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Cesium Tetrakis(1-(1,5-Dimethyl-1*H*-Pyrazol-4-yl)-4,4,4-Trifluorobutane-1,3-diono)europiate(III): Synthesis, Crystal Structure, and Luminescence Properties

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Abstract—Anionic complex $Cs^+[EuL_4]^-$ (**I**) is synthesized by 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**) and CsOH in an aqueous-alcohol medium. Unstable adduct $Cs^+[EuL_4]^- \cdot 2CH_2Cl_2$ (**Ia**) is obtained from a solution in CH_2Cl_2. The structure of complex **Ia** is determined by X-ray diffraction analysis. The crystals of complex **Ia** at 100 K are monoclinic, $a = 10.8435(5)$, $b = 20.1353(9)$, $c = 23.355(1)$ Å, $\beta = 92.548(1)°$, $V = 5094.3(4)$ Å^3, space group $P2_1/n$, $Z = 4$, and $R = 0.0294$. The coordination number of the Cs^+ ion is 9. The Cs^+ ion forms shortened (up to 3.3 Å) contacts with the O, N, and F atoms of four diketonate fragments joining the molecules into a three-dimensional structure.

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INTRODUCTION

Diverse rare-earth metal complexes, in particular, β-diketonates, are subjects of current intense investigation. Such an increased interest is due to the possibility to use these compounds as active layers of organic light-emitting diodes [1], active media for frequency-controlled lasers, fluorescent labels and dyes [2]. Many works are devoted to the study of the europium compounds emitting in the red spectral range [3].

As a rule, to obtain complexes with a high luminescence quantum yield, researchers try to avoid the inclusion of water molecules or hydroxyl-containing solvents into the internal sphere of the complex and to introduce (if possible) fluorinated substituents into the ligand composition to prevent nonradiative energy loss by the energy transfer to vibrational levels of the CH and OH oscillators [3].

We have previously described [4] the universal method for the synthesis of 1,3-diketones of the pyrazole series and demonstrated the possibility of their use for the synthesis of some neutral rare-earth metal derivatives [5].

Anionic rare-earth metal complexes with diketonate ligands have a number of interesting properties (intense photoluminescence, capability of triboluminescing, etc.) [6]. In this work, we describe the synthesis of an anionic europium complex with 1-(1,5-dimethyl-1*H*-pyrazol-4-yl)-4,4,4-trifluorobutane-1,3-dione (HL) containing a cesium atom at the external sphere: $Cs^+[EuL_4]^-$ (**I**).

EXPERIMENTAL

Ligand HL was synthesized according to [4]. Europium nitrate (99.9%) and solvents ("for synthesis" grade, Aldrich) were used as received.

Synthesis of $Cs^+[EuL_4]^-$ (I). HL (0.937 g, 4 mmol) was dissolved in ethanol (15 mL) on heating. The solution was filtered, and a 1M aqueous solution of CsOH (4 mL, 4 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 dropwise with stirring at 40°C. The mixture was kept at 40°C for 1 h and left to stay over day at ambient temperature. Then the mixture was evaporated to dryness in vacuo and extracted with a hot mixture (50 mL) of anhydrous ethanol with CH_2Cl_2 (2 : 1 vol/vol). The solution was filtered and evaporated to the beginning of crystallization, and the crystals were separated and dried in vacuo at 40°C to a constant weight. The yield of a white microcrystalline powder of compound **I** was 0.90 g (74%).

For $C_{36}H_{32}F_{12}N_8O_8CsEu$

anal. calcd., %:	C, 35.51;	H, 2.65;	N, 9.20;	Eu, 12.72.
Found, %:	C, 35.49;	H, 2.78;	N, 9.39;	Eu, 12.63.

