LUMINESCENT PROPERTIES OF DIBENZOYLMETHANE-PIPERIDINE CHELATES OF EUROPIUM[1]

By A. Bączyński

Institute of Physics, N. Copernicus University, Toruń*

And S. Zachara

Institute of Physics, University of Gdańsk**

Three kinds of chelates of europium with dibenzoylmethane and piperidine have been obtained by successive recrystallization from a methanol solution. It was ascertained that the role of piperidine is not only to compensate the excess negative charge of the ligands, but to form conditions under which concrete structures of hybrids are realized. At the same time, it was found that in the dibenzoylmethane chelates of europium with a piperidine addition a single europium ion may receive a larger number of piperidine molecules.

1. Introduction

Intramolecular transfer of excitation energy in metallo-organic complexes of rare earth elements is a factor which permits the conversion of energy absorbed within a broad spectral range into monochromatic radiation energy [1, 2]. In this phenomenon an important role is played by the absorption of radiation energy in the conjugated π-electron structure in the organic part of the complex and the transfer of this energy to the central ion. If the latter is an ionized atom belonging to the lanthanides, in which the bond with the organic part is due to hybridization of free $5d$, $6s$, and $6p$ orbitals, then the electronic transitions in the $4f$ shell do not loose their linear character. It follows thus that the $4f$ orbital is not engaged in the metal-ligand bond.
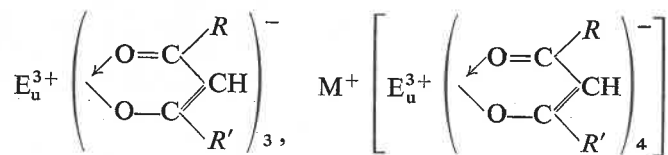
In this paper we present the results of our research on complexes of europium with a compound belonging to the group of β-diketones, namely, dibenzoylmethane. In a solution β-diketones exist in two tautomeric forms, the ketonic and enolic ones. In the enolic form they have a tendency to link coordinately with metals, including the rare earth

* Address: Instytut Fizyki, Uniwersytet M. Kopernika, Toruń, Grudziądzka 5, Poland.

** Address: Instytut Fizyki, Uniwersytet Gdański, Gdańsk, Sobieskiego 18, Poland.

elements, thus forming chelate bonds inner-complex (bonds) [3, 4]. An europium ion (Eu^{3+}) may form three- and four-ligand chelates of formulae

$$E_u^{3+}\left(\begin{array}{c} O=C{\diagup}R \\ \diagdown CH \\ O-C{\diagdown}R' \end{array}\right)_3^-, \quad M^+\left[E_u^{3+}\left(\begin{array}{c} O=C{\diagup}R \\ \diagdown CH \\ O-C{\diagdown}R' \end{array}\right)_4^-\right]$$

where R and R' are univalent aliphatic or aromatic radicals. In the four-ligand chelates an additional univalent metal ion (M^+) or an n-donor molecule being a Lewis base enters to compensate the negative charge of the enolic form.

The general outline of obtaining of such chelates is well known [5, 6]. There are justified implications, however, that chelate compounds obtained from the same reactants may have various spatial structures and chemical compositions. This appears to depend on the conditions under which the process of chelate formation occurs. In this work we present spectral analyses of metallo-organic compounds, with a particular attention being paid to finding the conditions under which any given complex form is realized. The subject of this study is the group of complexes of europium with benzoylmethane with an addition of piperidine. The trivalent ion of the lanthanide may have coordination numbers in the range from 6 to 12 [6]. This is conditioned by the participation of the $5d6s6p$ and $5f$ orbitals. A definite molecule symmetry strictly corresponds to each of the possible hybridizations.

2. Preparation of samples

The europium complexes were obtained from a solution of methanol with the use of the following reagents: europium chloride, manufactured by Johnson, Matthey and Co., London; dibenzoylmethane, manufactured by Koch — Light Laboratories, Ltd.; and piperidine, manufactured by R.C.B. — Bruxelles.

