

# Luminescent Properties of Europium(III) Complexes with Quinaldic Acid and Sulfur-Containing Neutral Ligands

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**Abstract**—The luminescent heteroligand complexes of europium(III) with quinaldic acid and sulfur-containing neutral ligands  $\text{Eu}(\text{Quin})_3 \cdot \text{D} \cdot 3\text{H}_2\text{O}$  (Quin – quinaldic acid, D – dimethyl sulfoxide or dihexyl sulfoxide) and  $\text{Eu}(\text{Quin})_3 \cdot 3\text{H}_2\text{O}$  have been obtained. Their composition and structure have been determined. The thermal and spectral-luminescent properties of the heteroligand europium(III) complexes have been studied. The quinaldate ion has been found to coordinate to the europium(III) ion as a bidentate ligand. The Stark structure of  ${}^5\text{D}_0$ – ${}^7\text{F}_j$  ( $j = 0, 1, 2$ ) transitions in the low-temperature luminescence spectra of the europium(III) complexes has been analyzed.

**Keywords:** luminescence, europium ion, europium complexes, quinaldic acid

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Complexes of rare-earth elements with carboxylic acids are among promising luminescent compounds [1–6]. Structural and compositional diversity of carboxylic acids makes them convenient model objects for the study of relationship between molecular structure of the components and their physico-chemical properties. Carboxylic acids are widely used as bridging ligands in the polynuclear complexes of *f*-elements and, similarly to other bridging ligands, determine the properties of the compounds and their ability to the formation of supramolecular systems [7–9]. Strong luminescence, photostability, and high thermal stability of rare-earth compounds allow their application as dopants in functional optical materials for optoelectronics and laser devices, for the creation of light-transforming polymer materials, etc. [10, 11].

The presence of two functional groups in quinaldic acid and the possibility of different types of coordination of the carboxylic groups can lead to the formation of different rare-earth elements quinaldates exhibiting interesting luminescent properties. For example, we have synthesized complex europium(III) quinaldates with island and polymeric structure [11–13]. The synthesis of heteroligand europium(III) complexes containing quinaldic acid is usually complicated: generally, the formed precipitate contains a mixture of several compounds [13]. Synthesis and luminescent properties of europium(III) quinaldates with N- and P-containing neutral ligands have been described in [14].

Herein we discuss the results of the study of thermal and spectral-luminescent properties of heteroligand europium(III) complexes with quinaldic acid and sulfur-containing neutral ligands:  $\text{Eu}(\text{Quin})_3 \cdot \text{D} \cdot 3\text{H}_2\text{O}$  with Quin being anion of quinaldic acid and D being dimethyl sulfoxide (DMSO) or dihexyl sulfoxide (DHSO) as well as  $\text{Eu}(\text{Quin})_3 \cdot 3\text{H}_2\text{O}$ .

The composition of the synthesized complexes,  $\text{Eu}(\text{Quin})_3 \cdot \text{D} \cdot 3\text{H}_2\text{O}$ , was confirmed by means of elemental analysis (see the table). The obtained yellow heteroligand europium(III) complexes were soluble only in polar solvents and were not decomposed during prolonged storage. The data on hydrate composition of the heteroligand complexes as well as their dehydration, composition, and decomposition were obtained by means of thermogravimetric analysis at 25–700°C. The decomposition of the europium(III) complexes was similar (Fig. 1), occurring in four stages. Thermogravimetric analysis of complex europium(III) quinaldates with sulfur-containing neutral ligands revealed a single endothermic effect accompanied by the mass loss in the TG and DTA curves (Fig. 1). The 90–135°C temperature range corresponded to a single-stage dehydration of the complexes accompanied by an endothermic effect. The water content determined from the samples mass loss corresponded to the calculated one. Further heating led to a single-stage endothermic elimination of the neutral ligands (DMSO, DHSO) at 130–155°C. The mass loss at

Data of element analysis of heteroligand compounds of europium(III) with quinaldic acid

Compound	Found, %						Formula	Calculated, %					
	C	H	N	H <sub>2</sub> O	Eu	S		C	H	N	H <sub>2</sub> O	Eu	S
Eu(Quin) <sub>3</sub> ·3H <sub>2</sub> O	50.4	3.3	6.0	7.7	21.4	0.0	EuC <sub>30</sub> H <sub>24</sub> O <sub>9</sub> N <sub>3</sub>	50.1	3.3	5.8	7.5	21.1	0.0
Eu(Quin) <sub>3</sub> ·DMSO·3H <sub>2</sub> O	48.3	4.1	5.1	6.7	18.8	4.3	EuC <sub>32</sub> H <sub>30</sub> O <sub>10</sub> N <sub>3</sub> S	48.0	3.8	5.3	6.8	19.0	4.0
Eu(Quin) <sub>3</sub> ·DHSO·3H <sub>2</sub> O	41.1	3.3	4.6	6.0	16.1	3.7	EuC <sub>42</sub> H <sub>54</sub> O <sub>10</sub> N <sub>3</sub> S	40.9	3.2	4.5	5.7	16.2	3.4

