

ION-ION INTERACTION EFFECT ON THE LUMINESCENCE OF EUROPIUM DIBENZOYLMETHANE COMPLEXES*

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New europium dibenzoylmethane complexes with sodium and potassium acetate were obtained. Energy level splitting in crystalline field, and an additional splitting is reported. It is suggested that this additional splitting is due to ion-ion interaction.

1. Introduction

Trivalent europium ions can easily form complexes with β -diketones. It is well known [1, 2, 3] that such complexes crystallize in organic solutions of β -diketones with europium salts and either organic or inorganic bases present. The role of bases in complex formation is as yet not completely understood, except the fact that they compensate the negative charge localized on ligands and influence the realization of definite spatial structures of complex molecules. Such a role is played by piperidine, morpholine, ethanalamine, NaOH, and KOH in dibenzoylmethane complexes of europium.

Europium dibenzoylmethane chelates show very strong luminescence. The excitation occurs by absorption of light in the organic part of the chelate — the energy of excitation is transferred by a radiationless transition to the europium ion which, going to its ground state, emits its characteristic radiation. The emission spectrum is a system of sharp lines originated from the ${}^5D_0 - {}^7F_J$ and ${}^5D_1 - {}^7F_J$ electronic transitions in trivalent europium ions. The large number of these lines is explained by the splitting of energy levels in electrostatic fields present in the complex molecule.

The crystal field approximation enables one to determine the symmetry of the field acting on the central ion when knowing the splittings of fine structures of energy levels.

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This gives us an information about the nearest neighbourhood of the central ion and about the structure of the complex molecule as a whole. When the symmetry of the field is low, the degeneracy is removed; for higher symmetries the number of spectral lines decrease. The crystal field does not influence an energy level with $J = 0$. In the case of trivalent europium ion, the 5D_0 and 7F_0 energy levels are not splitted in crystalline field — in the spectral region of the transition ${}^5D_0 - {}^7F_0$ a single, sharp spectral line should be observed.

In this paper spectroscopic investigations of europium dibenzoylmethane complexes obtained in the presence of sodium and potassium acetates are presented. It will be shown that new europium complexes are obtained, the emission spectra of which can be explained assuming splittings of the 5D_0 and 7F_0 levels.

2. Experimental

The europium complexes were obtained from a methanol solution of europium chloride, dibenzoylmethane and sodium or potassium acetate. The mole fractions of Eu:dbm:CH₃COOM was 1:4:10 (M being Na or K). The chelation procedure was as follows:

0.9 g of dibenzoylmethane was dissolved in 30 cm³ and 0.26 g of EuCl₃ in 10 cm³ of methanol. These solutions were mixed together and a solution of 0.82 g of sodium acetate in 30 cm³ of methanol was added. Such a mixture was heated and left for crystallization. After 2 hours yellow crystals could already be observed. The crystallization process was finished in 24 hours. As a result a mixture of two substances was obtained: a superior amount of a yellowish crystalline form and a brown form of the europium chelate. Both these forms exhibit strong luminescence in liquid air temperature but in room temperature only the brown crystals show luminescence when excited with uv-light. The separation of these two forms can be achieved *e. g.* by recrystallization in benzene. In the same way two kinds of products can be obtained when the potassium acetate is used instead of sodium acetate.

The contents of C and H in the obtained chelates, as given in the elementary analysis, is shown in Table I. Basing on these results and taking into account different possible stoichiometric compositions, chemical formulas were ascribed for each particular product of chelation. Only mixed complexes could account for the obtained results.

TABLE I

Elementary analysis data

Compound	Colour	% C		% H	
		Calc.	Found	Calc.	Found
[Eu(dbm) ₂ CH ₃ COO]·CH ₃ COOH	yellow	56.9	57.4	4.0	4.5
Eu(dbm) ₂ CH ₃ COO	brown	58.4	57.7	3.8	4.2

3. Results

Spectral investigation results confirmed the conclusion of elementary analysis that two kinds of complexes could be obtained in both cases with either sodium or potassium acetate present in methanol solution of benzoylmethane with EuCl_3 . In Fig. 1a and 1b