0.64 g of dibenzoylmethane was dissolved with an addition of 8 ml of piperidine in 160 ml of methanol. In 20 ml of methanol 0.21 g of europium chloride was dissolved. Then these solutions were mixed together, getting a turbid solution; this turbidity abated after several minutes passed. From this solution single crystals of the europium complex (chelate A) precipitated. After four days of crystallization the remainder of the solution was drawn off, while the single crystals, of which the largest had dimensions of the order of 0.2 cm, were rinsed in methanol. All single crystals obtained in this manner had identical structures.

When the chelate A was redissolved in methanol and submitted to recrystallization, an europium complex precipitated once again, but in polycrystalline form (chelate B). This chelate differed from the species A as far as its spectroscopic properties were concerned.

The product of a repeated recrystallization of chelate B from methanol is a two--component system, of which one is a bright yellow powder having the same spectroscopic

properties as chelate B, whereas the other is a substance of another colour in polycrystalline form. This second component (chelate C) possesses spectroscopic properties different than those of chelates A and B. It must be noted that subsequent recrystallizations of chelate C do not alter its properties.

It was anticipated that chelates B and C could be also obtained by altering the quantitative ratios of the components used in the first crystallization. Leaving the quantitative ratio of dibenzoylmethane and europium constant (5 : 1), but changing the piperidine content in the solution, the chelate C was produced when the amount of piperidine was decreased ten-fold. This prescription permits chelate C to be obtained in single-crystalline form. As it was expected, multiple recrystallizations in methanol do not change the spectroscopic properties of this chelate.

3. Emission spectrum measurements

Spectral analyses of the obtained chelates A, B, and C were performed at liquid air temperature. For this purpose, the examined chelate, placed in a quartz ampoule, was immersed directly in liquid air contained in a quartz Dewar. The sample was excited by means of an HBO-200 mercury lamp and an absorptive filter letting through the intense 3650 Å line of mercury. Instead of a photographic plate, the spectrograph was equipped with a photoelectric attachment designed in such a way that the exit slit of the spectrograph together with EMI-6094 B photomultiplier moved in the focal plane of the spectrograph. The amplified signal from the photomultiplier was recorded on a recorder whose tape motion was synchronized with the photomultiplier motion. The resolving power of the arrangement was about 1 Å in the spectral range where the principal europium lines are emitted.

4. Results of measurements

Because of the existing mechanism of energy migration from the ligands to the central ion *via* the triplet state of the complex's organic part, there are observed electronic transitions due to excitation of the first sublevels of the fine structure of the europium ion, ^5D [7]. The energy of the ligand's triplet state is about 19.000 cm^{-1}; hence, when excitation is accomplished by energy absorption in the organic part of the complex molecule, the $^5D_0$ and $^5D_1$ levels are primarily occupied. Since there is electronic relaxation which brings the system from the $^5D_1$ state to the $^5D_0$ state, the main contribution to the intensities of the observed lines has to come from electronic levels of the europium ion's excited state $^5D_0$ during transition to fine structure sublevels of the ground state ^7F [7].

This paper presents the emission spectra of chelates in the range from 5750 to 6300 Å. In this range mainly the electronic transitions $^5D_0 - {}^7F_0$, $^5D_0 - {}^7F_1$, $^5D_0 - {}^7F_2$ and the weaker transitions from $^5D_1$ to the higher ground state sublevels are observed. As seen from the spectra shown in Figs 1, 2, and 3, the spectral lines associated with the $^5D_0 - {}^7F_1$ and $^5D_0 - {}^7F_2$ transitions indicate that there is a splitting of the $^7F_1$ and $^7F_2$ states due to the existence of an intramolecular crystal field. The lines of the various chelates associated

