The Infrared, Raman, and Vibronic Spectra of Europium Chelates

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Absorption spectra in the far and intermediate infrared, as well as Raman and vibronic spectra were measured for three crystalline forms of four-ligand europium chelate with dibenzoylmethane and piperidine and a three-ligand chelate in the spectral ranges: 40–450, 450–4500, 0–4500 and 0–1600 cm^{-1}, respectively.

The analysis of the individual spectra enabled the identification of the frequencies corresponding to the vibrations of the Eu–O bond coupled with the lattice vibrations, and the frequencies of the intraligand vibrations. It is found that piperidine is bound to the complex molecule by hydrogen bond.

Introduction

The complex conpounds of europium with β-diketones are the reaction products of the enolic form of β-diketone and the three-positive europium ion. Such complexes crystallize in solutions in the presence of organic or inorganic bases, the role of which in the complex has not yet been elucidated. Not only its function consists in the compensation of one negative charge located on the ligand but it also enables certain spatial structures of the complex to be formed [1].

The complex of europium and dibenzoylmethane in the form of Eu(DBM)$_4$ HP, where DBM and P denote dibenzoylmethane, and piperidine, respectively, is an example of such a complex for which the organic base – piperidine – affects the formation of diversified spatial structures. Spectroscopic experiments show that the reaction yields three different crystalline forms of four-ligand chelate depending on the crystallization conditions [2, 3].

In the present paper, the infrared, Raman and vibronic spectra of the above chelates have been analyzed, with the possible bondings of piperidine in the complex molecule of the four-ligand chelates being presented and the interpretation of the identified vibrational modes being given.

Experimental

Molecular crystals were obtained from methanol solutions by the method described previously [3]. Three different crystalline forms of four-ligand chelates and one three-ligand chelate were obtained, which, for simplification, have been designated in the present paper by A, B, C and T, respectively. For chelates A and C, the molar ratio of europium:dibenzoylmethane:piperidine in the solution was 1:5:100 and 1:5:10, respectively. Chelate B was obtained by recrystallization of chelate A. Three-ligand chelate T was obtained by thermal decomposition of chelate A or B lasting for 6 hours at 460 K under a pressure of 10^{-6} mm Hg. All chelates were obtained as microcrystalline powders.

The spectra of chelates T, A, B, C and DBM, P in the far infrared (FIR), 40–450 cm^{-1}, and intermediate infrared (IR), 450–4500 cm^{-1}, were recorded by means of a Perkin-Elmer 180 spectrophotometer. For the recording of the FIR spectra, suspensions of microcrystalline powder of the chelates and DBM on Nujol mulls were used, whereas for the IR spectra tablets of KBr were prepared.

The Raman spectra (RS) were recorded in the range of 0–4500 cm^{-1} by means of a GDM-1000 Carl-Zeiss Jena Raman spectrophotometer after argon laser excitation at $\lambda = 488$ nm. The spectra were examined for the chelate and DBM microcrystalline powders.

The FIR, IR and Raman spectra were measured at room temperature. The frequencies of the spectra were read with an accuracy of ± 1 cm^{-1}.

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The vibronic spectra of the chelates were measured in the range of 0–1600 cm^{-1} using a PGS-2 spectrograph with photoelectric recording. The fluorescence spectra were measured for samples placed in liquid nitrogen. Microcrystalline powder was excited using an HBO-50 lamp, with a wavelength of 365 nm being selected with a filter. An FEU-51 photomultiplier was used in the experiment. The frequencies obtained from the spectra were determined within an accuracy of ± 3 cm^{-1}.

