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Tris(1,5-Dimethyl-1*H*-Pyrazol-4-Yl)-4,4,4-Trifluorobutane-1,3-Dionato)(dimethanol)terbium(III): Synthesis, Crystal Structure, and Luminescent Properties

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Abstract—The neutral complex $[Tb(L_3)(MeOH)_2]$ was unexpectedly formed as the major product of the reaction of $Tb(NO_3)_3 \cdot 6H_2O$ with 1-(1,5-dimethyl-1*H*-pyrazol-4-yl)-4,4,4-trifluorobutane-1,3-dione (HL) and CsOH in aqueous alcohol in 1 : 4 : 4 molar ratio of the reactants. The composition of the complex was confirmed by elemental analysis and X-ray diffraction stidy (CIF file CCDC no. 1876652); luminescent properties of the complex were investigated.

Keywords: terbium coordination compounds, 1,3-diketones, pyrazole, luminescence
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INTRODUCTION

Heterocyclic β-diketones represent an intensively studied class of chelating O^O-ligands used, in particular, for the synthesis of various lanthanide complexes [1, 2]. These complexes find various practical applications, for example, in the separation of products of nuclear fuel reprocessing [3], as luminescent materials [4], for CVD fabrication of inorganic coatings [5], and so on. The properties of coordination compounds largely depend on the nature of ligands; therefore, the synthesis of new complex-forming molecules is a highly important task. Previously, we described the synthesis of new β-diketones bearing pyrazole substituents [6]. A specific features of these ligands is the ability to form not only usual neutral tris- and anionic tetrakis-complexes [7–9], but also unusual polymeric structures (2D polymers) via additional coordination involving pyrazole nitrogen atoms [10]. Here we describe the unexpected formation of a neutral terbium tris-complex under conditions used previously to prepare anionic europium tetrakis-complexes with the same pyrazole type ligand [9].

EXPERIMENTAL

1-(1,5-Dimethyl-1*H*-pyrazol-4-yl)-4,4,4-trifluorobutane-1,3-dione (HL) was synthesized by a known procedure [6]. Terbium nitrate (99.9%, Aldrich, USA) was used as received. The other reagents and solvents were commercial chemicals of Acros Organics (Belgium) and were used as received.

Elemental CHN analysis was done on an Elementar Vario MicroCube analyzer (Elementar Analysensysteme GmbH, Germany). The metal was quantified by titration with EDTA after acid decomposition of the complex.

The UV/Vis spectra were recorded on a Shimadzu UV-1800 spectrophotmeter (Japan); the luminescence spectra and excited state lifetimes were measured on a Fluorolog 3-22 spectrofluorimeter (Horiba-Jobin-Yvon, USA) for solid samples placed into quartz tubes 4 mm in diameter. The absolute luminescence quantum yields were determined using the same instrument and integrating sphere (GMP, Switzerland) and averaged over at least three measurements. The error of quantum yield determination was ±15%.

Synthesis of $[Tb(L)_3(MeOH)_2]$ (I). A weighed portion of HL (0.937 g, 4 mmol) was dissolved in methanol (15 mL) with heating (40°C). The solution was filtered, and a 1 M aqueous solution of CsOH (4 mL, 4 mmol) was added. Then a solution of $Tb(NO_3)_3 \cdot 6H_2O$ (0.446 g, 1 mmol) in water (5 mL) was added dropwise with stirring at 40°C, then the mixture was kept for 1 h and allowed to stand for 24 h at room temperature. After that, the mixture was evaporated to dryness in vacuo and extracted with boiling MeOH (50 mL). The solution was filtered through a thin layer of Celite, concentrated to a volume of 5 mL, and kept until crystallization started. The crystals were collected on a filter, washed with hexane (5 mL), and dried to a constant weight in vacuo (50°C, 0.1 Torr).

