ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 6, pp. 437–441. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © I.V. Taidakov, A.N. Lobanov, A.G. Vitukhnovskii, Z.A. Starikova, 2013, published in Koordinatsionnaya Khimiya, 2013, Vol. 39, No. 6, pp. 334–339.

Synthesis and Unusual Crystal Structure of the Eu(III) Complex with 1-(1,5-Dimethyl-1*H*-Pyrazol-4-yl)-4,4,4-Trifluorobutane-1,3-Dione

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Received November 7, 2012

Abstract—The reaction of $Eu(NO_3)_3 \cdot 6H_2O$ with 1-(1,5-dimethyl-1*H*-pyrazol-4-yl)-4,4,4-trifluorobutane-1,3-dione (HL) in the presence of NaOH in aqueous ethanol gave neutral complex $[EuL_3(H_2O)]$ (**I**). The unstable adduct $[EuL_3(H_2O)] \cdot 1.3MeCN$ (**Ia**) was obtained from an acetonitrile solution and studied by X-ray diffraction. The crystals of **Ia** at 100 K are monoclinic, $a = 17.551(3)$ Å, $b = 11.532(2)$ Å, $c = 20.371(3)$ Å, $\beta = 110.886(3)°$, $V = 3852(1)$ Å^3, space group $P2_1/c$, $Z = 4$, $R = 0.0505$. The molecules are connected into chains by strong interactions between the europium atom of one molecule and the pyrazole N(2) atom of another molecule and additionally stabilized by strong hydrogen bonds O(1*w*)–H(1*w*1)···N(4)*. The chains are combined into layers by the hydrogen bonds (1*w*)–H(2*w*1)···N(2)*.

DOI: 10.1134/S1070328413050072

INTRODUCTION

Lanthanide complexes, in particular, β-diketonates are currently under intense research. The enhanced interest is caused, among other reasons, by the possibility of using these compounds as active layers of organic light-emitting diodes (OLED) [1], active media of frequency-tuned lasers, fluorescent markers, and dyes [2]. Numerous publications were devoted to europium compounds that emit in the red spectral region [3].

Previously we described [4] a versatile method for the synthesis of pyrazole 1,3-diketones and demonstrated the possibility of using these compounds for the synthesis of some lanthanide derivatives [5].

For the preparation of complexes exhibiting high luminescence quantum yields, one usually tries to avoid incorporation of water molecules or hydroxyl-containing solvents into the inner sphere of the complex and whenever possible to introduce fluorinated substituents in the ligand in order to avoid nonradiative energy loss upon transfer to the vibrational levels of the CH and OH oscillators [3].

Here we prepared the hydrated complex of europium with 1-(1,5-dimethyl-1*H*-pyrazol-4-yl)-4,4,4-trifluorobutane-1,3-dione (HL) to study the details of complexation of a new class of ligands, pyrazole 1,3-diketones.

EXPERIMENTAL

Ligand HL was synthesized by a known procedure [4]. Synthesis grade europium nitrate (99.9%) and solvents (Aldrich) were used as received.

Synthesis of $[EuL_3(H_2O)]$ (I). HL (0.702 g, 3 mmol) was dissolved in ethanol (15 mL) with heating. The solution was filtered, and 1 M aqueous NaOH (3 mL, 3 mmol) was added. Then a solution of $Eu(NO_3)_3 \cdot 6H_2O$ (0.446 g, 1 mmol) in water (5 mL) was added with stirring at 40°C. The mixture was maintained at 40°C for 4 h and then left at room temperature for 24 h. Then the mixture was vacuum concentrated to dryness and the residue was washed with water on a filter, dried at 40°C to a constant weight, and extracted with hot anhydrous ethanol. Ethanol was evaporated until crystallization started, and the crystals were separated and vacuum dried. The yield of the white microcrystalline powder of $[EuL_3(H_2O)]$ (**I**) was 0.34 g (39%).

For $C_{27}H_{26}N_6F_9O_7Eu$

anal. calcd., %:	C, 37.30;	H, 3.01;	N, 9.67;	Eu, 17.48.
Found, %:	C, 37.93;	H, 3.21;	N, 9.82;	Eu, 17.53.