that stage equaled 10.5% for Eu(Quin)<sub>3</sub>·DMSO·3H<sub>2</sub>O and 24.6% for Eu(Quin)<sub>3</sub>·DHSO·3H<sub>2</sub>O. The final stage of the neutral ligand elimination overlapped with the onset of the complexes decomposition; therefore, the Eu(Quin)<sub>3</sub> compound could not be obtained via heating. Vigorous decomposition of the quinaldates affording europium(III) oxide occurred at 380–500°C.

Thermal stability of the studied europium(III) complexes was lower in comparison with polymeric europium(III) quinaldates [13], being comparable with that of the island-type europium(III) quinaldates with neutral N-containing ligands [12]. Likely, the presence of the europium(III) ion with two functional groups in the case of the polymeric complexes [12, 13] significantly enhanced the complexes thermal stability.

IR spectra of the obtained europium(III) quinaldates were recorded over the 400–3600 cm<sup>-1</sup> range. The presence of the deprotonates carboxylic group in the complexes was evidenced by the absence of the OH deformation band at 990 cm<sup>-1</sup> [15, 16]. The absorption of the carbonyl group of the free quinaldic acid at 1705 cm<sup>-1</sup> was absent in the complexes spectra as well [17]. Strong bands at 800–807, 1620–1630, and 1372–1385 cm<sup>-1</sup> could be assigned to the  $\delta(\text{OCO}^-)$ ,  $\gamma_{\text{as}}(\text{COO}^-)$ , and  $\gamma_{\text{s}}(\text{COO}^-)$  absorption, respectively, of the carboxylic groups exhibiting bidentate binding, whereas the weaker bands at 1469–1474 and 1594–1597 cm<sup>-1</sup> could be due to the C–C and C–N bonds stretching [17, 18]. Similar bands have been observed in the IR spectra of island-type europium(III) quinaldates. Bidentate coordination of quinaldic acid in the island-type complex europium(III) quinaldates has been elucidated from the IR and X-ray electronic spectroscopy data [13]. IR spectra of the europium complexes obtained in this study revealed especially strong symmetric stretching band of the carboxylic group at 1372–1385 cm<sup>-1</sup>, pointing at the bidentate coordination of the carboxylic groups as well [16]. The  $\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$  difference exceeded 200 cm<sup>-1</sup>, evidencing the ionic character of the Eu–O bond involving the carboxylic group of quinaldic acid [17]. The  $\Delta\nu$  value exceeding

100 cm<sup>-1</sup> generally corresponds to bidentate coordination of the COO<sup>-</sup> group with europium(III) ion [18]. The  $\nu(\text{Eu-N})$  and  $\nu(\text{Eu-O})$  bands of the obtained complexes appear at frequency below 400 cm<sup>-1</sup> [16]. The spectra of the studied complexes contained the bands at 3300–3500 cm<sup>-1</sup> assignable to water molecules stretching [17, 18], whereas the band at 1018–1020 cm<sup>-1</sup> was related to the S=O stretching. The latter frequency was lower than that in the free dihexyl and dimethyl sulfoxides (1050–1100 cm<sup>-1</sup> [16]).

Electronic absorption spectra of the studied heteroligand europium(III) complexes are shown in Fig. 2. The maximum of the broad band  $\lambda_{\text{max}} = 300$  nm in the spectra was somewhat shifted to longer wavelength in comparison with the free quinaldic acid. Moreover, the absorption spectra of the heteroligand complexes contained the absorption bands of the sulfur-containing ligands at  $\lambda_{\text{max}} = 290$ –294 and 308–312 nm, absent in the spectrum of europium quinaldate hydrate (Fig. 2).

Analysis of the electronic absorption spectra revealed the position of the singlet levels S: Quin (34960–35240 cm<sup>-1</sup>), DMSO (47778–47790 cm<sup>-1</sup>), and DHSO (46882–46890 cm<sup>-1</sup>). The position of the quinaldic acid triplet level was determined from the fluorescence spectrum of gadolinium quinaldate (18602–17485 cm<sup>-1</sup> [13]).