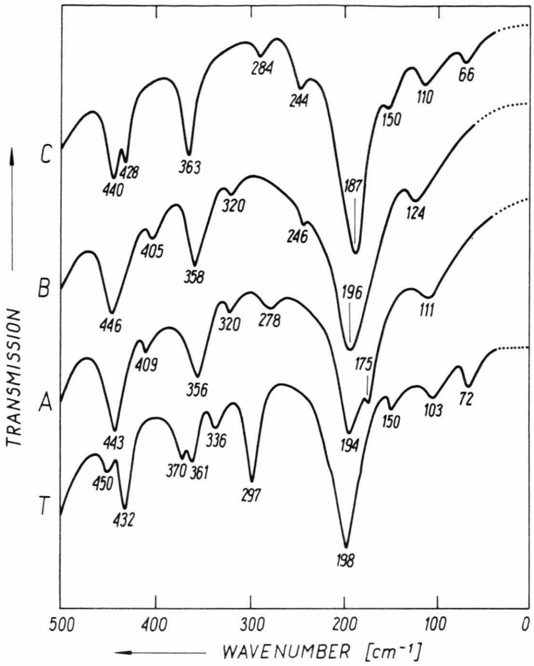

Fig. 1. Far infrared (FIR) absorption spectra in the region of 40–450 cm^{-1} for Eu (DBM)$_3$-T and Eu (DBM)$_4$ HP-A, B, C.

Results and Discussion

The FIR and Raman spectra of the chelates in the range of 40–450 cm^{-1} are shown in Figs. 1 and 2. The IR spectra in the range of 1500–2000 cm^{-1} and the Raman ones in the range of 1400–1700; 3150–3550 cm^{-1} are given in Figs. 3 and 4, respectively. Tables 1 and 2 present the vibration frequencies determined from the above and the vibronic spectra (VIB).

The vibration frequencies of the VIB were obtained from the fluorescence spectra as the differences between the wavenumbers of the pure electronic transition $^5D_0 \rightarrow {}^7F_0$ and the vibronic transitions, since at 77 K the transitions from the lowest vibrational level $^5D_0$ to those of level $^7F_0$ are predominant [4]. The change in the location of atoms surrounding the Eu^{3+} ion in the organic complex induces a local dynamic crystalline field which interacts with the electrons of the 4f shell of the Eu^{3+} responsible for the emission spectra [5, 6]. The interaction depends on the symmetry of the electronic states as well as on the vibrational modes. Thus, such bands occur only in VIB for which an interaction exists between the created phonon and the electronic transition. The frequencies of the phonons may correspond to the modes of normal vibrations of the complex molecule or to the modes of the crystalline lattice.

The frequencies in the VIB spectra of chelates investigated below 250 cm^{-1} correspond in principle to Eu–O vibrations coupled with those of the individual bondings in the complex, which in turn are coupled with the deforming vibrations of the chelate ring through which the interaction with the Eu^{3+} state occurs. The last column in Tables 1 and 2 gives the interpretation of the individual vibrations based on the data from literature and the analysis of the vibrational spectra of dibenzoylmethane (DBM) and piperidine (P) recorded in order to determine the characteristic frequencies of these molecules. It should be emphasized that the frequencies of the Eu–O vibrations (40–720 cm^{-1}) are in good agreement with the values obtained by Gouteron et al. for the single crystal of Eu_2O_3 [7].

Several frequencies in the IR and Raman spectra of the chelates investigated correspond to the vibrations of the phenyl group and the C–H bond in the ligand (Figs. 3, 4, Table 2) [8, 9]. The occurrence of two frequencies instead of one characterizing the vibration of the C=C bond in the chelate ring is related to its coupling with the phenyl group. The interaction of these groups causes the anharmonicity of the C=C bond vibrations resulting in the occurrence of two bands with frequencies 1550 and 1600 cm^{-1} (Figs. 3, 4, Table 2), [10–12].

As seen in Table 2, the frequencies characteristic of the intramolecular vibrations in the piperidine molecule occur in the vibrational spectra of chelates A, B and C. These frequencies do not occur for chelate T due to the removal of piperidine as a result of thermal decomposition. The analysis of the vibrations of the NH group in the range of 3300–3430 cm^{-1} leads to the conclusion that the P molecules exist in different

Table 1. Vibration frequencies determined from the FIR, Raman, and VIB spectra of the chelates investigated and their interpretation in the range of 40–450 cm^{-1}. [1] sh – shoulder; [2] vw – very weak; [3] w – weak; [4] m – medium; [5] s – strong; [6] vs – very strong.