X-ray diffraction. The crystals **I** · 1.3MeCN suitable for X-ray diffraction were prepared by slow evaporation of a saturated solution of complex **I** in acetonitrile. The experimental set of 34126 reflections was obtained on a Bruker APEX II diffractometer with a

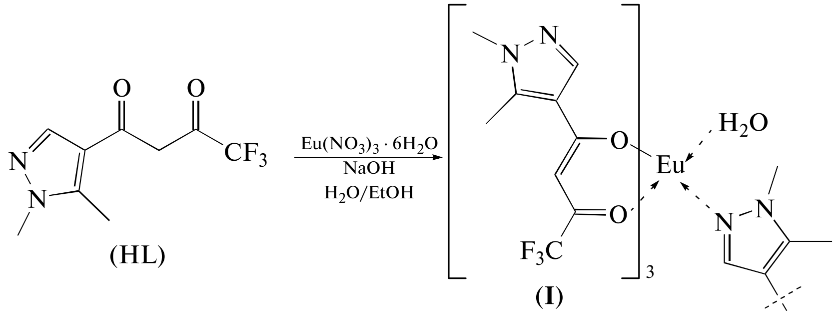
CCD area detector at 100 K from a 0.33 × 0.30 × 0.15 mm single crystal. The absorption corrections were applied by the SADABS program [6]. The structure was solved by the direct method, all non-hydrogen atoms were located in the difference electron density maps and refined on F^2_{hkl} in the anisotropic approximation. All hydrogen atoms (except for water hydrogen atoms located in the difference density maps) were placed in geometrically calculated positions and included in the isotropic refinement in the "rider" model with U(H) = *n*U(C), where U(C) is the equivalent thermal factor of the carbon atom bearing the given H atom, $n = 1.2$ for methine H atoms and $n = 1.5$ for methyl H atoms. All calculations were carried out using the SHELXTL PLUS 5 program package [7].

The crystal data and structure refinement parameters for compound **Ia** are summarized in Table 1. Selected bond angles and bond lengths of **Ia** are given in Table 2. The atom coordinates, bond lengths and bond angles, and the thermal parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 905941; deposit@ccdc.cam.ac.uk or www.ccdc.cam.uk/conts/retrieving.html).

The luminescence spectra of solid samples were recorded on a Perkin-Elmer SL-45 spectrofluorimeter in quartz cells at room temperature.

RESULTS AND DISCUSSION

Compound **I** was prepared by the following route:



The relatively low yield of the complex is probably attributable to the formation of basic salts. The method of choice was the two-step procedure according to which, first, water-soluble salts were washed out of the precipitate and then the mixture of basic salts and the target compound was separated employing the fact that the former were almost insoluble in anhydrous ethanol. Apparently, upon evaporation of the ethanol solution, a solvate is first formed; however, it is fully desolvated during the subsequent vacuum drying.

Solvate **Ia**, which is stable at 100 K and, hence, suitable for X-ray diffraction, is isolated from the acetonitrile solution. The structure contains neutral molecules $[EuL_3(H_2O)]$ and MeCN solvent molecules. The structure of the complex molecule is shown in Fig. 1.

The Eu atom is connected to the oxygen atoms of the chelate rings (Eu(1)–O, 2.348(4)–2.387(4) Å), the O(1*w*) atom (Eu(1)–O(1*w*), 2.389(4) Å), and the N(5*A*) atom (2.600(5) Å) of the neighboring molecule. These bond lengths are similar to those found, for example, for $[Eu(Tta)_3(4,4'\text{-Bipy})(H_2O)]$ [8]: Eu–O 2.335(11)–2.379(11) Å, Eu–O(1*w*) 2.429(13); and Eu–N, 2.621(12) Å. Thus, the Eu–N(5*A*) bond in **Ia** is nearly as strong as Ln–N bonds in complexes formed by bipyridine, phenanthroline, and other common nitrogen ligands.

