New Rare-Earth Metal Acyl Pyrazolonates: Synthesis, Crystals Structures, and Luminescence Properties

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Abstract—Ligand 3-methyl-1-phenyl-4-stearoylpyrazol-5-one (HQ) is synthesized and used to obtain new complexes of rare-earth metals (Eu, Gd, and Tb) of the composition $[Ln(Q)_3(H_2O)(EtOH)]$. The crystal structure of the terbium complex is determined by X-ray diffraction analysis (CIF file CCDC 975286). In a molecule of the complex, three aliphatic fragments n-C₁₇H₃₅ are codirected, which results in the formation of layers bound according to the fastener-sticker principle. The molecules of the complex are joined by a hydrogen bond network involving the pyrazolone rings and oxygen atoms of the inner-sphere solvent molecules (H₂O and EtOH). The terbium complex is luminescent at room temperature, whereas the luminescence of the europium complex is very weak at room temperature and increases by 60 times at lowered temperatures. This makes it possible to consider these compounds as a new class of "luminescent thermometers."

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INTRODUCTION

Permanent interest in luminescent complexes of lanthanides, first of all, terbium and europium complexes, is due to the possibility of their practical use in OLED devices [1] and luminescent sensors [2] and as biological labels [3]. The lanthanide complexes with 3-methyl-1-phenylpyrazol-5-ones are characterized by the simple synthesis, good luminescence characteristics, and the possibility of controlling the luminescence properties by the variation of the radical at the carbonyl group [4–9]. Interest in compounds containing the extended aliphatic chain is related to the possibility of their use for the deposition of Langmuir-Blodgett films and immobilization on the nanoparticle surface. It is also interesting to study processes of vibrational luminescence quenching from the viewpoint of the development of materials for luminescent thermometers.

Ligand HQ [10] was earlier studied for the purpose of possible applications in the extraction separation of rare-earth metals [11, 12]. However, the task of the synthesis and isolation of individual complexes was not stated and their luminescence properties were not studied. The synthesis of the cadmium complex $[Cd(Q)_2(EtOH)_2]$ was described in which individual molecules are linked into infinite chains through hydrogen bonds between the N(2) atom of each acylpyrazolone and ethanol molecule of the adjacent fragment [13]. In each molecule, the aliphatic residues $C_{17}H_{35}$ are linear and antiparallel to each other. Ligand HQ and some other acylpyrazolones forming complexes $[Ln(L)_3(H_2O)(EtOH)]$ are shown in the scheme.



The structures of the rare-earth metal complexes with ligand HQ were not studied. At the same time, three extended n-C₁₇H₃₅ fragments assume two possible structures of the complex: with differently directed aliphatic fragments to form a 2D network as in the case of [Cd(Q)₂(EtOH)₂] and with codirected aliphatic fragments.

We synthesized ligand HQ and complexes $[Ln(Q)_3(H_2O)(EtOH)]$, where Ln is Eu (I), Gd (II), and Tb (III). The crystal structure of complex III was determined and demonstrated the codirected arrangement of the aliphatic fragments. The photophysical properties of complexes I–III were studied.

Compound	Content (found/calculated), %			
	С	Н	Ν	
HQ	76.1/76.32	10.2/10.06	6.2/6.36	
Ι	67.1/67.29	9.1/9.00	5.3/5.47	
II	67.3/67.06	9.3/8.97	5.2/5.46	
III	66.7/66.99	9.1/8.96	5.3/5.45	

Table 1. Elemental analysis results for HQ andcompounds I–III

EXPERIMENTAL

The following commercially available reagents and solvents were used without additional purification: stearic acid, SOCl₂, 3-methyl-1-phenylpyrazol-5-one, potassium hydroxide, acetonitrile, and ethanol. Dioxane was dehydrated by storage above molecular sieves (4 Å) followed by distillation under argon. Terbium, gadolinium, and europium nitrates were obtained by the dissolution of the corresponding oxides (reagent grade) in nitric acid (special purity grade).

IR spectra in the attenuated total internal reflectance mode were recorded on a SpectrumOne spectrophotometer (PerkinElmer) in the range from 650 to 4000 cm⁻¹. A small amount of the triturated sample was placed in a cell and pressed to a diamond crystal, and the spectrum was recorded.

Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry was carried out on an Autoflex II instrument with a time-of-flight detector (Bruker Daltonics, Germany).

The photoluminescence spectra of powdered samples was measured using an S2000 multichannel spectrometer (Ocean Optics, US) and an LGI-21 nitrogen laser ($\lambda_{exc} = 337$ nm) as an excitation source. The measurements were carried out at 300 and 77 K. All luminescence and excitation spectra were measured with a correction to instrumental functions.