Table 1. Crystallographic data and X-ray diffraction experiment and structure refinement details for complex **I**

Parameter	Value
M	922.53
Temperature, K	120(2)
$\lambda(MoK_\alpha)$, Å	0.71073
System	Triclinic
Space group	$P\bar{1}$
a, Å	11.2242(4)
b, Å	11.6788(4)
c, Å	15.3556(6)
α, deg	88.7250(10)
β, deg	76.1870(10)
γ, deg	64.1270(10)
V, Å^3	1751.00(11)
Z	2
ρ(calcd.), g cm^{-3}	1.750
$\mu(MoK_\alpha)$, mm^{-1}	2.124
F(000)	916
Range of θ, deg	1.37–29.00
Number of collected reflections	20925
Number of unique reflections (R_{int})	9286 (0.0274)
Number of reflections with $I > 2\sigma(I)$	8465
T_{min}/T_{max}	0.817/0.902
Data of refined parameters	486
GOOF	1.014
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0266$, $wR_2 = 0.0604$
R factors (for the whole array)	$R_1 = 0.0307$, $wR_2 = 0.0626$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.855/–0.813

The yield of the colorless finely crystalline powder was 0.673 g (73%).

For $C_{29}H_{32}F_9N_6O_8Tb$				
Anal. calcd., %	C, 37.76	H, 3.50	N, 9.11	Tb, 13.63
Found, %	C, 37.94	H, 3.611	N, 9.02	Tb, 13.98

X-ray diffraction. The colorless plate-like crystals of complex **I** suitable for X-ray diffraction were prepared by slow evaporation of a saturated solution of **I** in dichloromethane at room temperature. The experimental set of 20925 reflections was collected on a Bruker APEX-II CCD diffractometer at 120 K from a 0.10 × 0.05 × 0.05 mm crystal. The structure was solved by direct methods, all non-hydrogen atoms were located in difference electron density Fourier maps and refined on F^2 in the anisotropic-isotropic approximation. All calculations were carried out using the SHELX program package [11]. Selected structural data and refinement parameters for compound **I** are summarized in Table 1.

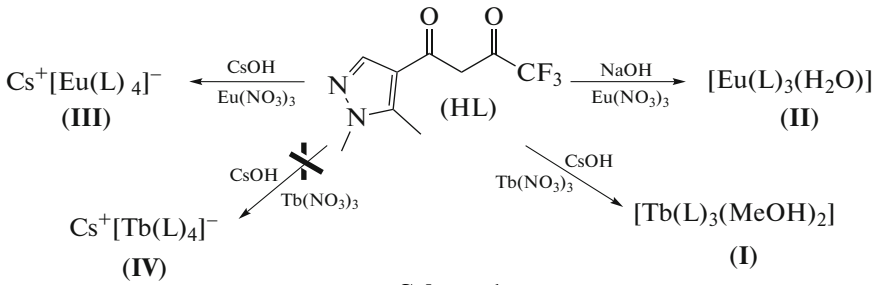
The crystallographic data for structure **I** are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1876652; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The generally accepted method for the synthesis of both tris- and tetrakis-complexes of lanthanides with β-diketones is the reaction between alkaline solutions of ligands with an appropriate amount of a metal salt, usually nitrate or chloride [12, 13]. As a rule, the reaction is carried out in aqueous alcohols. At a ligand : base : lanthanide salt molar ratio of 3 : 3 : 1, the tris-complex is formed, while the ratio of 4 : 4 : 1, results in the formation of the tetrakis-complex bearing an additional outer-sphere cation. However, in the case of HL, the dependence is more complex. The reaction of the ligand HL with terbium and europium nitrates in the presence of various bases is shown in the Scheme 1.