Note that the Cambridge Crystallographic Data Centre [9] lacks information on europium complexes with 1,3-diketones in which the polymer structure would form by coordination with different types of atoms contained in the same ligand molecule. In particular, the presence of such bonding might be suggested for well-known lanthanide complexes of N-substituted 4-acylpyrazolones [3]; however, we found no such examples.

The coordination polyhedron of Eu can be described as a highly distorted square antiprism, the caps of the antiprism are highly corrugated, being formed by the O(1), O(2), O(5), O(1*w*) and O(3), O(4), O(6), N(5*A*) atoms, which deviate from the mean planes of the caps by ±0.31 and ±0.28 Å, respectively. The mean planes of the caps are parallel, the dihedral angle being only 2.2°. Two chelate rings {O(1) ⟷ O(2) and O(3) ⟷ O(4)} are coplanar to the caps, while the third ring {O(5) ⟷ O(6)} draws the caps together.

The complex molecules are combined in the crystal into chains parallel to the *y*-axis (Fig. 2) by means of Eu–N bonds. The strong hydrogen bond O(1*w*)–H(1*w*1)···N(4)* additionally stabilizes the chain, whereas the second hydrogen bond, O(1*w*)–H(2*w*1)···N(2)* joins the chains into layers parallel to the *xy*0 plane (H(1*w*1)···N(5)* and H(2*w*1)···N(2)*, 1.87 Å each).

Table 1. Crystal data and X-ray experimental parameters for complex **Ia**

Parameter	Value
Molecular Formula	$C_{29.6}H_{29.9}N_{7.3}F_9O_7Eu$
Temperature, K	100(2)
Wavelength (MoK_α)	0.71073 Å
System	Monoclinic
Space group	$P2_1/c$
a, Å	17.551(3)
b, Å	11.532(2)
c, Å	20.371(3)
β, deg	110.886(3)
V, Å^3	3852(1)
Z	4
ρ(calcd.), g cm^{-3}	1.591
μ(MoK_α), mm^{-1}	1.723
T_{min}/T_{max}	0.782/0.600
F(000)	1834
θ_{min}–θ_{max}, deg	2.06–26.00
The number of measured reflections	34126
The number of independent reflections (R_{int})	7449 (0.0541)
The number of reflections with $I > 2\sigma(I)$	5970
The number of refined parameters	515
$R(F)$ ($I > 2\sigma(I)$)	0.0505
Rw (F^2)	0.1159
GOOF	0.991
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	3.974, 2.148