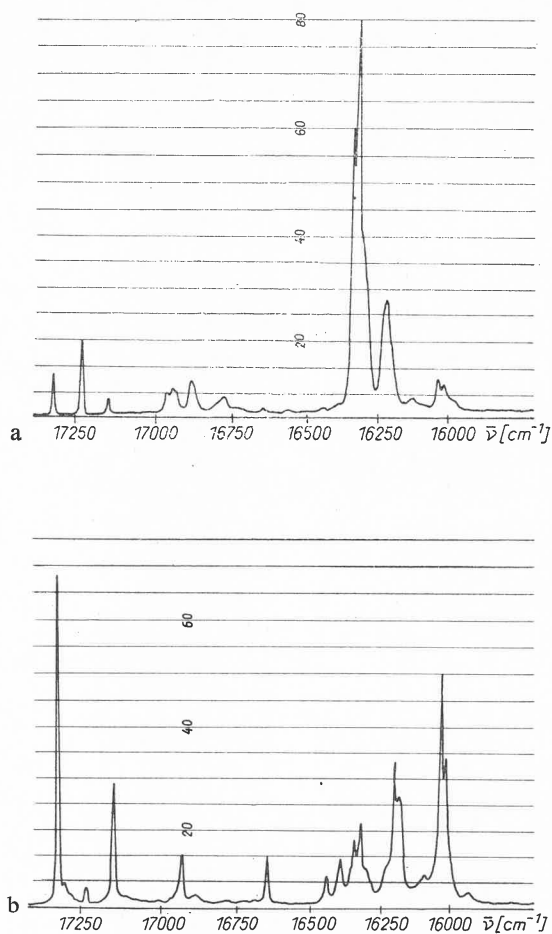


Fig. 1. Luminescence spectra of europium dibenzoylmethane complexes with sodium and potassium acetate (liquid air temp.), a) brown form — satellite line wave numbers: 17331 and 17156 cm^{-1} , b) yellow form — satellite line wave numbers: 17327 and 17150 cm^{-1}

emission spectra taken in liquid air temperature of the investigated chelates are presented. It has to be noted that in both cases of the obtained complexes new satellite lines can be observed in the region of the 5D_0 — 7F_0 transition. Figs 2a and b present emission spectra of the two kinds of investigated chelates in the region of this 5D_0 — 7F_0 transition. On the basis of spectral investigation results, an energy level diagram could be con-

structured (Fig. 3). The splittings of 7F_0 and 5D_0 levels are responsible for the appearance of the satellite lines. The temperature dependence of the intensity of the satellite lines was measured. It was found that the intensities of the short wave satellite lines as well as long wave ones decrease when the temperature increases. In room temperature the intensity of the satellite lines is hardly observable. Fig. 4 presents the emission spectrum of the brown

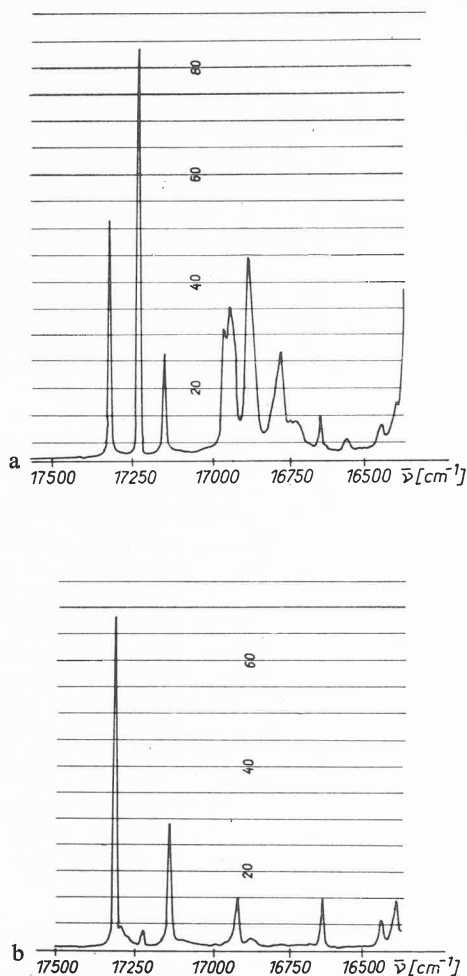


Fig. 2. Luminescence spectra in the ${}^5D_0-{}^7F_0$ and ${}^5D_0-{}^7F_1$ region (see Fig. 1)

form of europium complex taken in room temperature. The yellow form does not luminesce in room temperature at all. It has to be noted that the temperature influence on the intensity of the satellite lines is evident, whereas the positions of the energy levels are temperature-independent.