T			A			B			C			Type of vibrations
FIR	RS	VIB	FIR	RS	VIB	FIR	RS	VIB	FIR	RS	VIB	
72 w[3]	72 sh[1]	68 sh	–	–	54 w	–	–	60 vw[2]	66 w	–	62 m[4]	(Eu – O) and lattice [7]
–	92 s[5]	90 m	–	–	–	–	98 sh	105 m	–	98 sh	102 m	
103 w	110 sh	113 m	111 w	–	114 s	–	–	–	110 m	–	118 m	
–	116 vs	–	–	–	–	124 w	–	125 m	–	–	–	
150 vw	156 s	152 m	–	154 sh	145 w	–	156 sh	–	150 sh	156 sh	142 m	
–	–	–	175 sh	–	–	–	–	–	–	–	–	(Eu – O) [7]
–	–	–	–	188 m	186 s	–	188 w	182 m	187 vs	–	180 w	δ (NH . . . O) [10]
198 vs[6]	200 m	196 vs	194 vs	200 m	200 s	196 vs	200 m	200 m	–	197 s	–	(Eu – O) and lattice [7]
–	212 m	–	–	209 m	–	–	208 m	–	–	–	–	(Eu – O) [7]
–	244 w	–	–	240 sh	249 s	246 sh	236 m	248 s	244 sh	237 m	–	(Eu – O) and lattice [7]
–	256 w	–	–	–	–	–	250 vw	–	–	255 m	–	(Eu – O) [7]
–	–	–	278 w–	–	280 s	–	–	–	284 vw	–	–	(Eu – O) and δ chel. ring [7]
297 s	292 w	–	–	–	–	–	296 vw	–	–	–	–	def. chel. ring [12, 14]
336 w	320 w	–	320 w	–	–	320 vw	328 vw	327 vw	–	325 m	330 vs	
361 m	–	–	356 s	–	360 m	358 s	–	–	363 s	363 m	–	
370 m	–	377 vw	–	–	–	–	–	–	–	–	–	(Eu – O) and δ chel. ring [7]
–	–	413 sh	409 vw	410 m	–	405 vw	410 m	406 sh	–	410 m	–	(Eu – O); γ (C – C) ph. ring [7]
432 s	–	434 sh	–	–	–	–	–	–	428 m	430 m	–	(Eu – O) and δ chel. ring [7, 13]
450 w	452 m	–	443 s	452 m	451 sh	446 s	452 m	–	440 s	452 m	455 vs	

Table 2. Vibration frequencies determined from the IR, Raman, and VIB spectra of the chelates investigated and their interpretation in the range of 1400–2000 cm^{-1} and 3150–3550 cm^{-1}.