Table 2. Selected bond lengths and bond angles in **Ia**

Bond	d, Å	Bond	d, Å
Eu(1)–O(1)	2.363(4)	N(5)–C(23)	1.33(1)
Eu(1)–O(2)	2.357(4)	N(6)–C(25)	1.343(8)
Eu(1)–O(3)	2.387(5)	N(6)–C(27)	1.44(1)
Eu(1)–O(4)	2.349(5)	C(1)–C(2)	1.51(1)
Eu(1)–O(5)	2.368(4)	C(2)–C(3)	1.363(9)
Eu(1)–O(6)	2.383(4)	C(3)–C(4)	1.42(1)
Eu(1)–O(1w)	2.398(5)	C(4)–C(5)	1.471(9)
Eu(1)–N(5)	2.599(5)	C(5)–C(6)	1.38(1)
O(1)–C(4)	1.259(7)	C(5)–C(7)	1.415(9)
O(2)–C(2)	1.293(7)	C(6)–C(9)	1.49(1)
O(3)–C(13)	1.259(8)	C(10)–C(11)	1.52(1)
O(4)–C(11)	1.264(8)	C(11)–C(12)	1.376(9)
O(5)–C(22)	1.259(6)	C(12)–C(13)	1.43(1)
O(6)–C(20)	1.263(7)	C(13)–C(14)	1.463(9)
N(1)–N(2)	1.355(9)	C(14)–C(15)	1.414(9)
N(1)–C(6)	1.348(7)	C(14)–C(16)	1.39(1)
N(1)–C(8)	1.45(1)	C(16)–C(18)	1.50(1)
N(2)–C(7)	1.322(9)	C(19)–C(20)	1.53(1)
N(3)–N(4)	1.36(1)	C(20)–C(21)	1.37(1)
N(3)–C(16)	1.336(8)	C(21)–C(22)	1.418(9)
N(3)–C(17)	1.45(1)	C(22)–C(24)	1.476(9)
N(4)–C(15)	1.32(1)	C(23)–C(24)	1.390(8)
N(5)–N(6)	1.374(8)	C(24)–C(25)	1.39(1)
Angle	ω, deg	Angle	ω, deg
O(1)Eu(1)O(2)	72.3(2)	O(4)Eu(1)O(6)	73.7(1)
O(1)Eu(1)O(3)	74.7(2)	N(6)N(5)Eu(1)	123.5(4)
O(1)Eu(1)O(4)	78.4(2)	O(4)Eu(1)N(5)	96.4(2)
O(1)Eu(1)O(5)	130.3(2)	O(5)Eu(1)O(6)	72.4(1)
O(1)Eu(1)O(6)	134.7(1)	O(5)Eu(1)O(1w)	77.5(1)
O(1)Eu(1)N(5)	141.8(2)	O(5)Eu(1)N(5)	72.2(2)
O(2)Eu(1)O(3)	77.9(1)	O(6)Eu(1)O(1w)	77.2(1)
O(2)Eu(1)O(4)	142.4(2)	O(6)Eu(1)N(5)	77.0(2)
O(2)Eu(1)O(5)	71.4(1)	O(1) Eu(1)N(5)	144.8(2)
O(2)Eu(1)O(6)	143.8(1)	Eu(1)O(1)C(4)	137.2(4)
O(2)Eu(1)N(5)	92.5(2)	Eu(1)O(2)C(2)	132.5(4)
O(3)Eu(1)O(4)	72.0(2)	Eu(1)O(3)C(13)	138.7(4)
O(3)Eu(1)O(5)	127.6(1)	Eu(1)O(4)C(11)	134.2(4)
O(3)Eu(1)O(6)	126.7(1)	Eu(1)O(5)C(22)	137.6(4)
O(3)Eu(1)N(5)	67.8(2)	Eu(1)O(6)C(20)	133.1(4)
O(4)Eu(1)O(5)	145.9(2)	N(6)N(5)Eu(1)	123.5(4)

The bond lengths in the chelate rings attest to some double bond localization; the average bond lengths are as follows: O(1)–C(1), 1.27; C(1)–C(2), 1.37; C(2)–C(3), 1.42; and C(3)–O(2), 1.26 Å. The C(1)–C(2) bond is much shorter than C(2)–C(3). The average distances in the pyrazole ring (C(4)–C(5), 1.41; C(4)–C(6), 1.39; N(1)–N(2), 1.36; N(1)–C(5), 1.33; N(2)–C(6), 1.34 Å) attest to bond delocalization in the ring. The exocyclic C(3)–C(4) bond (1.47 Å) is substantially elongated. This bond length redistribution may be due to the effect of methyl groups (at N(2) and C(6)) and to

