Reversible temperature changes of photoluminescence spectra of crystalline europium(III) carboxylatodibenzoylmethanates

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The X-ray structural data[1] indicate several types of coordination of carboxyl groups in lanthanide carboxylates, depending on the number of the rare-earth element (REE) and the electron-donating properties of the carboxylate ion.

The spectroscopic properties of carboxylatodibenzoylmethanates of REE have been described.[2,3] Based on analysis of the IR spectroscopic and spectral-luminescence data, a dimeric structure with bridging carboxylate groups was assigned to the complexes. Continuing the study of the temperature effect on photoluminescence of REE complexes, we studied the behavior of crystalline europium carboxylatodibenzoylmethanates $[Eu(DBM)_2RCOO] \cdot 2H_2O$, where R = Me, Et, Pr, and Bu. We found that, unlike the known REE chelates, in the case of the complexes indicated, the Stark structure of luminescence spectra changes substantially on going from 77 K to room temperature and back (Fig. 1).

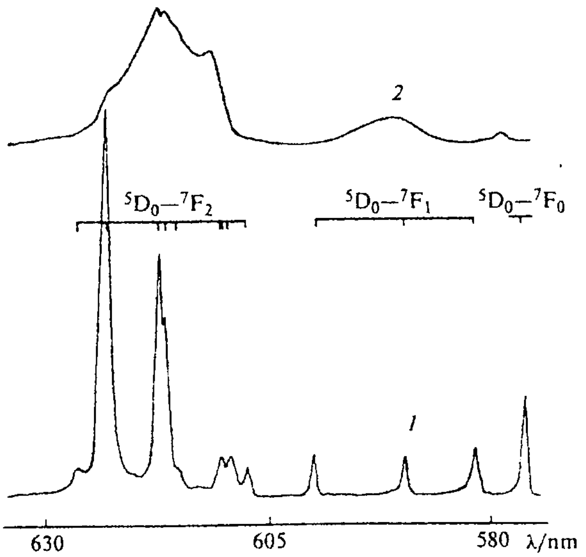

Fig. 1. Luminescence spectra of the $[Eu(DBM)_2BuCOO] \cdot 2H_2O$ complex at 77 (*1*) and 300 (*2*) K. Excitation at 365 nm.

The luminescence spectra of the compounds under study at 77 K differ significantly from those of standard europium chelates by the character of distribution of bands and splitting of intensities: the relative intensity of the line of the $^5D_0-^7F_0$ singlet transition is unusually high and the Stark components of the $^5D_0-^7F_1$ transition are considerably remote from each other (~500 cm^{-1}). At ~20 °C, the luminescence spectra become similar to those of the majority of europium chelates: the main fraction of the radiation energy falls on the $^5D_0-^7F_2$ transition, and the intensity of the $^5D_0-^7F_0$ transition is insignificant. The activation energies obtained by us for temperature quenching of luminescence (~14 kcal mol^{-1}) are substantially higher than the distance between the $^5D_0$ level and the triplet T_1 level of the ligand. It is difficult to explain such a considerable deactivation of the luminescent D_0-state of Eu^{3+} by traditional deactivation mechanisms: electron-vibrational energy transfer to overtones of high-frequency vibrations of C—H groups of the ligand or transitions to higher-lying states of the ion ($^5D_1$, $^5D_2$) or ligand (T_1). The mechanism of electron transfer, where Eu^{3+} plays the role of an acceptor and the ligand is a donor, seems more probable.

References

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