The lifetimes of the excited state were determined from the spectra recorded using an EG&G system (Princeton applied research) containing the averaging scheme with a narrow-band filter (model 162). The system included a gated oscillator (model 164) and a broad-band preamplifier (model 115) with the excitation of the organic ligands ($\lambda_{exc} = 337$ nm) and detection of the transitions ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ of terbium and europium ions, respectively. The lifetimes were averaged by three independent measurements.

The synthesis of HQ was carried out according to a modified standard procedure for the synthesis of acylpyrazolones [14], replacing calcium hydroxide by freshly calcined CaO. Stearyl chloride was preliminarily obtained by the reaction of stearic acid with an excess of SOCl₂ followed by the distillation of unre-

acted $SOCl_2$. The reaction product was purified by recrystallization from *n*-hexane. The yield was 76%.

¹H NMR (CDCl₃), δ , ppm: 0.86–0.89 (3H, m, <u>CH₃</u>-C₁₆H₃₂), 1.26–1.41 (28H, m, (<u>CH₂</u>)₁₄–CH₃), 1.70–1.78 (2H, m, <u>CH₂</u>–C₁₅H₃₁), 2), 2.47 (3H, s., <u>CH₃</u>–Pz), 2.71–2.75 (2H, t, <u>CH₂</u>-C₁₆H₃₃), 7.54–7.29 (3H, m, *p*- and *m*-H-Ar), 7.82–7.84 (2H, d, *o*-H-Ar).

The syntheses of I–III were carried out by dropping an alcohol solution of the corresponding rare-earth metal (70 mmol, 5 mL) to an alcohol solution of the in situ obtained KQ (210 mmol, 10 mL). The reaction mixture was refluxed for 20–30 min and cooled, chloroform (5 mL) was added, and potassium nitrate precipitated from the solution was filtered off. Solutions of compounds I–III in an ethanol–chloroform mixture were evaporated to 2 mL and cooled, and the crystallized reaction mixture was filtered off. The precipitates were washed on the filter with diethyl ether and dried in a vacuum drying box over P₂O₅ for 48 h. The yield was ~70%. The elemental analysis results for compounds I–III are given in Table 1.

Complex I: IR, v, cm⁻¹: 3739 (OH), 3573, 2931– 2856 (CH), 1941, 1868, 1740, 1636, 1508 v(C=C, C=O), 1470, 1151, 1083, 996, 760, 630, 496, 483.

MALDI: 592 (EuQ), 1031, 1259 (EuQ₂), 1493 (EuQ₃ + C₂H₅), 1593 (Eu₂Q₂(Q-C₂H₅)), 1621 (Eu₂Q₂(Q-C₁₇H₃₅)).

Complex II: IR, v, cm⁻¹: 3667 (OH), 3317, 2952– 2859 (CH), 1944, 1871, 1786, 1740, 1560, 1491 v(C=C, C=O), 1364, 1210, 1151, 1082, 984, 906, 758, 642, 509.

Complex III: IR, v, cm⁻¹: 3662 (OH), 3318, 2926–2854 (CH), 1941, 1859, 1652, 1549, 1527 v(C=C, C=O), 1467, 1343, 1205, 1151, 1064, 962, 803, 746, 652, 526, 450.

Single crystals of complex **III** were obtained as colorless needles at the slow evaporation of a solution of the complex in ethanol.

The X-ray diffraction analysis of complex III was carried out on a Bruker SMART APEX2 automated diffractometer ($\lambda Mo K_{\alpha}$, graphite monochromator) at 160 K. The structure was solved by a direct method. The positions of hydrogen atoms were found in difference Fourier syntheses. Non-hydrogen atoms were refined by least squares in the anisotropic approximation, and all hydrogen atoms were determined in the isotropic approximation. The APEX2, SAINT, SADABS, and XPRE programs were used for the collection and processing of the I(hkl) array [15]. The calculations were performed using the SHELX97 program package [16]. The crystallographic parameters for structure III are given in Table 2. The coordinates of atoms and other parameters for structure III were deposited with the Cambridge Crystallographic Data Centre (CCDC 975286; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data request/cif).

RESULTS AND DISCUSSION

Structure III is built of Tb(Q)₃(H₂O)(EtOH) molecules (Fig. 1). The coordination polyhedron of the central atom can be described as a strongly distorted square antiprism with the bases O(1), O(2), O(6), $O(7)(H_2O)$ and O(3), O(4), O(5), O(8)(EtOH). The L-O distances in structure III and in complexes $[Ln(Q)_3(H_2O)(EtOH)]$ are presented in Table 3.