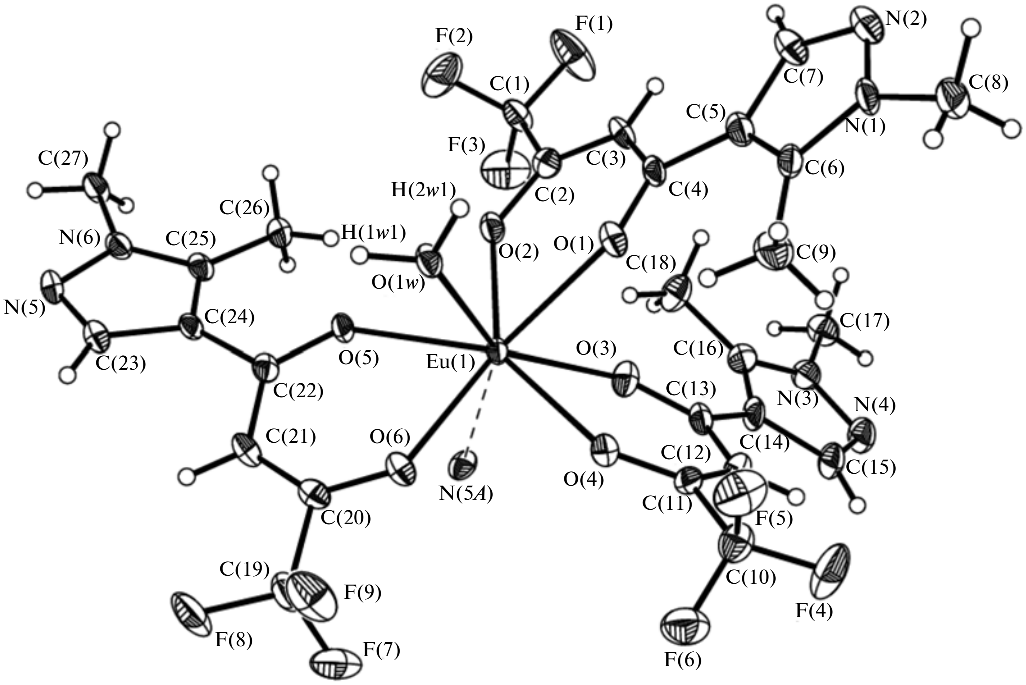


Fig. 1. Molecular structure of complex **Ia**. The thermal ellipsoids are presented to a 30% probability.

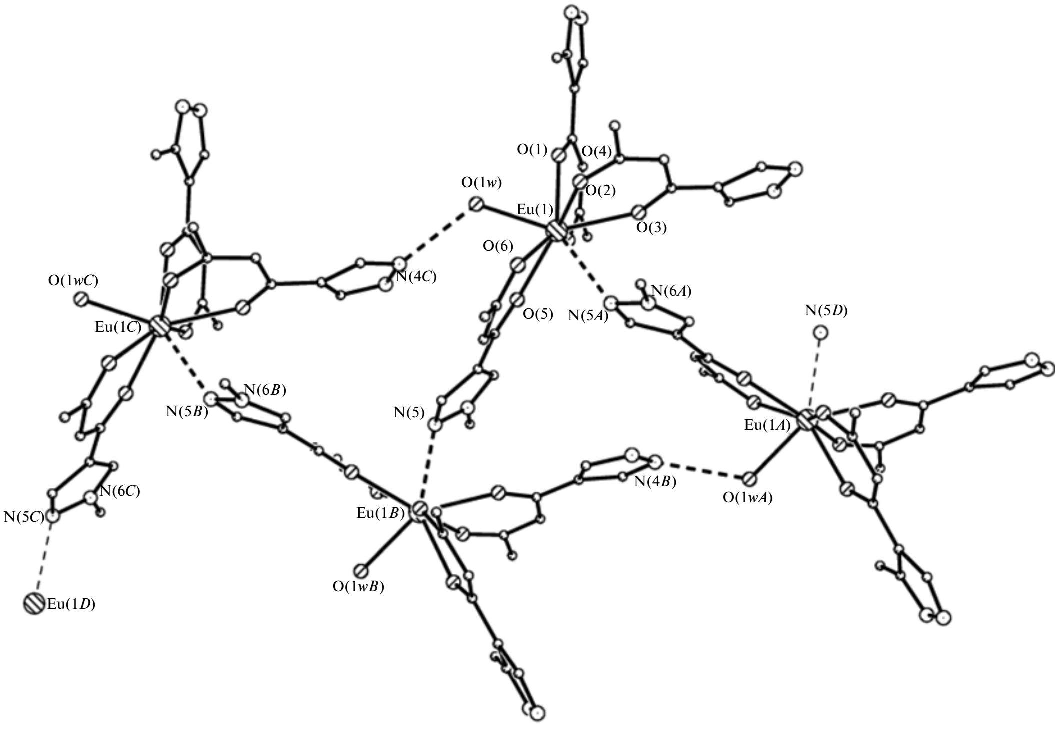


Fig. 2. Fragment of the chain parallel to the *y*-axis.

involvement of N(5)* in the coordination to Eu or involvement of N(4) and N(2) in short hydrogen bonds.

