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Morphological Structure and Dispersity of Luminescent Heteroligand Europium Cinnamates

I. V. Kalinovskaya, V. G. Kuryavyi, A. N. Zadorozhnaya, and V. A. Karasev

Institute of Chemistry, Far-Eastern Division, Russian Academy of Sciences,
pr. 100 let Vladivostoku 159, Vladivostok, 690022 Russia
e-mail: Kalinovskaya@ich.dvo.ru

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Abstract—The luminescence characteristics of heteroligand europium cinnamates are reported. As follows from the IR spectra, cinnamic acid coordinates with europium in these compounds in the bidentate fashion. The shape, size, and surface morphology of particles of heteroligand europium cinnamates were determined by scanning electron and atomic force microscopy. Heteroligand europium complexes usually form plate-like and needle-like microcrystals of size 0.1–15 μm.

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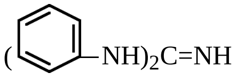
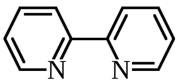
Preparation of finely dispersed powders of luminescent heteroligand compounds is an urgent problem, because many practically important properties of such compounds depend on the particle size [1, 2]. Heteroligand europium cinnamates with nitrogen- and phosphorus-containing neutral ligands are formed in the amorphous state or as fine crystalline druses with the crystal size insufficient for an X-ray analysis. These compounds exhibit strong luminescence. It is interesting to study the morphological structure and dispersity of europium cinnamates by scanning electron and atomic force microscopy.

Heteroligand europium cinnamates that we obtained in [3], $Eu(C_8H_7COO)_3 \cdot nD \cdot xH_2O$, where D = 2,2'-bipyridine ($C_{10}H_8N_2$, $n = 2$, $x = 0$), triphenylphosphine oxide ($C_{18}H_{15}PO$, $n = 1$, $x = 1$), or diphenylguanidine ($C_{13}H_{13}N_3$, $n = 1$, $x = 2$), show red luminescence both at room temperature and at 77 K.


$C_{13}H_{13}N_3$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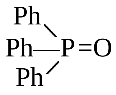
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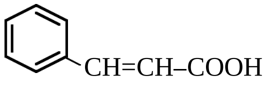
C_8H_7COOH

The luminescence spectra of europium compounds (77 K) are shown in Fig. 1. The strongest bands in the luminescence spectra belong to the eletrodipole $^5D_0$–$^7F_2$ transition, which is characteristic of the majority of luminescent europium compounds [4, 5]. The low-temperature luminescence spectra of these compounds consist of narrow lines. Europium cinnamate hydrate shows the strongest luminescence, exceeding in the intensity that of the heteroligand compounds by a factor of several tens.

The main absorption bands in the IR spectra of europium cinnamates were assigned on the basis of the published data [6, 7]. The disappearance of the OH bending band at 1000 cm^{-1} indicates that the carboxylic group in the complexes is deprotonated [6].

Strong bands at 760–785, 1390–1420, and 1635–1640 cm^{-1} belong, respectively, to the $\delta(OCO^-)$, $\nu_s(COO^-)$, and $\nu_{as}(COO^-)$ modes of bidentate carboxylic groups [6, 7]. The difference $\Delta\nu = \nu_{as}(COO^-) - \nu_s(COO^-)$ is 220–240 cm^{-1}, which corresponds to the bidentate coordination of the carboxylic group with the rare-earth element [6]. The weaker band at 1460–1470 cm^{-1} can be assigned to the stretching vibrations of the C=C bonds of the benzene ring, and the band at 1530–1540 cm^{-1} in the spectrum of the complex