T			A			B			C			Type of vibrations
IR	RS	VIB	IR	RS	VIB	IR	RS	VIB	IR	RS	VIB	
1440 sh	–	–	1440 sh	–	–	1440 sh	–	–	1440 sh	–	–	$\nu(\mathrm{C-C_6H_5}) + \nu(\mathrm{C-C})$ [12, 13, 14]
1451 s	1448 m	1452 sh	1460 vs	1448 m	1466 s	1460 vs	1452 m	1450 s	1460 vs	1457 w	1465 vw	$\nu(\mathrm{C-C_6H_5}) + \nu(\mathrm{C-C})$ [12, 13, 14]
1477 vs	–	1472 m	1477 vs	–	–	1475 vs	–	–	1477 vs	–	–	$\nu(\mathrm{C-C})$ ph. ring [8, 9]
–	1496 m	1497 m	–	–	–	–	1496 vs	–	–	1493 m	–	$\nu(\mathrm{C-C})$ ph. ring [8, 9]
1517 vs	–	–	1515 vs	1516 s	–	1515 vs	1508 m	–	1515 vs	1516 w	–	$\nu(\mathrm{C=O}) + \delta(\mathrm{C-H})$ and $\gamma(\mathrm{C-H})$ [8, 9]
1545 vs	–	–	1550 vs	–	1560 s	1555 vs	–	1550 s	1552 vs	–	1559 m	$\nu(\mathrm{C=C})$ [10, 11, 12]
1593 vs	1592 s	1591 m	1595 vs	1601 vs	1606 w	1600 vs	1604 vs	1606 s	1598 vs	1601 vs	1605 m	$\nu(\mathrm{C=C})$ [10, 11, 12]
–	–	–	1728 m	–	–	1728 w	–	–	1710 m	–	–	$\nu(\mathrm{C=O})$ [10, 11]
1760 w	–	–	–	–	–	–	–	–	–	–	–	$\nu(\mathrm{C=O})$ [10, 11]
1807 w	–	–	1815 w	–	–	1810 w	–	–	1810 m	–	–	ph. ring comb. [8, 9]
1892 w	–	–	1895 w	–	–	1900 w	–	–	1895 m	–	–	
1958 w	–	–	1958 w	–	–	1955 w	–	–	1957 m	–	–	
–	–	–	–	3152 vs	–	–	3164 s	–	–	–	–	$\nu(\mathrm{C-H})$ [8, 9]
–	3184 m	–	–	–	–	–	–	–	–	–	–	$2\nu(\mathrm{C=C})$
–	–	–	–	3202 m	–	–	3202 w	–	–	3201 m	–	$2\nu(\mathrm{C=C})$
–	3260 vs	–	–	–	–	–	–	–	–	–	–	?
–	–	–	–	3298 m	–	–	3304 m	–	–	–	–	$\nu(\mathrm{NH \ldots O})$ [10, 11]
–	–	–	–	–	–	–	3316 vw	–	–	3313 m	–	$\nu(\mathrm{NH \ldots N})$ [10, 11]
–	–	–	–	3352 m	–	–	–	–	–	3356 m	–	$\nu\,\mathrm{NH}$ [10]
–	–	–	–	3426 m	–	–	3426 m	–	–	3426 m	–	$\nu\,\mathrm{NH_2}$ [10, 11]

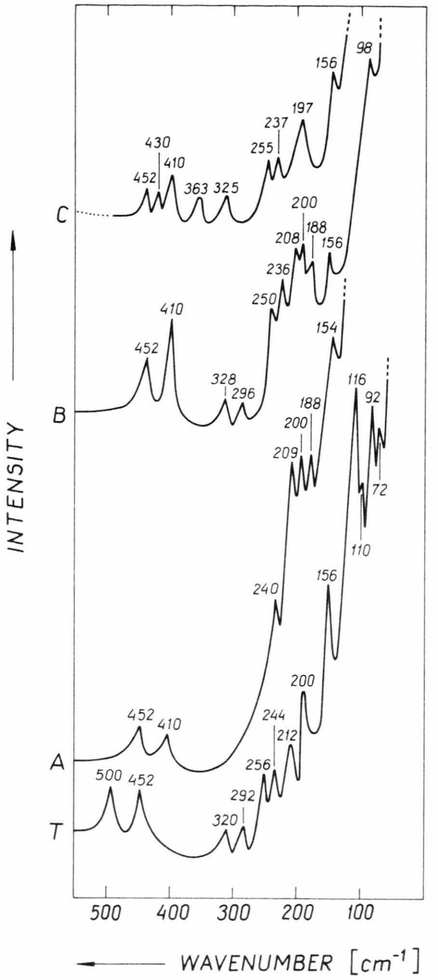

Fig. 2. Raman spectra (RS) in the region of 0 – 450 cm^{-1} for Eu $(DBM)_3$-T and Eu $(DBM)_4$ HP-A, B, C.

