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Orange Luminescence from Europium(III) Compounds

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In a recent communication Blasse [1] commented on the appearance of orange luminescence from europium(III) in three compounds in which the symmetry is approximately D_{4d}. One of these, the Eu^{3+}–decatungstate is a molecular compound and the other two, $YF_3:Eu^{3+}$ and $GdB_3O_6:Eu^{3+}$, are non-molecular solids. In the present communication we wish to elaborate on the examples quoted by Blasse and to point out additional examples of orange luminescence in non-centrosymmetric europium(III) complexes.

Europium(III) compounds having a center of inversion exhibit emission spectra dominated by the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$, which occurs at approximately 590 nm, and consequently are orange. Examples of these would be $Cs_2NaEuCl_6$ at 77 K (O_h), Eu(antipyrene)$_6$I$_3$ (S_6), and $Cs_2NaEu(NO_2)_6$ (T_h) [2]. When a europium(III) compound does not have a center of inversion, the luminescence is generally dominated by the $^5D_0 \rightarrow {}^7F_2$ forced-electric dipole transition at about 615 nm and the luminescence is red. (The possibility that there may be significant vibronic intensity in the $^5D_0 \rightarrow {}^7F_2$ transition cannot be dismissed and occasionally a compound that has an inversion center may appear pink. Such is the case for $Cs_2NaEuCl_6$ at room temperature.)

One of the idealized coordination polyhedra for eight-coordination is the square antiprism which has D_{4d} symmetry [3]. This point group does not possess a center of inversion and the number of lines predicted in the luminescence from $^5D_0$ is given in Table I [4]. Since the $^5D_0 \rightarrow {}^7F_2$ transition is forbidden, europium(III) compounds having D_{4d} symmetry should give an orange luminescence corresponding to the $^5D_0 \rightarrow {}^7F_1$ transition.

As pointed out by Blasse [1], this is an uncommon symmetry in non-molecular solids. However, in addition to the molecular decatungstate mentioned by Blasse there are other examples of complexes in which the coordination polyhedron approximates this symmetry. In particular, the complex Eu(4-picoline-*N*-oxide)$_8$(PF$_6$)$_3$ might be mentioned. This compound was studied in 1965 by Rose and Abramson and gives a very strong orange luminescence [5]. Although the group theoretical analysis in this paper is incorrect, the conclusion that the symmetry is D_{4d} is correct and is based on essentially the same arguments as those presented by Blasse [1]. The crystal structure of this compound has never been determined but that of Eu(pyridine-*N*-oxide)$_8$(ClO$_4$)$_3$ has [6]. This latter compound has an idealized coordination polyhedron that approximates the square antiprism and also gives an intense orange luminescence when excited with UV light. The spectrum is that which is expected in the first approximation for D_{4d} symmetry [7].

TABLE I. Number of Allowed Transitions for $^5D_0 \rightarrow {}^7F_{1,2,4}$ in Three Symmetries

Symmetry	Transition		
	$^5D_0 \rightarrow {}^7F_1$ (magnetic dipole)	$^5D_0 \rightarrow {}^7F_2$ (electric dipole)	$^5D_0 \rightarrow {}^7F_4$ (electric dipole)
D_3	2	2	4
D_{3h}	2	1	3
D_{4d}	2	0	2

The qualitative visual determination of color (that is, orange or red) cannot be used to draw even the limited conclusions mentioned above. A wide variety of europium(III) complexes have spectra in which the contribution of $^5D_0 \rightarrow {}^7F_1$ is sufficiently large that the luminescence appears to be orange to the naked eye even though the compound cannot have a center of inversion nor approximate D_{4d} symmetry.

The compound Na$_3$[Eu(oxydiacetato)$_3$]$\cdot$2NaClO$_4\cdot$6H$_2$O contains the complex ion [Eu(oxydiacetato)$_3$]$^{3-}$ and yields decidedly orange luminescence [2]. The symmetry of this complex ion can be approximated as D_3 in which both the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions are allowed (see Table I). Both transitions are observed but the magnetic dipole-allowed $^5D_0 \rightarrow {}^7F_1$ is the more intense which leads to the orange color. Calculations of the theoretical oscillator strengths are consistent with this observation [8]. Again, as in D_{4d}, substantial intensity is observed in the region of the $^5D_0 \rightarrow {}^7F_4$ transition.

The complex ion [Eu(terpy)$_3$]$^{3+}$ is a second example of a discrete complex which has essentially D_3 symmetry and in which the magnetic dipole transition is substantially more intense (approximately 6 times) than the electric dipole transition again resulting in a decidedly orange luminescence [9]. The $^5D_0 \rightarrow {}^7F_4$ emission is also relatively intense.

Finally it should be pointed out that even quite simple complex ions can give the orange luminescence even though they have a relatively high symmetry. The ion [Eu(H$_2$O)$_9$]$^{3+}$ occurs in the bromate, ethylsulfate, and trifluoromethylsulfonate [10, 11].

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The site symmetry around the europium(III) ion is C_{3h} and if only the oxygen atoms are considered, it is D_{3h}. Again, there is no center of inversion and both the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions are allowed. in each case the luminescence is orange and the 590 nm emission is considerably more intense than that at 616 nm. (In the case of the ethylsulfate it is a factor of five [12]. Moreover, the $^5D_0 \rightarrow {}^7F_4$ emission intensity is even slightly greater than that of $^5D_0 \rightarrow {}^7F_1$.)

In conclusion, the purpose of this brief communication has been to expand on the observation of Blasse [1] that a low $^5D_0 \rightarrow {}^7F_2$ emission intensity does not mean that a compound of europium(III) that yields an orange luminescence necessarily possesses a center of inversion. To this end we have presented some additional examples of non-centrosymmetric complexes in which the $^5D_0 \rightarrow {}^7F_2$ transition is weaker than the $^5D_0 \rightarrow {}^7F_1$ transition. These examples, which are not intended to be all-inclusive, include complexes in which the symmetry around the europium(III) ion is D_3 or D_{3h} as well as D_{4d}.

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