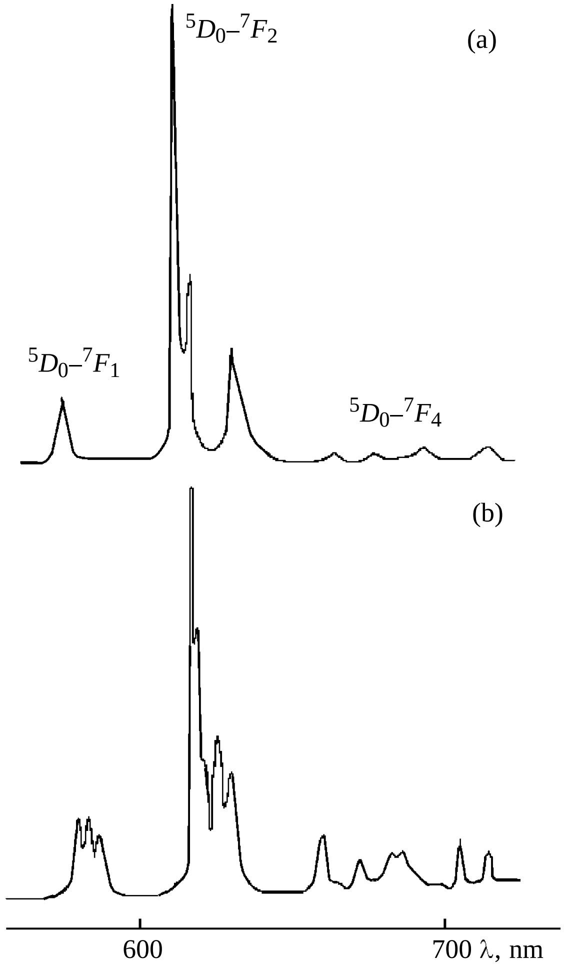

Fig. 1. Luminescence spectra (77 K) of (a) $Eu(C_8H_7 \cdot COO)_3 \cdot H_2O$ and (b) $Eu(C_8H_7COO)_3 \cdot 2C_{10}H_8N_2$.

of europium cinnamate with bipyridine, to the C=N vibrations. The coordination of bipyridine to the europium ion is also indicated by a high-frequency shift of the ligand absorption bands at 1415, 1560, and 1585 cm^{-1} in the spectrum of the complex relative to the free ligand [7]. In the IR spectrum of the complex, the characteristic absorption band of the out-of-plane bending vibrations of the ring hydrogen atoms of bipyridine δ(CH) at about 740 cm^{-1} is split into a doublet (737, 731 cm^{-1}).

The ν(P=O) band in the IR spectrum of the triphenylphosphine oxide complex of europium cinnamate (1170 cm^{-1}) is shifted by ~25 cm^{-1} toward lower frequencies relative to free triphenylphosphine oxide (1195 cm^{-1}), suggesting the coordination of the ligand through the oxygen atom of the P=O group. The IR spectrum of the complex of europium cinnamate with diphenylguanidine contains an absorption band at 3418 cm^{-1} belonging to the NH stretching vibrations. The coordination of diphenylguanidine caused splitting of the bands belonging to the out-of-plane vibrations of hydrogen atoms in the range 685–720 cm^{-1}. In the range 3600–3200 cm^{-1}, there is a weak band assignable to stretching vibrations of water [7].

According to the X-ray diffraction patterns, most of the compounds prepared are X-ray amorphous. Some compounds consist of very fine crystalline druses, but the crystal size is insufficient for an X-ray analysis. It is interesting to examine the size and shape of the compounds by scanning electron and atomic force microscopy.

$Eu(C_8H_7COO)_3 \cdot H_2O$. According to data of the scanning electron microscopy, the compound consists of microcrystalline druses combined in coarser aggregates. These particles consist of plate-like or needle-like crystals of rectangular shape with the size from 0.1 to 15 μm (Fig. 2a). The orientations of microcrystals in druses are diverse and in some cases opposite.

The atomic-force microscopic pattern additionally reveals that these microcrystals have a block substructure and consist of nanocrystallites with approximately triangular faces along with nanocrystallites with rectangular faces, forming a lamellar structure.

$Eu(C_8H_7COO)_3 \cdot 2C_{10}H_8N_2$. The compound consists of druses formed by crystals of parallelepiped shape, or of separate crystals in the form of parallelepipeds of size from 3 to 20 μm (Fig. 2b). Finer (by a factor of 10–20) plate-like crystals in the form of flat chips are disseminated on the face surfaces.

Crystal faces forming three-dimensional right angles are clearly seen in the atomic-force microscopic pattern (Fig. 2b). On the face surfaces, there are oval structures with transverse size of ~0.1 μm, forming a fractal-like pattern. A block substructure in the form of edges of rectangular plates constituting the whole crystal is observed.

$Eu(C_8H_7COO)_3 \cdot C_{18}H_{15}PO \cdot H_2O$. Scanning electron microscopy shows that the substance consists of petals of round or rounded polygonal (triangles or distorted parallelograms) shape, 1–6 μm in size (Fig. 2c).

Atomic force microscopy reveals crystallites of irregular hexagonal of parallelogram-like faces. The particle size is 3–6 μm. The particles are composed of plate-like structures. Dendritic crystallites are also observed. The external perimeter of the dendrites is hexagonal. Also, lamellar structures with a layer thickness of ~0.1 μm are observed.

$Eu(C_8H_7COO)_3 \cdot C_{13}H_{12}N_3 \cdot 2H_2O$. According to scanning electron microscopy, the substance consists