Table 2. Selected bond lengths (Å) and bond angles (deg.) in complex **I**

Bond	*d*, Å	Bond	*d*, Å
Tb(1)–O(6)	2.3343(16)	Tb(1)–O(5)	2.3706(16)
Tb(1)–O(3)	2.3373(16)	Tb(1)–O(4)	2.3847(15)
Tb(1)–O(1)	2.3417(16)	Tb(1)–O(2S)	2.4184(16)
Tb(1)–O(2)	2.3600(16)	Tb(1)–O(1S)	2.4198(16)
Angle	ω, deg	Angle	ω, deg
O(6)Tb(1)O(3)	143.34(6)	O(5)Tb(1)O(2S)	71.18(6)
O(6)Tb(1)O(1)	74.59(6)	O(4)Tb(1)O(2S)	140.63(6)
O(3)Tb(1)O(1)	142.01(6)	O(6)Tb(1)O(1S)	88.02(6)
O(6)Tb(1)O(2)	145.61(6)	O(3)Tb(1)O(1S)	101.00(6)
O(3)Tb(1)O(2)	70.70(6)	O(1)Tb(1)O(1S)	76.83(6)
O(1)Tb(1)O(2)	71.91(6)	O(2)Tb(1)O(1S)	77.09(6)
O(6)Tb(1)O(5)	72.60(5)	O(5)Tb(1)O(1S)	139.76(5)
O(3)Tb(1)O(5)	78.06(6)	O(4)Tb(1)O(1S)	68.88(5)
O(1)Tb(1)O(5)	127.86(6)	O(2S)Tb(1)O(1S)	149.02(6)
O(2)Tb(1)O(5)	136.38(5)	O(3)Tb(1)O(4)	72.26(5)
O(6)Tb(1)O(4)	78.33(6)	O(1)Tb(1)O(4)	136.58(6)
O(2)Tb(1)O(4)	122.64(6)	O(3)Tb(1)O(2S)	85.27(6)
O(5)Tb(1)O(4)	72.76(5)	O(1)Tb(1)O(2S)	79.78(6)
O(6)Tb(1)O(2S)	105.05(6)	O(2)Tb(1)O(2S)	76.53(6)



Scheme 1.

According to our earlier data, the reaction of the ligand with $Eu(NO_3)_3$ in 3 : 1 molar ratio in the presence of 3 equiv. of NaOH affords the expected tris-complex **II** ($[Eu(L)_3(H_2O)]$) with the structure of a 2D coordination polymer [9], while the ratio of 4 : 1 and 4 equiv. of a base (CsOH) give cesium tetrakis-complex **III** ($Cs^+[EuL_4]^-$) [10]. When CsOH is replaced by NaOH or KOH, the reaction gives a complex mixture of unidentified products. Thus, the radius of the alkali metal cation has a pronounced effect on the stability of the resulting complex anions. However, the nature of the lanthanide ion was also found to be significant. Attempted synthesis of terbium tris-complexes by the same procedure as used for europium complexes yielded a mixture of basic salts and hydroxides. When the ligand amount was increased to 4 moles per mole of $Tb(NO_3)_3$ and, correspondingly, 4 equiv. of the base were taken, a product could be isolated and identified only in the case of CsOH. It is noteworthy that, instead of the expected tetrakis-complex **IV** ($Cs^+[TbL_4]^-$), the monomeric tris-complex **I** without coordination of pyrazole nitrogen atom to the metal, like in its europium analogue **II**, was isolated in this case as the only product. The coordination sphere of the Tb^{3+} ion is completed by the oxygen atoms of the OH groups of coordinated methanol molecules. Thus, minor changes of the lanthanide ion radius are probably sufficient to considerably affect the stability of the resulting coordination compounds and completely change the distribution of the reaction products with this ligand. It is also possible that the reaction pathway markedly depends on stabilization of the anion of the HL enol form and, correspondingly, the complex tetrakis-anion via specific Cs···F interactions. Multi-

