Photophysical Properties of $Eu(SiW_{11}O_{39})_2^{13-}$ and $Eu(BW_{11}O_{39})_2^{15-}$

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Received April 28, 1984

The photophysical properties (absorption, emission, and excitation spectra; luminescence quantum yields; luminescence decay lifetimes) of $K_{13}[Eu(SiW_{11}O_{39})_2]$ and $K_{15}[Eu(BW_{11}O_{39})_2]$ in aqueous solution and in the solid state are reported. Both complexes exhibit broad and very intense O → W charge transfer bands in the U.V. region and weak and narrow f → f Eu^{3+} bands in the visible. At 77 K the luminescence emission of both complexes, which consists of $^5D_0 \rightarrow {}^7F_J$ bands split by the local crystal field, can be pumped very efficiently via both the O → W CT levels and the f → f Eu^{3+} levels, whereas at 298 K only pumping via the f → f Eu^{3+} is efficient. The values of the luminescence decay lifetimes in H_2O and D_2O solution are quite similar, showing that no water molecule is coordinated to the central Eu^{3+} ion. The high resolution emission spectra are discussed in an attempt to define the coordination symmetry of Eu^{3+}.

Introduction

The iso- and hetero-polyoxomolybdates and polyoxotungstates constitute a particularly interesting family of chemical compounds because of their great variety of compositions and structures [1, 2]. Eu^{3+} may coordinate some of these anions to give rise to luminescent complexes [3–6] which, in principle, might be interesting as inorganic photosensitizers or relay species [6]. We report here the photophysical characterization (absorption, emission, and excitation spectra; luminescence quantum yields; luminescence decay lifetimes) of two of these compounds, $Eu(SiW_{11}O_{39})_2^{13-}$ and $Eu(BW_{11}O_{39})_2^{15-}$, in aqueous solution and in the solid state. Spectral data on $Eu(SiW_{11}O_{39})_2^{13-}$ were previously reported by Stillman and Thomson [3] and by Blasse *et al.* [4].

In these complexes the ligands are $XW_{11}O_{39}$ units (X = Si or B) which are obtained from the Keggin $XW_{12}O_{40}$ structure by removal of the tungsten atom and its unshared oxygen from one of the twelve octahedra (Fig. 1). The complexes are formed by coordination of two such ligands to Eu^{3+}, which is thus coordinated to eight oxygen atoms [4, 7].

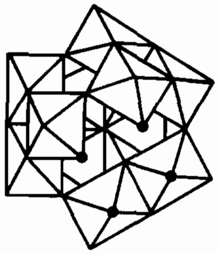

Fig. 1. Schematic representation of the $XW_{11}O_{39}$ unit. The X atom (Si or B) occupies the tetrahedral central cavity. The four oxygen atoms which coordinate Eu^{3+} in the $Eu(XW_{11}O_{39})_2^{z-}$ complexes are indicated by dots.

Experimental

$K_{13}Eu(SiW_{11}O_{39})_2\cdot 30H_2O$ was prepared following the method given by Peacock and Weakley [8] for the analogous Ce(IV) compound. Calc. for $K_{13}Eu(SiW_{11}O_{39})_2\cdot 30H_2O$: Eu, 2.30; W, 61.4; K, 7.72; Si, 0.8; H_2O, 8.20; found: Eu, 2.22; W, 61.8; K, 7.68; Si, 0.7; H_2O, 8.23.

$K_{15}Eu(BW_{11}O_{39})_2\cdot 16H_2O$ was prepared from $K_5BW_{12}O_{40}\cdot nH_2O$ [9] and $EuCl_3\cdot 6H_2O$ following a procedure similar to that used to prepare the compound containing Si. Calc. for $K_{15}Eu(BW_{11}O_{39})_2\cdot 16H_2O$: Eu, 2.40; W, 63.8; K, 9.25; H_2O, 4.56; found: Eu, 2.53; W, 64.2; K, 9.15; H_2O, 4.46. Thermogravimetric analysis showed that both complexes are completely dehydrated below 200 °C without apparent decomposition. $Na_9Eu(W_5O_{18})_2\cdot 18H_2O$ was available from a previous study [6].