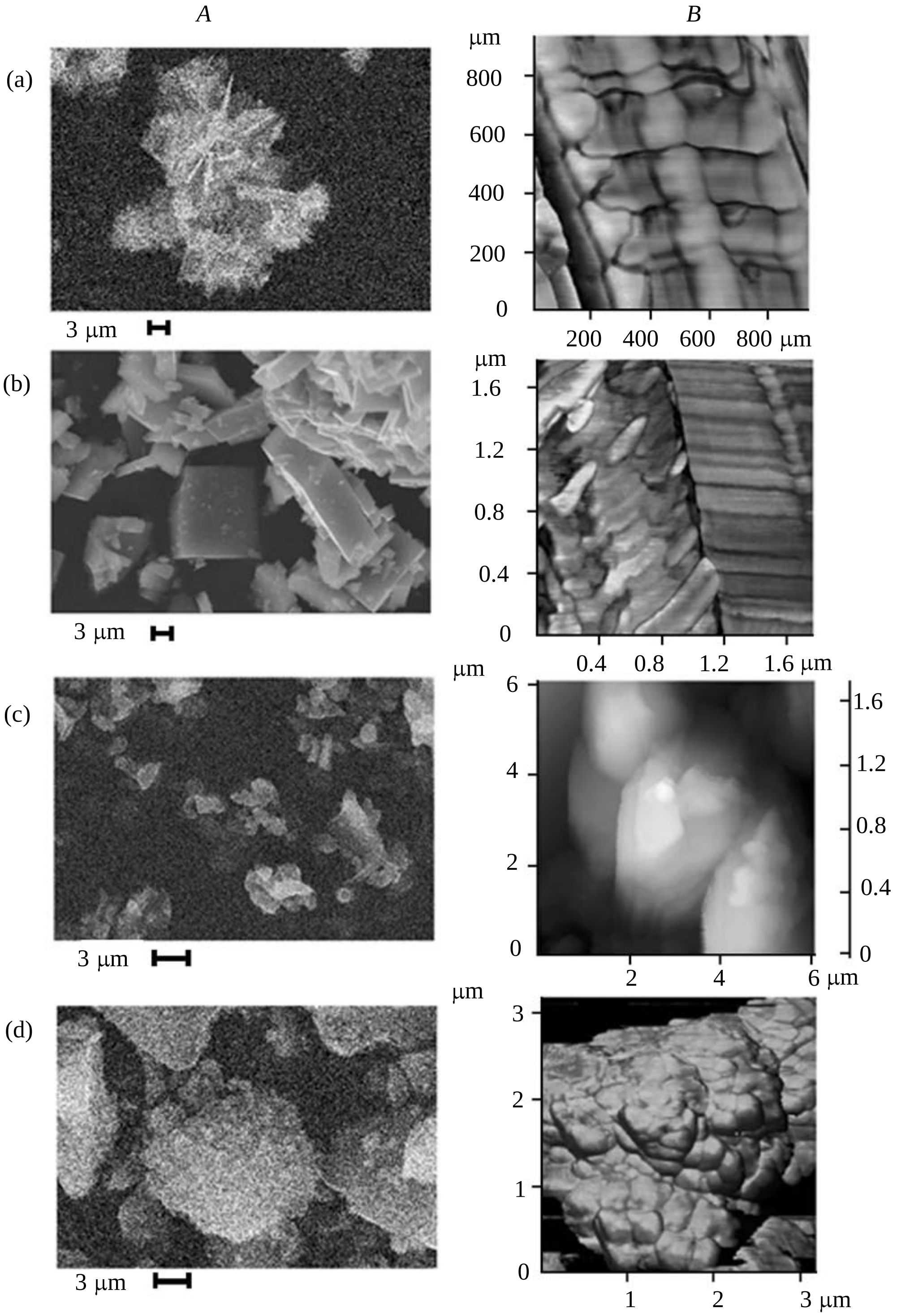

Fig. 2. Morphological structure of europium cinnamates: (a) $Eu(C_8H_7COO)_3 \cdot H_2O$, (b) $Eu(C_8H_7COO)_3 \cdot 2C_{10}H_8N_2$, (c) $Eu(C_8H_7COO)_3 \cdot C_{18}H_{15}PO \cdot H_2O$, and (d) $Eu(C_8H_7COO)_3 \cdot C_{13}H_{12}N_3 \cdot 2H_2O$. (*A*) Scanning electron and (*B*) atomic force microscopy.

of irregular-shaped particles ~10 μm in size consisting, in turn, of finer particles (~0.5 μm). The atomic-force microscopic patterns mainly reveal oval particles of size 0.1–0.5 μm (Fig. 2d), although needle-like parallelepiped crystallites are also sometimes observed.

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer 557 spectrophotometer. The samples were prepared as KBr pellets. The luminescence spectra were taken on an SDL-1 diffraction spectrometer at 77 K. The excitation was provided by a DRSh-250 lamp.

The morphological structure of powders of the europium cinnamates obtained was examined with a DRON-3 X-ray diffractometer (CuK_α radiation), an LEO-430 scanning electron microscope, and an atomic force microscope.

The complexes were prepared from the following pure grade chemicals: $Eu(NO_3)_3 \cdot 6H_2O$, cinnamic acid C_8H_7COOH, nitrogen bases $C_{13}H_{13}N_3$, $C_{10}H_8N_2$, and phosphine oxide $C_{18}H_{15}PO$.

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