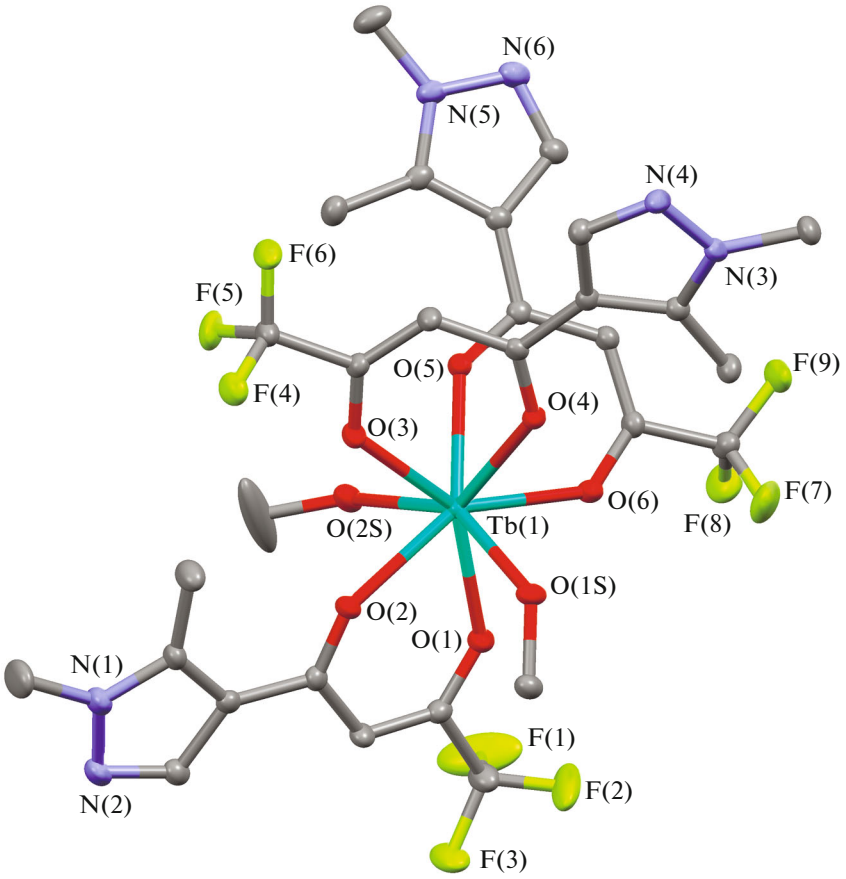


Fig. 1. Molecular structure of $[Tb(L)_3(MeOH)_2]$. The hydrogen atoms are omitted, the thermal ellipsoids are drawn at 50% probability level.

ple Cs···F contacts were observed previously in the crystals of compound **III**.

The crystal structure of compound **I** is shown in Fig. 1. The coordination number (CN) of the Tb^{3+} ion in **I** is 8 and the $\{TbO_8\}$ coordination polyhedron is best described as a triangular dodecahedron (TDD-8), as follows from analysis of the corresponding bond lengths and bond angles. Note that the crystals of **I** do not contain solvent molecules, apart from those incorporated in the local coordination sphere of terbium. The Tb–O bond lengths in the diketonate groups are in the range of 2.334(2)–2.385(2) Å. The Tb–O bonds with the methanol molecules are longer (2.418(3) and 2.420(3) Å). Selected bond lengths and bond angles for compound **I** are presented in Table 2.

In the crystal, single molecules form zigzag chains (Fig. 2) due to the presence of numerous contacts of various types: hydrogen bonds, O(1S)–H(1S)···N(4) (O···N 2.725(3) Å) and O(2S)–H(2S)···N(6) (O···N 2.776(3) Å), and weak interactions, CF···H(Me), F···C, and F···F, with average bond lengths of 3.228(3), 3.374(3), and 2.833(2) Å, respectively. It is noteworthy that no π···π interactions are observed between the pyrazole rings in these structures.

In an acetonitrile solution, complex **I** shows an intense absorption of UV radiation in the 250–370 nm wavelength range, with the maximum being at ~315 nm (Fig. 3). The absorption is due to the $\pi \rightarrow \pi^*$ electronic transitions in the conjugated system of the ligand formed by the pyrazole ring and the enolyzed diketone moiety. The weak lines of the Tb^{3+} intrinsic absorption arising due to the forbidden $4f \rightarrow 4f$ transitions are not observed in the spectrum under these conditions.