The Tb-O(Q) bonds in complex III are shorter, on the average, than those in other studied complexes by 1.5–2%. This is due to the fact that the $C_{17}H_{35}$ group occupies a smaller volume near the central atom than the cyclic substituents in the complexes described earlier. For the same reason, the $Tb-O(H_2O)$ and Tb-O(EtOH) bonds in complex III are shorter than those in other similar complexes by 2-4% on the average.

Molecules of complex III are packed in infinite planar layers formed by a hydrogen bond network between the oxygen atoms of the solvents and unsubstituted nitrogen atoms of ligands O of three adjacent molecules of the complex. The $O(7)(H_2O)-N(6)$, $O(7)(H_2O)-N(2)$, and O(8)(EtOH)-N(4) distances are 2.832(13), 2.874(12), and 2.748 Å, respectively. The shortest Tb–Tb distance in the layer is 9.357 Å.

Individual layers (Fig. 2) in structure III are surrounded from two sides by extended fragments $C_{17}H_{35}$. The aliphatic residue of the first acylpyrazolone molecule (C(12)-C(28)) exists in the conformation similar to an ideal one for the untwisted aliphatic chain. The residue of the second molecule (C(12A)-C(28A)) is after the C(15A) atom bv 46° turned $(C(13A)C(15A)C(17A) 134.42^{\circ})$ and then by 77° $(C(24A)C(26A)C(28A) = 102.87^{\circ})$ after the C(26A) atom. Finally, the residue of the third molecule (C(12B)-C(28B)) is turned by 52° after the C(14B)

Table 2.	Crystallographic data and the experimental and re-
finemen	t parameters for structure III

Parameter	Value	
M	1535.89	
Crystal system	Triclinic	
Space group	$P\overline{1}$	
a, Å	14.871(4)	
<i>b</i> , Å	15.311(4)	
<i>c</i> , Å	20.446(5)	
α, deg	82.410(4)	
β, deg	73.482(3)	
γ, deg	66.011(3)	
$V, Å^3$	4076.9(17)	
$\rho_{calcd}, g/cm^3$	1.251	
Ζ	2	
Scan range, θ , deg	2.07-26.37	
Index range	$-18 \le h \le 17, -19 \le k \le 19, \\ -24 \le l \le 25$	
Goodness-of-fit for F^2	2.110	
Number of measured/indepen- dent reflections	31248/14791	
Number of refined parameters	910	
<i>R</i> factors $(I > 2\sigma(I))$	$R_1 = 0.1088, wR_2 = 0.3247$	
<i>R</i> factors (all reflections)	$R_1 = 0.1411, wR_2 = 0.3323$	
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min}, e {\rm \AA}^{-3}$	3.244/-2.742	

atom $(C(12B)C(14B)C(16B) 127.92^{\circ}))$. Due to these bents, all three residues become codirected and have approximately the same extension (the Tb-C(28),



Fig. 1. Molecular structure of complex III. The phenyl groups at the N(1), N(3), and N(5) atoms and hydrogen atoms are omitted.

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Bond	<i>d</i> , Å				
	III	$Tb(L^{1})_{3}(H_{2}O)(EtOH)$ [7]	$Tb(L^2)_3(H_2O)(EtOH)$ [17]	$Eu(L^3)_3(H_2O)(EtOH)$ [18]	
Ln–O(1)	2.276	2.347	2.356	2.396	
Ln–O(2)	2.364	2.349	2.362	2.357	
Ln–O(3)	2.325	2.301		2.412	
Ln-O(4)	2.341	2.324	2.363	2.352	
Ln–O(5)	2.398	2.369	2.352	2.391	
Ln–O(6)	2.303	2.353	2.331	2.382	
Av. Ln–O(L)	2.3345	2.3590	2.341	2.3816	
$Ln-O(7)(H_2O)$	2.410	2.470	2.456	2.497	
Ln–O(8)(EtOH)	2.404	2.391	2.430	2.514	

Table 3. Comparison of the Ln–O bond lengths in structure III and in some other terbium and europium acyl pyrazolonates

Tb-C(28*A*), and Tb-C(28*B*) distances are 20.213, 19.681, and 21.145 Å, respectively). The layers are linked by the interpenetration of these fragments

according to the fastener-sticker principle (Fig. 3). The Tb–Tb distance between the nearest terbium atoms of two adjacent layers is 30.336 Å.



Fig. 2. Layer of molecules III bound by hydrogen bonds: along the (a) *x* and (b) *y* axes.