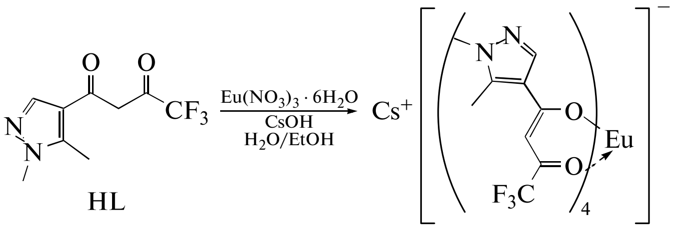
X-ray diffraction analysis. Colorless needle-like crystals of compound **I** · $2CH_2Cl_2$ (**Ia**) suitable for X-ray diffraction analysis were obtained by the slow evaporation of a saturated solution of complex **I** in dichloromethane. An experimental set of reflections was obtained on a Bruker APEX II CCD area detector diffractometer at 100(2) K from a single crystal 0.35 × 0.25 × 0.20 mm in size. An absorption correction was applied using the SADABS program [7]. The crystallographic data and refinement parameters for compound **Ia** are listed in Table 1. The structure was solved by a direct method. All non-hydrogen atoms were localized in the difference electron density syntheses and refined for F_{hkl}^2 in the anisotropic approximation. All hydrogen atoms were placed in geometrically calculated positions and taken into account by refinement in the anisotropic approximation in the riding model with $U(H) = nU(C)$, where U(C) is the equivalent temperature factor of the carbon atom to which the corresponding H atom is bonded; $n = 1.2$ for the methine H atoms and $n = 1.5$ for the H atoms of the methyl groups. Selected bond angles and bond lengths for compound **Ia** are given in Table 2.

All calculations were performed using the SHELXTL PLUS 5 program package [8]. The coordinates of atoms, bond lengths and bond angles, and temperature parameters were deposited with the Cambridge Crystallographic Data Centre (no. 922987, deposit@ccdc.cam.ac.uk).

The luminescence spectra of the solid samples were recorded on a PerkinElmer SL-45 spectrofluorimeter in quartz cells at ambient temperature.

RESULTS AND DISCUSSION

Compound **I** was synthesized according to the following scheme:



HL

I

The anionic complex is readily formed when mixing the reactants in an Eu : HL : CsOH ratio of 1 : 4 : 4. A minor amount of basic salts is separated by the filtration of a solution of the complex before crystallization.

Probably, a solvate is primarily formed when the solution in an EtOH–CH_2Cl_2 mixture is evaporated. However, the solvate is completely desolvated upon the subsequent drying in vacuo.

Solvate **Ia** is also formed from the solution in pure CH_2Cl_2. Solvate **Ia** is stable at 100 K, which makes it possible to determine its structure by X-ray diffraction analysis. The structure contains Cs^+ cations, $[Eu(L)_4]^-$ anions, and CH_2Cl_2 solvate molecules. The structure of the $[Eu(L)_4]^-$ complex anion is shown in Fig. 1.

The coordination polyhedron of the Eu atom is a distorted tetragonal antiprism $\{EuO_8\}$. The caps of the antiprism formed by the O(1), O(2), O(3), O(7) and O(4), O(5), O(6), O(8) atoms are strongly corrugated, the deviations of the atoms from the mean planes are ±0.25 and ±0.28 Å, respectively, and the dihedral angle between the planes is 6.8°.

The Eu–O bonds related to the same cap (average length 2.382 Å) are somewhat shorter than the Eu–O bonds of the second cap (average length 2.397 Å). The average Eu–O bond lengths in complex **Ia** are comparable to those in similar complexes with other ligands. For example, for complex $K[Eu(Hfac)_2(Btfac)_2]$, the average Eu–O bond lengths are 2.336 and 2.405 Å for each ligand, respectively [9].

Two chelates O(3)↔O(4) and O(7)↔O(8) pull together the caps. Two cycles O(1)↔O(2) and O(5)↔O(6) are arranged under the caps and form with the cap planes dihedral angles of 39.7° and 68.9°, respectively.

The coordination number of the Cs^+ ion is 9. The Cs^+ ion forms shortened contacts (up to 3.3 Å) with the O, N, and F atoms of four diketonate ligands. Due to these contacts, individual molecules of the complex are joined into a complicated three-dimensional network (Fig. 2).