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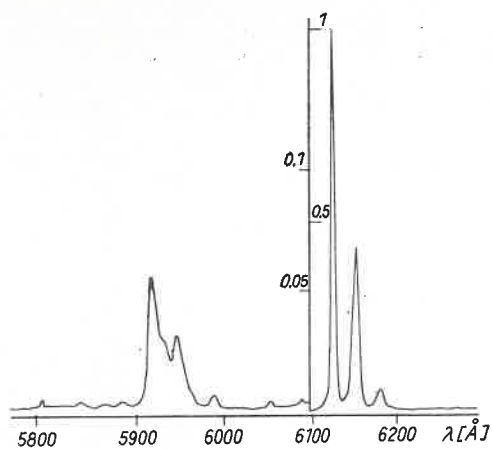
Fig. 1. Emission spectrum of chelate *A*
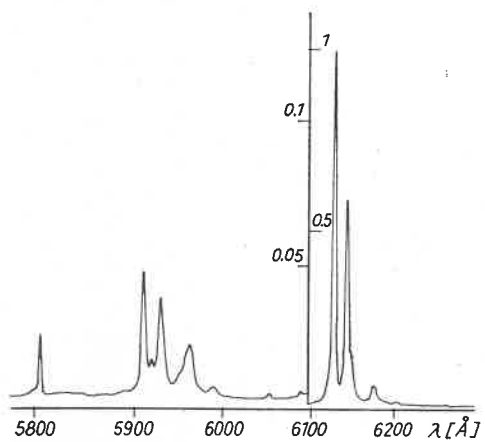
Fig. 2. Emission spectrum of chelate *B*
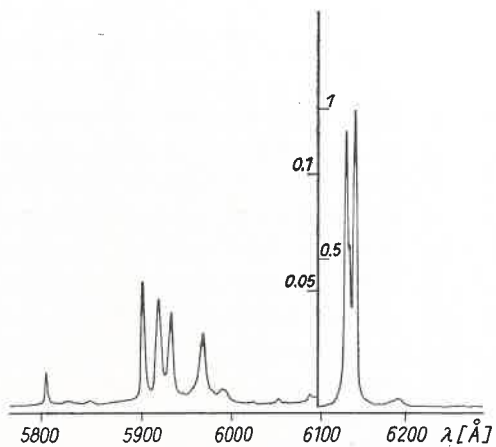
Fig. 3. Emission spectrum of chelate *C*

with the $^5D_0 - {^7F_0}$ transition are unsplit because these states have a quantum number $J = 0$. In the present study, as in others, the shape of this line was a check on the purity and homogeneity of the obtained material. In the case of chelate A this transition is forbidden, whereas in chelates B and C this forbiddenness is relaxed in the crystal field. The weak $0-0$ line appearing in the chelate A spectrum proved to be a sharp line when examined with an improved sensitivity of the detecting system.

In the spectrum recordings presented in Figs 1–3 the axis of ordinates separates spectral regions in which the spectral lines recorded at different sensitivities of the detection equipment. This is conditioned by the large differences in intensities of the set of lines falling within the spectral region of the $^5D_0 - {^7F_2}$ transition as compared with the intensities of the other lines.

In addition, spectral examination of the various chelates was carried out in alcohol solution at the temperature of liquid air. Chelate concentration in solution was $5 \times 10^{-4} g/cm^3$. It was found that in the alcohol solution the obtained chelates A, B, and C have identical
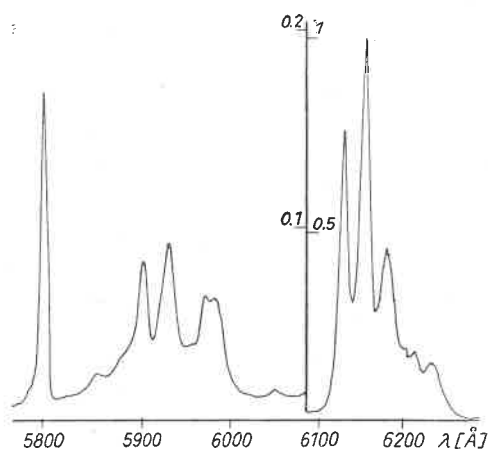

Fig. 4. Emission spectrum of europium chelate in methanol solution

emission spectra. Figure 4 shows the spectrum of one of the chelates in methanol. It is seen here that the $0-0$ transition is much stronger than in the case of the chelates themselves in crystalline form.