In the energy level diagrams (Fig. 3) additional splittings for 5D_1 and 7F_2 levels had to be assumed. The number of these sublevels cannot be explained by the complete removal

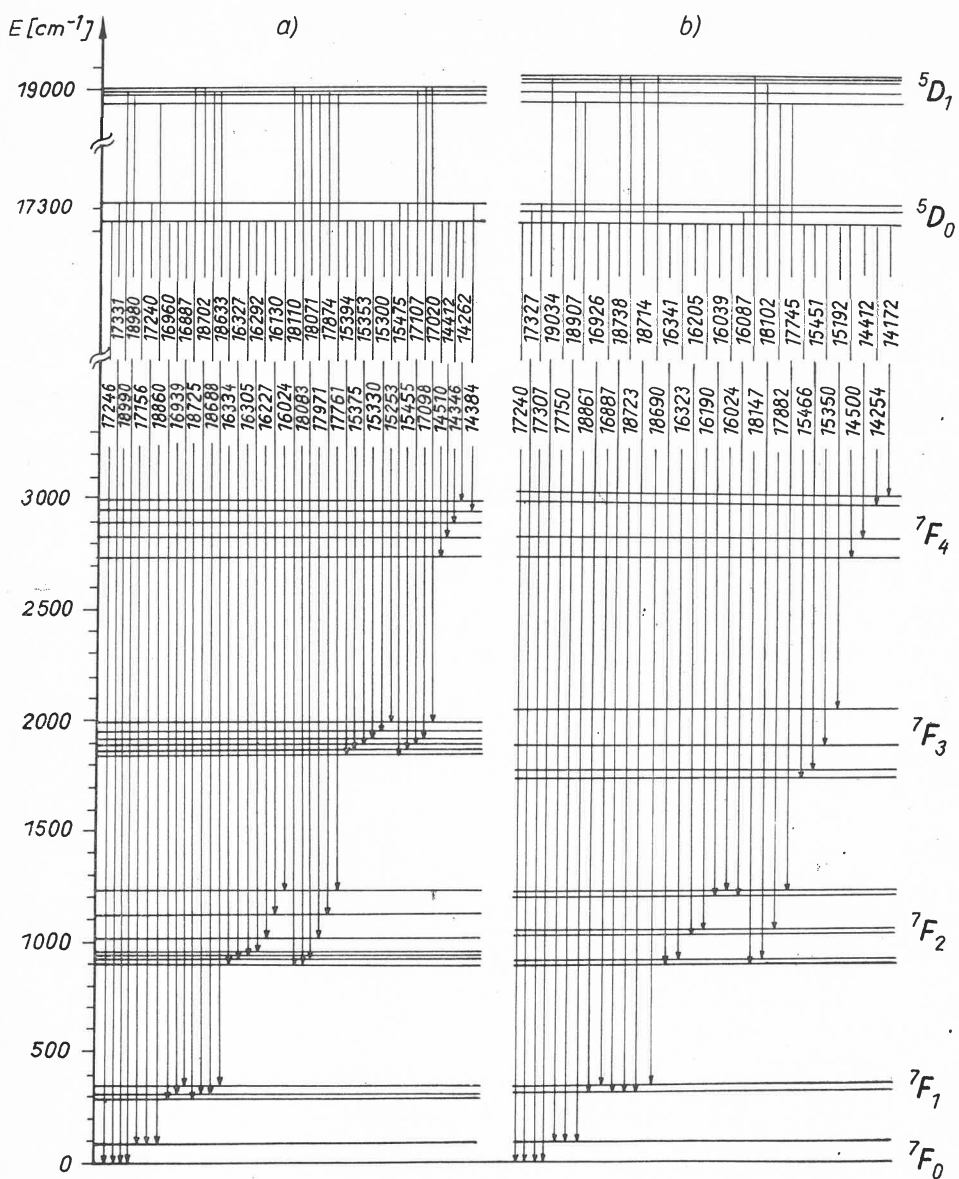


Fig. 3. Energy level diagrams of investigated europium complexes; a) brown form, b) yellow form

of degeneracies. It is not certain, that additional satellite lines do not occur in regions of other electronic transitions. This experimental fact makes it difficult to use the crystal field approximation to assign the symmetry of the obtained chelates.