Fig. 3. Packing of the layers in structure III according to the fastener-sticker principle (along the x axis).

The sizes of thermal ellipsoids of atoms in the molecule are not uniformly distributed: they increase significantly on going from the nearest coordination sphere of the metal (3-methyl-1-phenylacypyrazolone ring) to less structurally rigid aliphatic chains.

The space between the layers linked by hydrogen bonds contain cavities infinite along the x axis and having linear sizes of 2.7×11.5 Å. Similar cavities are also arranged along the y axis but their sizes are smaller $(1.7 \times 11$ Å). We believe that these cavities can be filled with various molecules of an appropriate size to approach the synthesized complex to materials of the class of metal-organic framework (MOF) structures.

The photoluminescence spectrum of gadolinium complex II was recorded at 77 K (Fig. 4) to estimate the position of the triplet level of ligand HQ. The spectrum exhibits three bands with maxima at 21800, 19200, and 16300 cm⁻¹, i.e., they differ by ~2800-3000 cm⁻¹. These values correspond to the frequencies of intense vibrations of the OH and CH groups of the complex, which allows us to ascribe the corresponding bands to the transitions from the excited triplet state to different vibrational levels of the ground singlet state and to estimate the position of the triplet level of the acylpyrazolone ligand as $T_1 = 21800 \text{ cm}^{-1}$. This value corresponds to the efficient energy transfer to the excited ${}^{5}D_{4}$ level of the terbium ion ($\Delta E(T_{1} \rightarrow {}^{5}D_{4}) =$ 1400 cm⁻¹), whereas the gap between the T_1 and ${}^{5}D_{0}$ levels of the europium ion is too large, being 4400 cm^{-1} .

In fact, the study of the photoluminescence spectra of complexes I and III shows that at room temperature only complex III exhibits an intense luminescence (Fig. 5a). The luminescence of the Tb^{3+} ion appears as

the characteristic narrow intense bands with maxima at 490, 545, 583, and 621 nm and the unresolved broadened peak with a maximum at 651 nm corresponding to the electron transitions ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 6, 5, 4, 3, 2–0) inside the *f* shell of the terbium ion. Both the intensity and character of the luminescence spectrum of complex **III** remains almost unchanged as the temperature decreases (Fig. 5a). The absence of a temperature dependence of the luminescence is confirmed by the data of measurements of the lifetime



Fig. 4. Normalized photoluminescence spectrum of complex II at 77 K ($\lambda_{exc} = 337$ nm).

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Fig. 5. Normalized photoluminescence spectra of complexes (a) III and (b) I ($\lambda_{exc} = 337$ nm) at room and lowered (77 K) temperatures.

 $(\tau, \mu s)$ of the excited state ($\lambda_{exc} = 337$ nm), which is also temperature-independent:

Compound	77 K	300 K
Ι	332(13)	No data
III	610(10)	610(10)

The luminescence of complex I at room temperature is very low-intensity but is significantly enhanced at a lowered temperature (to 77 K) and appears as four peaks with maxima at 590, 613, 650, and 697 nm corresponding to the electron transitions $5 {}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J =1, 2, 3, 4) inside the *f* shell of the europium ion (Fig. 5b). The ratio of luminescence intensities (I_{77}/I_{300}) was chosen as a parameter characterizing the temperature dependence of the luminescence properties. This ratio for complex I is 60. This value is high: for example, in [19] the record value for the studied terbium compounds was $I_{77}/I_{300} = 80$. This allows one to ascribe complex I to the class of "luminescent thermometers" [19–23].

The reason for the temperature dependence of the luminescence of complex I is too high position of the T_1 level and the presence of the long alkyl substituent in the acylpyrazolone ligand. This results in the nonradiative vibrational relaxation of the excited state at room temperature and luminescence at a lowered temperature, when the vibrational levels are "frozen out." The phenomenon is also confirmed by the fact that the lifetime of the excited state of complex I, which is about 330 µs at 77 K, at room temperature is reduced to several µs (measurement limit of the used instrument).

Thus, the introduction of an extended aliphatic substituent into the acylpyrazolone ligand does not

substantially change the nearest coordination environment of the central atom compared to the earlier known acyl pyrazolonates. Three aliphatic fragments of ligand HQ are codirected. The intense luminescence of the terbium ion in complex **III** makes it possible to consider complex **III** and related structures as promising for problems of modifying the surfaces of hydrophobic particles and preparing porous framework structures of the MOF class. At the same time, the temperature dependence of the luminescence intensity in complex **I** is interesting from the viewpoint of developing "luminescent thermometers."

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