Complex **I** has a bright red fluorescence. The excitation spectrum ($\lambda_{em} = 617$ nm) and the luminescence and phosphorescence spectra ($\lambda_{exe} = 350$ nm) of compound **I** are shown in Figs. 3 and 4, respectively. The

Table 1. Crystallographic data and experimental parameters for complex **Ia**

Parameter	Value
Empirical formula	$C_{38}H_{36}Cl_4F_{12}N_8O_8CsEu$
Wave length (MoK_α), Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	10.8435(5)
b, Å	20.1353(9)
c, Å	23.3552(10)
β, deg	92.5480(10)
V, Å^3	5094.27
Z	4
ρ_{calcd}, g/cm^3	1.809
$\mu(MoK_\alpha)$, mm^{-1}	2.245
T_{min}/T_{max}	0.507/0.662
$F(000)$	2712
$\theta_{min}-\theta_{max}$, deg	1.75–27.00
Number of collected reflections	51826
Number of independent reflections (R_{int})	11111 (0.0486)
Number of reflections with $I > 2\sigma(I)$	9274
Number of refined parameters	659
$R(F)$ ($I > 2\sigma(I)$)	0.0294
$R_w(F^2)$	0.0641
Goodness-of-fit	1.016
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.992, –0.699

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

Bond	d, Å	Bond	d, Å
Eu(1)–O(1)	2.375(2)	Cs(1)–O(5)	3.058(2)
Eu(1)–O(2)	2.378(2)	Cs(1)–O(7)	3.086(2)
Eu(1)–O(3)	2.362(2)	Cs(1)–F(1)	3.449(2)
Eu(1)–O(4)	2.419(2)	Cs(1)–F(2)	3.222(2)
Eu(1)–O(5)	2.437(2)	Cs(1)–F(9)	3.276(2)
Eu(1)–O(6)	2.376(2)	Cs(1)–F(12)	3.210(2)
Eu(1)–O(7)	2.413(2)	Cs(1)–N(7)	3.216(3)
Eu(1)–O(8)	2.356(2)	Cs(1)–N(3)	3.177(3)
Cs(1)–O(1)	3.085(2)	Cs(1)–F(11)	3.462(2)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)Eu(1)O(3)	71.12(7)	O(1)Cs(1)F(1)	55.00(5)
O(1)Eu(1)O(4)	101.10(7)	O(1)Cs(1)F(2)	49.04(5)
O(1)Eu(1)O(5)	146.95(7)	O(1)Cs(1)F(9)	52.49(5)
O(1)Eu(1)O(6)	77.40(7)	O(1)Cs(1)F(12)	105.28(5)
O(1)Eu(1)O(7)	102.88(7)	O(1)Cs(1)N(7)	97.44(6)
O(1)Eu(1)O(8)	73.04(7)	O(1)Cs(1)N(3)	157.00(7)
O(1)Eu(1)O(3)	140.23(7)	O(1)Cs(1)F(11)	109.16(7)
O(2)Eu(1)O(4)	82.50(7)	O(1)Cs(1)F(12)	126.18(5)
O(2)Eu(1)O(5)	75.95(7)	O(1)Cs(1)O(7)	98.86(6)
O(2)Eu(1)O(6)	127.61(7)	O(5)Cs(1)F(1)	57.07(5)
O(2)Eu(1)O(8)	130.41(7)	O(5)Cs(1)F(9)	94.47(5)
O(2)Eu(1)O(4)	148.59(7)	O(5)Cs(1)F(12)	50.45(5)
O(3)Eu(1)O(5)	71.47(7)	O(5)Cs(1)N(7)	102.41(6)
O(3)Eu(1)O(6)	145.23(7)	O(5)Cs(1)N(3)	112.04(7)
O(3)Eu(1)O(7)	141.60(7)	O(5)Cs(1)F(11)	101.84(7)
O(3)Eu(1)O(8)	72.02(7)	O(5)Cs(1)F(12)	172.87(5)
O(3)Eu(1)O(5)	87.50(7)	O(5)Cs(1)F(1)	150.04(6)
O(4)Eu(1)O(6)	127.24(7)	O(7)Cs(1)F(2)	84.31(5)
O(4)Eu(1)O(7)	72.04(7)	O(7)Cs(1)F(9)	106.15(5)
O(4)Eu(1)O(8)	130.16(7)	O(7)Cs(1)F(12)	98.32(5)
O(4)Eu(1)O(6)	72.64(7)	O(7)Cs(1)N(7)	51.31(6)
O(5)Eu(1)O(7)	69.99(7)	O(7)Cs(1)N(3)	102.01(7)
O(5)Eu(1)O(8)	74.45(7)	O(7)Cs(1)F(11)	157.49(7)
O(5)Eu(1)O(7)	74.07(7)	O(7)Cs(1)F(12)	129.57(5)
O(6)Eu(1)O(8)	144.15(7)	O(7)Cs(1)F(2)	94.44(6)
O(6)Eu(1)O(8)	92.79(7)	F(1)Cs(1)F(9)	37.11(5)
O(7)Eu(1)O(5)	73.02(7)	F(1)Cs(1)F(12)	145.77(5)
O(1)Cs(1)O(7)	58.66(5)	F(1)Cs(1)N(7)	91.90(5)