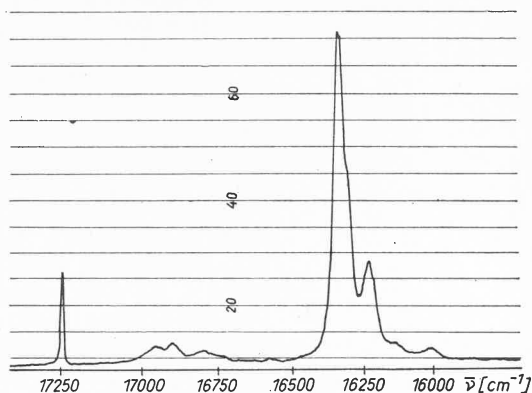


Fig. 4. Luminescence spectrum of europium dibenzoylmethane complex in room temperature

4. Discussion

In the so far known europium dibenzoylmethane complexes the appearance of a single line in the region of ${}^5D_0 - {}^7F_0$ electronic transition was used as a criterion for the homogeneity of the compound. The energy difference between the 5D_0 and 7F_0 states depends

TABLE II

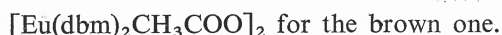
Compound	Wave number of ${}^5D_0 - {}^7F_0$ transition [cm^{-1}]
Europium dibenzoylmethane complex with sodium hydroxide	17228
Europium dibenzoylmethane complexes with piperidine [4]	17232
	17238
Europium dibenzoylmethane complex with potassium hydroxide	17240
Europium dibenzoylmethane complex with morpholine	17244
Europic ethylsulphate nonahydrate [5]	17257
Europium chloride [6]	17267
Europium dibenzoylmethane complexes with sodium and potassium acetate:	
brown form	17246
	17331 ^a
	17156 ^a
yellow form	17240
	17327 ^a
	17150 ^a

^a — satellite line

on the arrangement of the europium ion in the complex molecule. As it can be seen in Table II the wave numbers corresponding to ${}^5D_0 - {}^7F_0$ transitions for different complex compounds lie in the 40 cm^{-1} interval except for the investigated complex molecules. The appearance of additional lines in the ${}^5D_0 - {}^7F_0$ spectral region observed in the investigated complexes cannot be ascribed to the existence of an unhomogeneous product of the complex formation. The appearance of satellite lines cannot be explained on the basis of crystalline field (approximation) theory. Similar satellite lines were observed by [7] for ruby with high concentration of chromium ions. This effect was explained assuming an ion-ion interaction.

In all the other europium dibenzoylmethane complexes known in the literature no additional energy level splittings were observed. This can be understood because of rather large distances between europium ions making the interaction energy negligible. The appearance of additional energy level splittings can be explained by the appearance of coupled-ion effects. Such effects would be observed in many-centre complexes, *i. e.* in such complexes, where at least two europium ions are in a close neighbourhood. Many-centre complexes of lanthanides were obtained previously (see *e. g.* [8]).

The following chemical formulas can be suggested for the investigated complexes:



On the basis of the investigations so far performed, we cannot state whether these formulas are the only possible ones. The results of the elementary analysis presented in Table I do not allow an unambiguous ascription to be made, of the suggested chemical formulas to the investigated complexes. Taking into account the trend in changes of the values obtained in the analysis, it can merely be supposed that there are more acetate ligands in the case of the yellow form than the brown one.

The spectral investigations described here have shown that the splittings of the 5D_0 and 7F_0 levels for both the yellow and brown forms have the same values within experimental errors. This seems to indicate that the distances between the neighbour europium ions are the same. In consequence, such a result confirms the suggested chemical formulas, when assuming that in both cases the europium ions are connected with the same ligands.

For inorganic crystals with rare earth ions some anomalies in the results of measurements of migration, absorption, and emission of radiation have sometimes been observed. Such effects are called cooperative absorption and cooperative emission. They can only be observed in the case of close neighbourhood of interacting ions. In all the europium chelates no influence of interactions between the rare earth ions on the position of energy levels have been checked except those described above.

The lack of the influence of such interactions in inorganic crystals doped with europium is probably caused by the fact that the distances between the rare earth ions are not strictly fixed, but there exists a statistical distribution of their mutual distances. In the investigated complexes the distances between the europium ions are the same for all the elementary cells. This leads to a small half-width of the satellite lines and in consequence

to a possibility of checking of a small splittings (of the order $80\text{--}90\text{ cm}^{-1}$) caused by mutual interaction.

The information concerning the structures of the obtained complexes and particularly the exact distances between the interacting europium ions would allow a description of the character of the interaction to be made. There is also the problem of vanishing satellite lines in room temperature which needs explanation. As it is well known, the increase of temperature augments the oscillation amplitude and probably a consideration of the influence of oscillations on the interaction between the ions would be of importance in solving the problem.

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