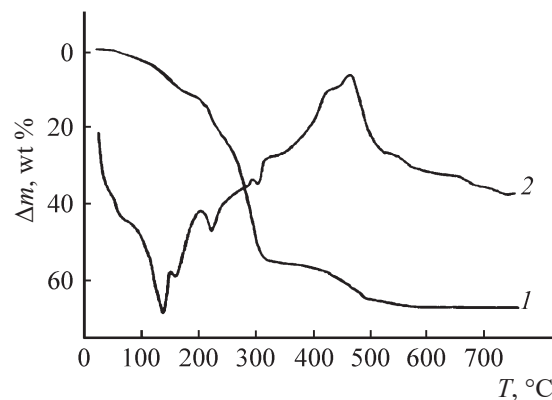
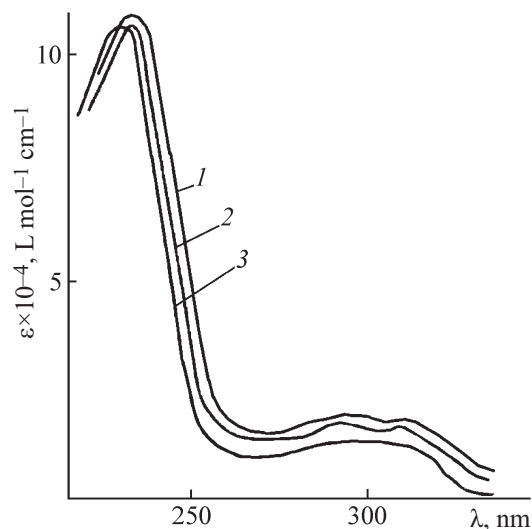
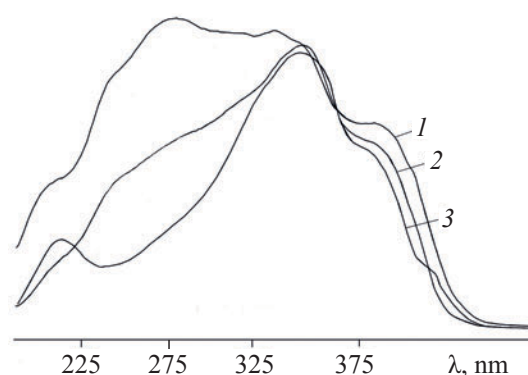


Fig. 1. Thermogravimetric analysis data for Eu(Quin)<sub>3</sub>·DMSO·3H<sub>2</sub>O: (1) TG, and (2) DTA.



**Fig. 2.** Electronic absorption spectra of  $\text{Eu}(\text{Quin})_3 \cdot \text{DMSO} \cdot 3\text{H}_2\text{O}$  (1),  $\text{Eu}(\text{Quin})_3 \cdot \text{DHSO} \cdot 3\text{H}_2\text{O}$  (2), Hquin (3), and  $\text{Eu}(\text{Quin})_3 \cdot 3\text{H}_2\text{O}$  (4) in ethanol ( $c = 10^{-4}$  mol/L).

Excitation spectra of the studied europium(III) complexes luminescence are shown in Fig. 3. In contrast to that of europium(III) quinaldate hydrate, the excitation spectra contained the bands at 250–320 nm assigned to the transitions of the sulfur-containing neutral ligands. That fact pointed at efficient energy transfer from quin-



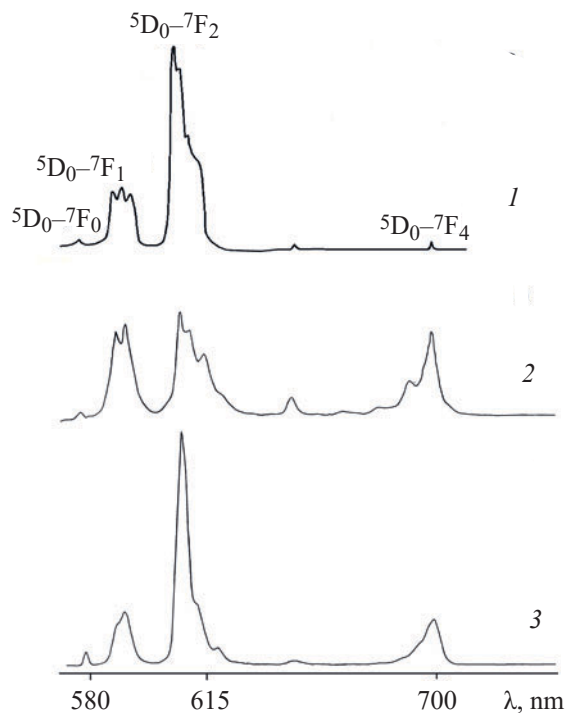
**Fig. 3.** Excitation spectra of  $\text{Eu}(\text{Quin})_3 \cdot \text{DMSO} \cdot 3\text{H}_2\text{O}$  (1),  $\text{Eu}(\text{Quin})_3 \cdot \text{DHSO} \cdot 3\text{H}_2\text{O}$  (2), and  $\text{Eu}(\text{Quin})_3 \cdot 3\text{H}_2\text{O}$  (3) at 300 K ( $\lambda_{\text{lum}} = 615$  nm).

aldic acid and sulfur-containing neutral ligands levels to europium(III) ion.