The relative intensities of the strongest lines belonging to the $^5D_0 - {^7F_2}$ set of the various chelates in crystalline forms were also measured. At liquid air temperature the ratios of intensities of these lines in chelates A, B, and C are $1 : 0.8 : 0.6$, respectively. Apart of the relative intensities (as compared with the strongest line), Table I also includes the wavelengths of the various spectral lines, and the positions of the terms found as the differences between the wave numbers of the $0-0$ transition and those of the various lines. Energy schemes of the obtained chelates, resulting from the observed electronic transitions, are presented in Fig. 5. Assignment of some lines to transitions other than $^5D_0 - {^7F_1}$ (Table I) was done on the basis of analyses of other europium complexes [8, 9].

TABLE I

No	Symbol of chelate	$^5D_0-{}^7F_0$ [Å] λ [cm^{-1}]	$^5D_0-{}^7F_1$ [Å] λ [cm^{-1}]	Position of term [cm^{-1}]	$\dfrac{I}{I_{max}}$	$^5D_0-{}^7F_2$ [Å] λ [cm^{-1}]	Position of term [cm^{-1}]	$\dfrac{I}{I_{max}}$
1	A	5809 17215	5922 16886	329	1.00	6122 16334	881	1.00
			5948 16812	403	0.57	6151 16257	958	0.39
			5987 16703	a	0.12	6180 16181	1034	0.05
2	B	5810 17212	5912 16915	297	1.00	6123 16332	880	1.00
			5922 16886	326	0.31	6139 16289	923	0.59
			5929 16866	346	0.81	6173 16200	1012	0.06
			5960 16778	a	0.44			
			5984 16711	a	0.17			
3	C	5809 17215	5905 16935	280	1.00	6125 16326	889	0.93
			5922 16886	329	0.85	6135 16300	915	1.00
			5933 16855	360	0.78	6187 16163	1052	0.03
			5965 16764	a	0.59			
			5987 16703	a	0.15			
4	in methanol solution	5803 17232	5901 16940	292	0.91	6122 16334	898	0.78
			5927 16872	360	1.00	6146 16271	961	1.00
			5965 16764	a	0.71	6174 16197	1035	0.45
			5976 16734	a	0.70	6209 16106	1126	0.18
						6230 16051	1181	0.15

[a] vibronic transition.

5. Discussion of results

In triply ionized atoms of the lanthanides, five $5d$ orbitals, one $6s$ orbital, and three $6p$ orbitals are wholly unoccupied, and they are responsible for the bonds in metallo-organic complexes. Depending on the number of orbitals engaged in the bonds, there is a definite number of possible spatial distributions of the hybrids. Not all hybrid arrangements lead to the formation of stable bonds. If in the Eu^{3+} complex with β-diketone the europium ion has a coordination number of 8, there are three possible spatial structures of the complex [12], whereas if the coordination number is 9, there is only one. The electrically neutral complex of Eu^{3+} with dibenzoylmethane forms as a result of the addition of three β-diketone molecules (in enolic form). In this case the coordination number of Eu^{3+} is 6. Such complexes may be achieved by appropriate thermal processing of four-ligand complexes [11].