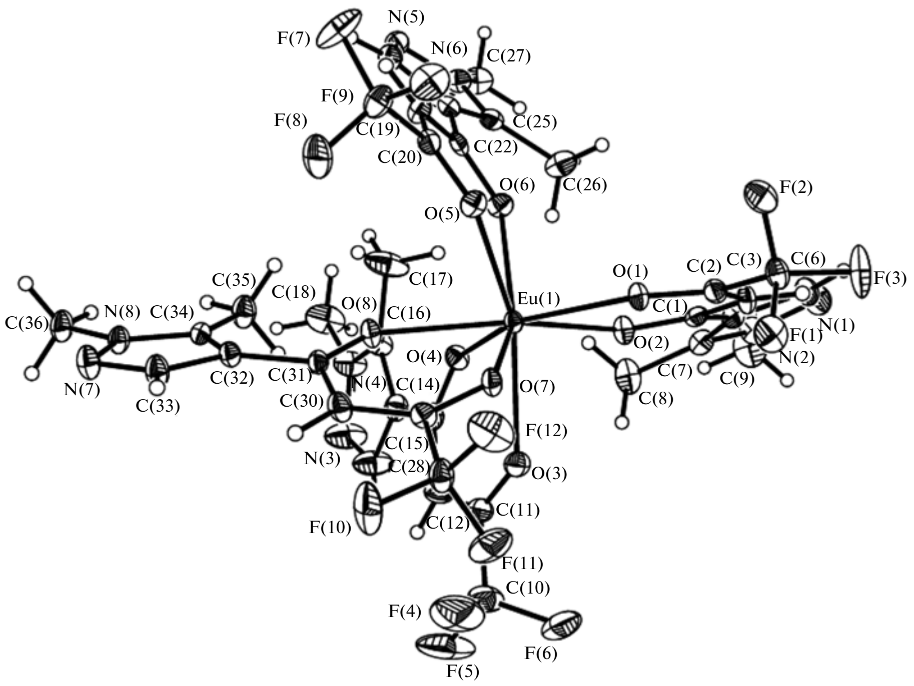


Fig. 1. Molecular structure of complex **Ia**. Thermal ellipsoids are presented with 50% probability.