Absorption spectra were recorded with a Cary 219 spectrophotometer. Emission and excitation spectra (under low resolution) were recorded with a Perkin-Elmer 650-40 spectrofluorimeter equipped with a R 928 phototube. High resolution emission spectra were obtained by a Jasco R 300 Raman Spectrophotometer using a Spectra-Physics Ar laser for excitation at 465.8 nm. Emission lifetimes were measured by a JK System 2000 neodymium Yag DLPY 4 laser (λ_{exc} = 532 nm) and by the Perkin-Elmer LS-5 spectrofluorimeter used in its phosphorescence decay mode (λ_{exc} = 315 or 394 nm). In both cases the experimental uncertainty is estimated

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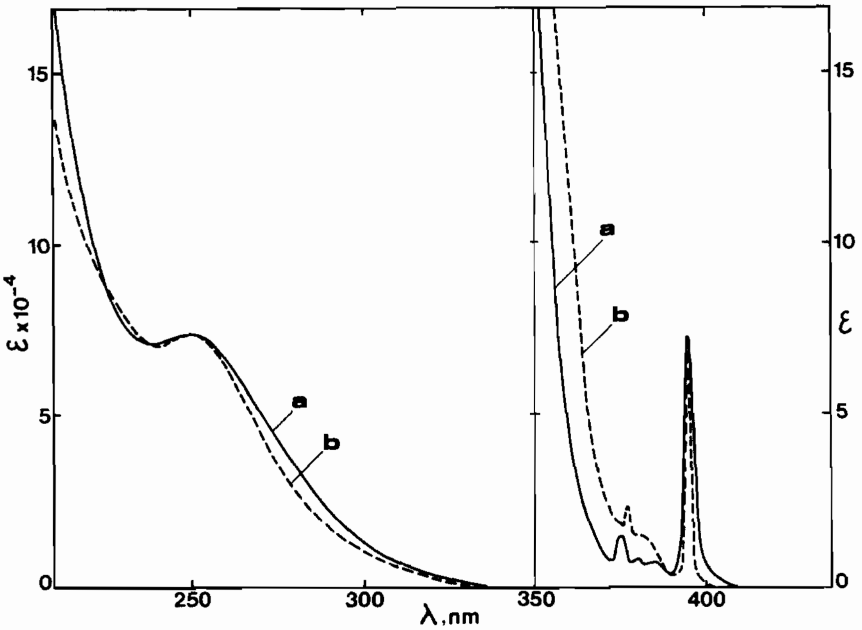

Fig. 2. Absorption spectra of (a) $Eu(SiW_{11}O_{39})_2{}^{13-}$ and (b) $Eu(BW_{11}O_{39})_2{}^{15-}$ in aqueous solution.

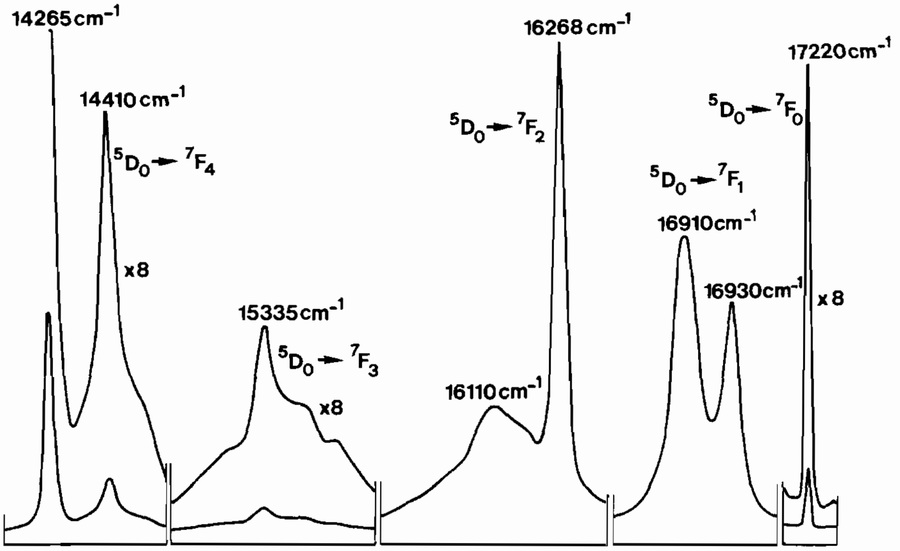

Fig. 3. High resolution emission spectrum of $K_{13}[Eu(SiW_{11}O_{39})_2]$ in the solid state at room temperature.

to be 10%. When the same sample was examined with the two methods, the agreement between the lifetime values obtained was better than 10%. The emission quantum yields in fluid solution were evaluated by the method described by Haas and Stein [10] using as standards $Eu(ClO_4)_3$ in D_2O (ϕ_{em} = 0.20) for 394 nm excitation and $Ru(bpy)_3{}^{2+}$ (ϕ_{em} = 0.042 [11]) for 305 nm excitation. The estimated uncertainty is 10% for excitation at 394 nm, where the samples were strongly luminescent, and 20% for excitation at 305 nm, where the luminescence was very weak. For solid samples, the emission quantum yields were estimated using $K_9[Eu(W_5O_{18})_2]$ as standard (ϕ_{em} = 0.9 and 0.8 at 77 and 298 K) [5]. The estimated uncertainty is 30%.