Although the structure contains coordinated water molecules, complex **I** shows rather bright red fluorescence. Figures 3 and 4 show the excitation

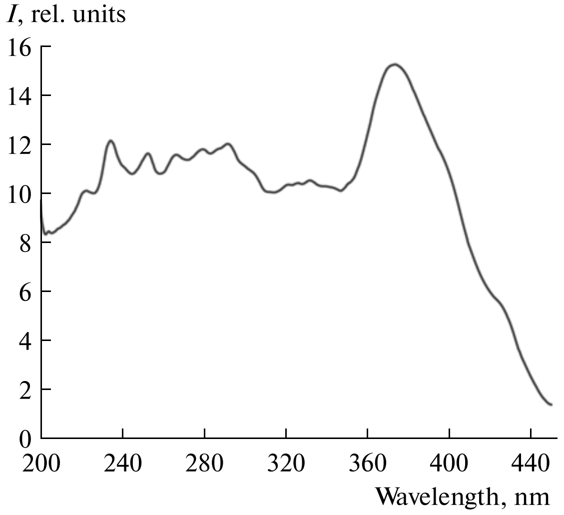


Fig. 3. Excitation spectrum of complex **I** (λ_{em} = 618 nm).

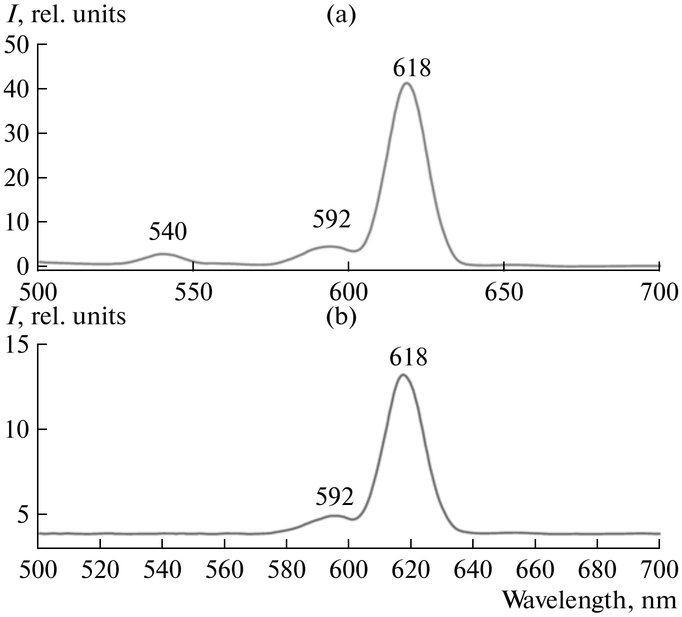


Fig. 4. (a) Luminescence and (b) phosphorescence spectra of complex **I** (λ_{excit} = 370 nm).

spectra (λ_{em} = 618 nm) and luminescence and phosphorescence spectra (λ_{excit} = 370 nm) of compound **I**. The excitation spectrum indicates efficient sensitization of the europium ion by the ligand.

The luminescence spectrum (Fig. 4) is typical [10] of the Eu^{3+} ion: the key lines at 540, 592, and 618 nm correspond to transitions from the $^5D_0$ resonance level to the $^7F_0$, $^7F_1$, and $^7F_2$ levels, respectively. As was to be expected, the presence of coordinated water markedly decreases (more than 4-fold) the phosphorescence intensity (Fig. 4) of the complex due to the nonradiative energy transfer from the ligand triplet level to the vibrational levels of water molecules.

ACKNOWLEDGMENTS

This work was partially supported by the Russian Foundation for Basic Research (project no. 12-03-00839-a) and by the State Contract no. 16.516.11.6071 with the RF Ministry of Science and Education.

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