In obtaining four-ligand complexes, an addition of some substance is used to compensate excess negative charge. The role of the piperidine used in obtaining the examined chealtes, however, is not only compensation of charge of the four-ligand complex, but,
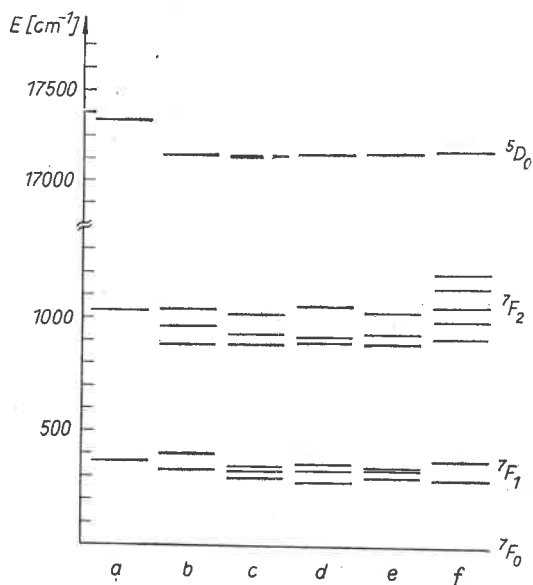

Fig. 5. Energy level scheme of Eu^{3+} ion, a) free ion, after [10], b) chelate A, c) chelate B, d) chelate C, e) according to data of Ref. [11], f) in solution

as it stems from the presented results of our research, also the formation of conditions under which definite spatial structures of the hybrids are realized. It should be emphasized that only three crystalline forms with different field distributions acting on the central ion were obtained, although a greater number of forms was sought. This may imply that in the Eu^{3+}-dibenzoylmethane complex with an addition of piperidine the central ion accepts a coordination of 8 and that structures of the symmetries of a dodecahedron, an antiprism and a face-centered prism are realized [12]. This conclusion, however,

requires a confrontation with an X-ray structural analysis of the obtained forms, or a theoretical verification on the basis of the experimental splittings of Eu^{3+} energy levels in the existing electric field produced by the ligands and acting on the central ion.

Slight changes in the symmetry of this field distinctly affect the positions of the spectral lines, their numbers and intensities. Chelates A, B, and C were obtained under conditions in which the quantity of piperidine in solution varied in each case. As given in the description of sample preparation, chelate A was obtained when most piperidine was contained in the solution. The emission spectrum of this chelate has some lines which are diffused. As it stems from the energy level scheme (Fig. 5), under the effect of the crystal field the $^7F_1$ level is split into two sublevels, of which one is degenerated. The degeneration of this level vanishes in the case of the chelates B and C, what implies that there is a lower-symmetry crystal field. The obtained results may be interpreted in the following way: when chelate formation occurs in the presence of a large excess of piperidine, crystals of relatively high symmetry are formed, with such a number of piperidine molecules in the complex that there are a few of them per complex molecule. When the amount of piperidine in the solution, where the chelates are being formed, becomes decreased, a complex is formed in crystalline form of a spatial structure different than that in the former case. This is clearly seen in the energy level scheme, where the $^7F_1$ level is split into three sublevels.

It appears that the existing differences in the emission spectra of chelate B and C may be explained by a stronger binding of the piperidine in the complex, what is revealed in the larger splitting of the sublevels of the $^7F_1$ level. It cannot be determined from the obtained spectra whether the symmetries of the crystal fields in the B and C chelates are different. To do so, the spectral range would have to be broadened to include transitions other than $^5D_0-{}^7F_0$, $^5D_0-{}^7F_1$, and $^5D_0-{}^7F_2$. The spectral range corresponding to the $^5D_0-{}^7F_2$ provides little information, as only two strong lines are observed, whereas the intensities of the remaining lines, observed at increased instrumental sensitivity, are comparable with those of lines associated with vibronic transitions and lines coming from the $^5D_1-{}^7F_4$ transition.

All of these chelates feature identical emission spectra when dissolved in alcohol. Owing to molecular dispersion and strong interaction of the solvent with the complex, the specific influence of piperidine disappears and the spectra become more diffuse. The increased number of spectral lines seen primarily in the region of the $^5D_0-{}^7F_2$ transition indicates a change in complex symmetry. It may be presumed that solvent molecules form associates with complex molecules. The identity of the emission spectra in alcohol solutions implies that either piperidine molecules detach from the complex in solution, or such a number of them is detached in chelates A and B that they become identical with the molecules of complex C in solution.

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