Results

Both complexes were stable in aqueous solution for several days. The absorption spectra of the two complexes (Fig. 2) show a very intense, broad band with maximum at 250 nm with $\epsilon \simeq 75\,000$ and very weak and narrow absorption bands in the U.V. and visible region.

TABLE I. Luminescence Quantum Yields.

Experimental Conditions			Luminescence Quantum Yield, ϕ^a		
Sample	T (K)	Exc. band	$Eu(SiW_{11}O_{39})_2{}^{13-}$	$Eu(BW_{11}O_{39})_2{}^{15-}$	$Eu(W_5O_{18})_2{}^{9-}$
H_2O solution	295	$^5L_6(Eu^{3+})$	0.35	0.17	–
H_2O solution	295	O → W CT	1×10^{-4}	$<5 \times 10^{-5}$	–
D_2O solution	295	$^5L_6(Eu^{3+})$	0.56	0.31	0.5^b
D_2O solution	295	O → W CT	3×10^{-4}	1×10^{-4}	0.2^b
solid state	295	$^5L_6(Eu^{3+})$	~1	–	$\sim 1^c$
solid state	295	O → W CT	$<1 \times 10^{-3}$	–	0.8^d
solid state	77	$^5L_6(Eu^{3+})$	~1	–	$\sim 1^c$
solid state	77	O → W CT	1	–	0.9^d

[a] For experimental errors, see text. [b] Ref. [6]. [c] Assumed value. [d] Ref. [5].

TABLE II. Luminescence Decay Lifetimes.

Experimental Conditions		Luminescence decay lifetime, τ(ms)^{a,b}		
Sample	T (K)	$Eu(SiW_{11}O_{39})_2{}^{13-}$	$Eu(BW_{11}O_{39})_2{}^{15-}$	$Eu(W_5O_{18})_2{}^{9-}$
H_2O solution	295	3.3	2.2	0.25^c
D_2O solution	295	5.2	4.3	3.7^c
H_2O solution	77	2.2	1.0	$\sim 2^d$
D_2O solution	77	4.3	1.7	–
solid state	295	2.4	1.8	2.8
solid state	77	2.7	1.9	3.3
solid state $(D_2O)^e$	295	2.4	–	3.1^c

[a] For experimental errors, see text. [b] The same values were obtained upon excitation in either the $^5L_6(Eu^{3+})$ band or in the O → W CT band. [c] Ref. [6]. [d] Decay not exponential. [e] Solid crystallized from D_2O solution.

Figure 3 shows the high resolution emission spectrum of $K_{13}[Eu(SiW_{11}O_{39})_2]$ at 295 K. The spectrum of the complex in aqueous solution is exactly the same. The emission spectra of $K_{15}[Eu(BW_{11}O_{39})_2]$ in the solid state and in solution are quite similar to that shown in Fig. 3 except for a smaller resolution of the two components of the $^5D_0 \rightarrow {}^7F_1$ transition and the presence of a small peak on the high energy side of the $^5D_0 \rightarrow {}^7F_0$ transition.

At room temperature, the ratio between the intensity of the broad U.V. band and the intensity of the narrow visible bands is very much smaller in the excitation spectra than in the absorption spectra both in the solid state and in aqueous solution. At 77 K, however, the intensity of the broad U.V. band in the excitation spectra becomes noticeably stronger than at room temperature.

The values obtained for the luminescence quantum yields upon excitation in the broad U.V. band or in the narrow band at 394 nm (which, as we shall see in the discussion, correspond to excitation of O → W CT and Eu^{3+} (f → f) transition, respectively) under different experimental conditions are shown in Table I.

The luminescence decay was strictly exponential in all cases and independent of excitation wavelength. The values of the luminescence lifetimes are given in Table II.

Some previously available [5, 6] and new data concerning $Eu(W_5O_{18})_2{}^{9-}$ are also reported in Tables I and II for comparison purposes.

For the experiments carried out in solution, the results obtained were in all cases independent of the complex concentration (5×10^{-4}–1×10^{-2} M).

Discussion

It is well known that a detailed analysis of the luminescence properties of Eu^{3+} in its coordination compounds can allow the elucidation of the composition, structure, and geometry of the coordination environment [12–17] and of the efficiency of the communication between the coordination environment and the central metal ion [4, 13, 17–19].