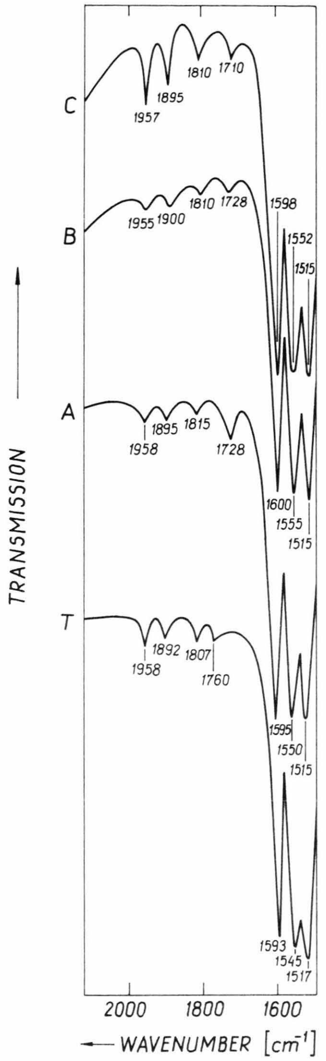

Fig. 3. Absorption spectra in the intermediate infrared (IR) region of 1500 – 2000 cm^{-1} for Eu $(DBM)_3$-T and Eu $(DBM)_4$ HP-A, B, C.

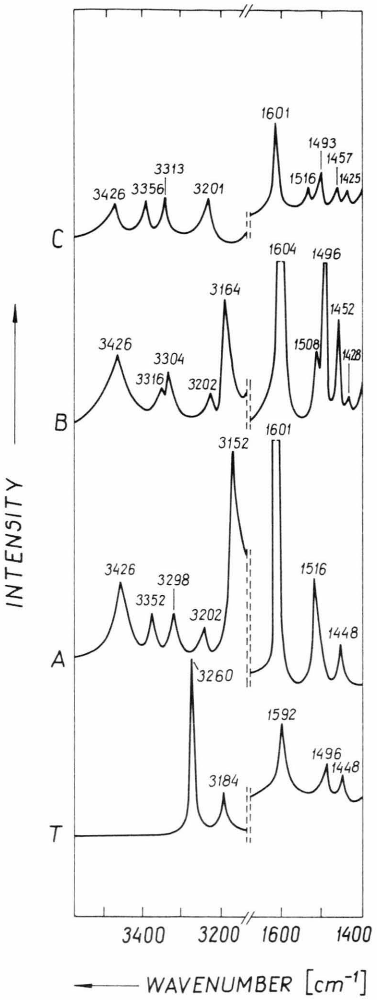

Fig. 4. Raman spectra (RS) in the region of 1400 – 1700 and 3150 – 3550 cm^{-1} for Eu $(DBM)_3$-T and Eu $(DBM)_4$ HP-A, B, C.

energetic configurations with respect to the complex. A frequency of 3352 cm^{-1} occurring for chelates A and C is characteristic of the vibrations of the “free” NH group, which suggests that molecules P could conceivably fill up the crystalline lattice without creating bonds between each other (this is possible thanks to the excess of piperidine in the crystallization process), as well as with the complex. A frequency of 3315 cm^{-1} obtained from the Raman spectra for chelates B and C indicates the existence of hydrogen bonding (NH . . . N) between the P molecules, whereas a frequency of 3426 cm^{-1} for chelates A, B and C is characteristic of the NH_2 group vibration in the piperidine ion [11]. The occurrence of frequency 3300 cm^{-1} for chelates A and B, characteristic of the stretching vibration of the NH group bounded by hydrogen bridge with oxygen [10] enables to conclude that part of molecules P are bound to the complex by hydrogen bonding. This could be supported by the occurrence of frequency $\sim 185\ \mathrm{cm}^{-1}$ in the vibrational spectra (Figs. 1 and 2, Table 1) corresponding to the deforming vibration of NH ... O. The fact of lowering the carbonyl group vibration frequency from $1760\ \mathrm{cm}^{-1}$ for chelate T (no bonding with P) to $1728\ \mathrm{cm}^{-1}$ for chelates A, B, and $1710\ \mathrm{cm}^{-1}$ for chelate C additionally provide evidence for the existence of hydrogen bonding. Such a marked change ($50\ \mathrm{cm}^{-1}$) in the frequency for chelate C may indicate piperidine to be strongest bound with the complex in the case of this form of chelate.

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