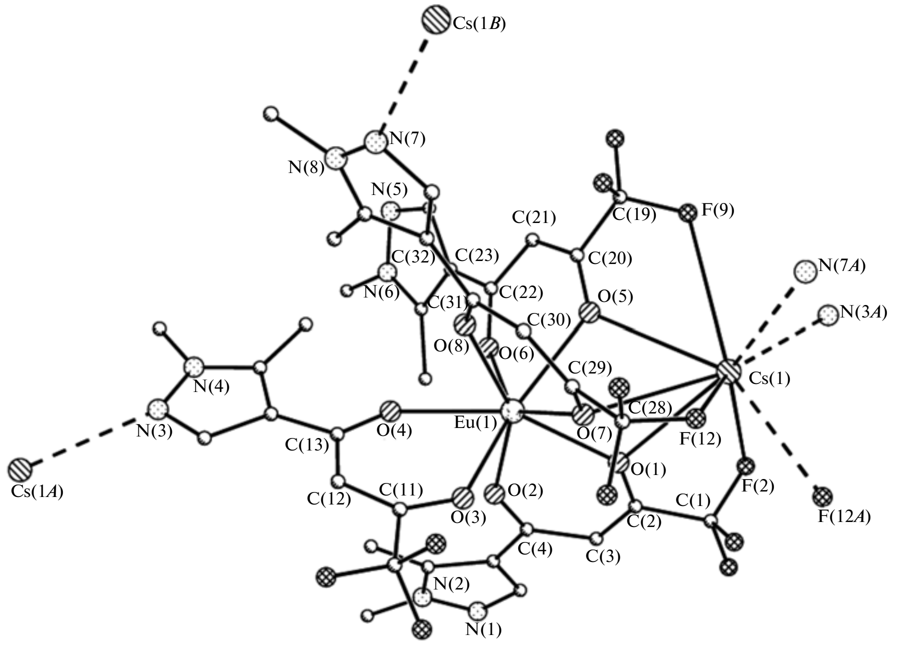


Fig. 2. Fragment of the molecular structure of solvate **Ia**. Solvent molecules are omitted.

excitation spectrum indicates the efficient sensibilization of the europium ion by the ligand.

The luminescence spectrum (Fig. 4) is typical [10] of the Eu^{3+} ion: the main lines at 538, 593, 617, and 691 nm correspond to transitions from the $^5D_0$ resonance level to the ^7F_n levels ($n = 0–3$), respectively.

The phosphorescence intensity (Fig. 4) is higher than the luminescence intensity because of signal inte-

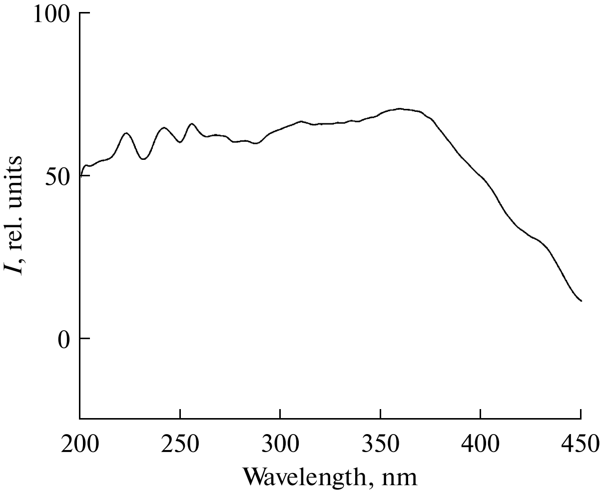


Fig. 3. Excitation spectrum of complex **I** ($\lambda_{em} = 617$ nm).

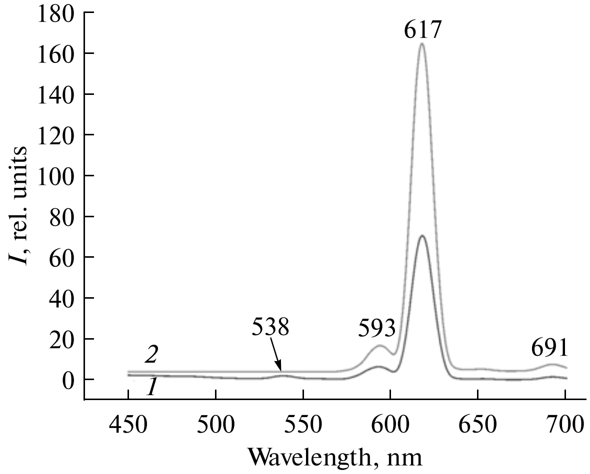


Fig. 4. (*1*) Luminescence and (*2*) phosphorescence spectra of complex **I** ($\lambda_{exe} = 350$ nm).

gration during spectra recording. The phosphorescence spectrum exhibits only three main lines corresponding to the $^5D_0 \rightarrow {}^7F_{1-3}$ transitions, and the line at 617 nm is the most intense in this case.

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