Before comparing the results obtained for the $Eu(XW_{11}O_{39})_2^{z-}$ (X = Si, B) complexes studied in this paper with those previously reported for $Eu(W_5O_{18})_2^{9-}$ [4–6], we would like to emphasize an important difference between the two types of complexes. In aqueous solution, $Eu(W_5O_{18})_2^{9-}$ is subject to equilibria among different species as is shown by the dependence of the emission and excitation spectra and luminescence lifetime on the complex concentration [6]. By contrast the emission and excitation spectra and the luminescence lifetimes of $Eu(XW_{11}O_{39})_2^{z-}$ do not depend on the complex concentration, showing that these complexes behave as single species*.

Communication between Tungstate Levels and Europium Levels

The broad, high intensity absorption band exhibited by the $Eu(XW_{11}O_{39})_2^{z-}$ complexes in the U.V. region (Fig. 2) is also present in the free $SiW_{11}O_{39}^{8-}$ ligand with extinction coefficient about half that found for the two complexes [20]. Such a band can thus be safely assigned to oxygen-to-tungsten charge transfer (O → W CT) transitions of the ligands, which are practically unaffected by coordination. The tail of the O → W CT band extends down to the visible, where the weak and narrow bands due to the Eu^{3+} (f → f) transitions can also be observed. The O → Eu CT bands are expected to lie in the 240–250 nm region [18, 21] but they have small extinction coefficients [18, 22] and thus they are covered by the intense ligand bands. The bands shown in the emission spectra (Fig. 3) of both complexes correspond to radiative transitions from the $^5D_0$ excited level to the ^7F_J ground state manifold within the Eu^{3+} ion. The emitting $^5D_0$ level can be reached by exciting both the various f → f bands of Eu^{3+} and the O → W CT band of the ligand. However, in the excitation spectra at 295 K the latter band appears with a much lower intensity (compared with the intensity of the f → f bands) than in the absorption spectra, showing that the efficiency of conversion of the O → W CT levels to the $^5D_0$ Eu^{3+} emitting level is much smaller than unity. This behaviour, which was previously noticed for $Eu(SiW_{11}O_{39})_2^{13-}$ by Blasse *et al.* [4] is placed on a quantitative basis by the quantum yield values reported in Table I. For both the $Eu(XW_{11}O_{39})_2^{z-}$ complexes the luminescence quantum yield at 295 K is very high upon excitation in the $^5L_6$ Eu^{3+} level, but it drops by a factor larger than 10^3 when excitation is performed into the O → W CT band. By contrast, at 77 K the quantum yield of the $Eu(SiW_{11}O_{39})_2^{13-}$ luminescence is the same (and about equal to unit) for excitation in the $^5L_6$ Eu^{3+} level and in the O → W CT band. These results show that the conversion from the O → W CT levels to the excited Eu^{3+} levels occurs with unitary efficiency at 77 K, while at room temperature another deactivation channel of the O → W CT levels predominates, thus reducing drastically the communication between O → W CT levels and excited Eu^{3+} levels. It should be noted that the temperature effect on the communication between ligand levels and Eu^{3+} levels is much smaller for $Eu(W_5O_{18})_2^{9-}$ (Table I). The reason why $Eu(XW_{11}O_{39})_2^{z-}$ and $Eu(W_5O_{18})_2^{9-}$ behave so differently is probably related, as suggested by Blasse *et al.*, [4] to the relative importance of a thermally activated radiationless deactivation path leading from the O → W CT levels to the ground state. Some role could also be played by the energy position of the O → Eu^{3+} CT excited states.

Interaction with Solvent

Because of its relatively large size and low tendency to give directional bonds, Eu^{3+} exhibits high coordination numbers and its first coordination sphere is often completed by water molecules both in aqueous solution and in the solid state [12–16]. Since the radiationless deactivation of the $^5D_0$ emitting level is strongly enhanced by coupling with the high frequency O–H oscillators, the luminescence lifetime is strongly affected by the presence of water molecules in the first coordination sphere [10, 13]. On the basis of this observation, Horrocks *et al.* [12, 13] have developed a method to estimate the number of water molecules coordinated to Eu^{3+} in Eu(III) complexes. This number is given, with an estimated uncertainty of 0.5, by the following equation:

$$n = 1.05(k_{H_2O} - k_{D_2O})$$

where k_{H_2O} and k_{D_2O} are the reciprocal (in ms^{-1}) of the experimental excited state lifetimes in a H_2O or D_2O environment. Using the lifetime values obtained for H_2O and D_2O solutions at 295 K (Table II), n results to be 0.1 ± 0.5 for $Eu(SiW_{11}O_{39})_2^{13-}$ and 0.2 ± 0.5 for $Eu(BW_{11}O_{39})_2^{15-}$, which means that in both cases there is no water molecule in the first coordination sphere of Eu^{3+}. The same conclusion can be drawn for rigid solution at 77 K and for solid samples when the relevant lifetime values reported in Table II are used. The situation is quite different from that of the previously studied $Eu(W_5O_{18})_2^{9-}$ complex which, in diluted aqueous solutions at room temperature, has four water molecules coordinated to Eu^{3+}. The number of coordinated water molecules however, was found to decrease with increasing complex concentration because of the formation of ion-pairs and it was found to be zero in the solid

