579 (1967).
10 G. Blasse and A. Bril, *Philips Res. Repts., 21,* 368 (1966).
11 P. Caro, *J. Less-Common Met., 126,* 239 (1986).
12 J. G. Bünzli and G. Pradervand, *J. Chem. Phys., 85,* 2489 (1986).
13 M. Stavola, L. Isganitis and M. G. Sceats, *J. Chem. Phys., 74,* 4228 (1981).
14 F. Kellendonk and G. Blasse, *J. Chem. Phys., 75,* 561 (1981).
15 J. P. M. van Vliet, G. Blasse and L. H. Brixner, *J. Electrochem. Soc.,* in press.
16 G. Blasse and A. Bril, *Philips Res. Repts., 22,* 481 (1967).
17 W. de W. Horrocks, Jr. and D. R. Sudnick, *Acc. Chem. Res., 14,* 384 (1981).