The obtained heteroligand europium(III) complexes exhibited strong room-temperature red luminescence, the emission maximum appearing at 612 nm (Fig. 4), similarly to the island-type heteroligand europium(III) complexes with quinaldic acid and nitrogen-containing neutral ligands [13]. The strongest bands in the luminescence spectra of europium(III) quinaldates with sulfur-containing neutral ligands were those assigned to the electro-dipole  $^5\text{D}_0-^7\text{F}_2$  transition, whereas the bands corresponding to triplet magnitodipole  $^5\text{D}_0-^7\text{F}_1$  transition were weaker.

The luminescence spectrum of  $\text{Eu}(\text{Quin})_3 \cdot \text{DMSO} \cdot 3\text{H}_2\text{O}$  was of interest, since the intensity of the  $^5\text{D}_0-^7\text{F}_1$  and  $^5\text{D}_0-^7\text{F}_4$  transitions were practically the same as that of the  $^5\text{D}_0-^7\text{F}_2$  transition.

As for majority of europium(III) complexes, the intensity of the forbidden  $^5\text{D}_0-^7\text{F}_0$  transition was low. The relative intensity of the band of the electro-dipole  $^5\text{D}_0-^7\text{F}_0$  transition was increased along the  $\text{Eu}(\text{Quin})_3 \cdot 3\text{H}_2\text{O}$ – $\text{Eu}(\text{Quin})_3 \cdot \text{DMSO} \cdot 3\text{H}_2\text{O}$ – $\text{Eu}(\text{Quin})_3 \cdot \text{DHSO} \cdot 3\text{H}_2\text{O}$  series. That could be caused by the increase in the distortion of the coordination polyhedron in the europium complex due to the adduct formation. The shape of the luminescence spectra was similar for the studied complexes. However, the change of the sulfur-containing neutral ligand led to significant rearrangement of the intensities of the bands of the  $^5\text{D}_0-^7\text{F}_{1,2}$  transitions. The



**Fig. 4.** Luminescence spectra of  $\text{Eu}(\text{Quin})_3 \cdot 3\text{H}_2\text{O}$  (1),  $\text{Eu}(\text{Quin})_3 \cdot \text{DMSO} \cdot 3\text{H}_2\text{O}$  (2), and  $\text{Eu}(\text{Quin})_3 \cdot \text{DHSO} \cdot 3\text{H}_2\text{O}$  (3) at 300 K.

change of the neutral ligand in the  $\text{Eu}(\text{Quin})_3 \cdot 3\text{H}_2\text{O}$ – $\text{Eu}(\text{Quin})_3 \cdot \text{DMSO} \cdot 3\text{H}_2\text{O}$ – $\text{Eu}(\text{Quin})_3 \cdot \text{DHSO} \cdot 3\text{H}_2\text{O}$  series affected the energy gap of the resonance  ${}^5\text{D}_0$ – ${}^7\text{F}_0$  transition (the O–O band exhibited red shift) and reduced the splitting of the Stark components of the  ${}^7\text{F}_1$  ( $\Delta F_1$ ) term.

#### EXPERIMENTAL

The heteroligand complexes of europium(III) were prepared from europium(III) nitrate hexahydrate, quinaldic acid, dimethyl sulfoxide, and dihexyl sulfoxide (all of the “pure” grade). Quinaldic acid was recrystallized from 96% ethanol. The complexes were prepared as described elsewhere [13].

The obtained yellow heteroligand europium(III) complexes were soluble only in polar solvents. The thermograms were obtained using a Paulik–Paulik–Erdey derivatograph (heating rate 5 deg/min,  $\alpha\text{-Al}_2\text{O}_3$  as reference).

Low-temperature luminescence spectra were recorded using an SDL-1 spectrometer (77 K,  $\lambda_{\text{exc}} = 365$  nm). The excitation was performed using a DRSh-250 mercury lamp. The electronic absorption spectra were recorded using an RF-2550 Shimadzu spectrometer (concentration  $10^{-4}$  mol/L in 96% ethanol). The excitation spectra were recorded using an RF-5301 pc Shimadzu instrument. Nitrogen content was determined via the Dumas method, water content was determined via the Fischer titration. Sulfur content was determined using a Shimadzu EDX-800 HS energy-dispersive X-ray fluorescence spectrometer. The samples were pressed with boric acid as substrate. Duration of the measurement in the Ti–U and C–Sc was 100 s (each). IR spectra were recorded using a Tensor-27 Bruker spectrometer ( $4000$ – $350$   $\text{cm}^{-1}$ , KBr pellets).

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#### CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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