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*The small peak on the high energy side of the $^5D_0 \rightarrow {}^7F_0$ band of $Eu(BW_{11}O_{39})_2^{15-}$ is present both in the solid state and in solution, showing that it is due to some minor impurity.

state [6]. Comparing the different size and structure of the W_5O_{18} and $XW_{11}O_{39}$ ligands, it does not seem likely that the larger steric hindrance of the ligand can fully account for the lack of coordinated water molecules in aqueous solution. Another factor which can make water coordination more difficult is certainly the large negative charge (−8 or −9) of the $XW_{11}O_{39}$ ligands, which better compensates the positive charge of Eu^{3+} and can also favor the formation of ion pairs with K^+ even in very dilute solutions.

Coordination Geometry

According to Blasse *et al.*, [4] the structure of $K_{13}[Eu(SiW_{11}O_{39})_2]$ is similar to that of $Cs_{12}[U(GeW_{11}O_{39})_2]$ described by Tourné *et al.* [7]. In the latter complex U is coordinated by eight oxygen atoms forming a distorted Archimedean antiprism. The polytungstate groups consist of distorted tungstate octahedra having approximate C_{4v} (actual C_s) symmetry [7].

Stillman and Thomson [3] reported that the distinct feature of the high-resolution emission spectrum of $K_{13}[Eu(SiW_{11}O_{39})_2]$ is an intense single line in the $^5D_0 \rightarrow {}^7F_2$ region. On the basis of this observation, they suggested a D_4 or D_{3h} symmetry. We would like to note, however, that in the $^5D_0 \rightarrow {}^7F_2$ region there are at least two bands at room temperature (Fig. 3) and clearly three maxima at 77 K. According to the same authors, when $K_{13}[Eu(SiW_{11}O_{39})_2]$ was dissolved, two different species were present, as indicated by the appearance of two $^5D_0 \rightarrow {}^7F_0$ bands having approximately the same intensity. Our $K_{13}[Eu(SiW_{11}O_{39})_2]$ sample, however, exhibits the same emission spectrum (and, in particular, only one $^5D_0 \rightarrow {}^7F_0$ component) in the solid state and in aqueous solution.

Blasse *et al.*, [4] excluded a D_{4d} site symmetry which would imply no allowed $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$ bands. On the basis of the two components found for the $^5D_0 \rightarrow {}^7F_2$ transition in a low resolution spectrum they also considered the possibility of a C_{4v} symmetry, which, however, was discarded because only 2 bands were observed (*vs.* four transitions expected) in the $^5D_0 \rightarrow {}^7F_4$ region. Our high resolution spectrum (Fig. 3) in fact shows four components (two maxima and two shoulders) in the $^5D_0 \rightarrow {}^7F_4$ region, but also at least three components in the $^5D_0 \rightarrow {}^7F_2$ region, which is again in disagreement with an undistorted C_{4v} symmetry.

Although the assignment of the Eu^{3+} site symmetry on the basis of the Stark components of the emission spectra is an appealing and very popular subject (see, for example, Table X of Ref. [13]), it should be pointed out that in several cases the assignment is made on the basis of a partial analysis of low resolution emission spectra. When high resolution spectra and at least five $^5D_0 \rightarrow {}^7F_J$ regions are considered, a straightforward assignment to a defined geometry often proves difficult because (i) slight deviation from an ideally high symmetry may cause the appearance of 'forbidden' bands and, *vice versa*, (ii) for a low symmetry species some sublevels may accidentally almost coincide or may be close enough to prevent resolution in the observed fluorescence spectrum. This is clearly the case for $Eu(SiW_{11}O_{39})_2{}^{13-}$ where the symmetry of the first coordination sphere of Eu^{3+} may be close to D_{4d} but the actual symmetry of the molecule is probably as low as C_1.

Acknowledgements

We would like to thank Dr. G. Fini for assistance and suggestions concerning the recording of high resolution emission spectra. Financial support from Ministero della Pubblica Istruzione and the Consiglio Nazionale delle Ricerche is gratefully acknowledged.

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