In the crystalline state, complex **I** shows a bright green luminescence under the action of UV radiation. The excitation spectrum of solid complex **I** exhibits strong absorption bands corresponding to $\pi \rightarrow \pi^*$ transitions in the ligand; they can also be observed in solution, which indicates efficient electronic excitation energy transfer from the ligands to the central terbium ion, together with weaker bands related to intrinsic $4f \rightarrow 4f$ absorption of the Tb^{3+}. The wavelengths of the absorption maxima and the corresponding transitions are presented in Fig. 4.

The emission spectrum of crystalline complex **I** recorded upon excitation at 365 nm is depicted in Fig. 5. No luminescence of the ligand is observed, and the four major lines can be assigned to transitions from the

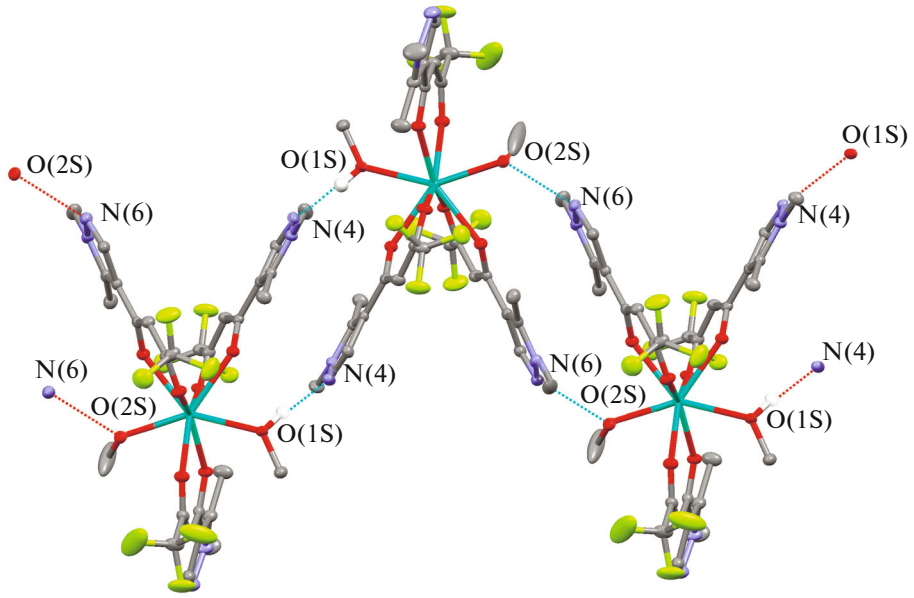


Fig. 2. Fragment of the crystal packing of $[Tb(L)_3(MeOH)_2]$.

$^5D_4$ resonance level of Tb^{3+} to lower $^7F_{6-3}$ levels. The most intense $^5D_4 \rightarrow {}^7F_4$ transition gives rise to a band with a peak at 548 nm (green spectral region). All bands are markedly split, which attests to a low symmetry of the Tb^{3+} ligand environment.

The lifetime of the Tb^{3+} excited state (τ_{obs}) of complex **I** is 305 μs (excitation at 365 nm and recording at 548 nm), and the absolute quantum yield of luminescence is 6.5%. Previously, we determined the triplet energy T_1 of the ligand HL (19800 cm^{-1}) from the phosphorescence spectra of the $[Gd(L)_3(EtOH)_2]$ complex at 77 K and showed that this ligand efficiently sensitizes luminescence of Eu^{3+} ions [14]. The energy of the first singlet excited level S_1 of the ligand (36650 cm^{-1}) was found from analysis of its absorption spectra. Since the energy of the $^5D_4$ resonance level of Tb^{3+} is 20430 cm^{-1}, one cannot expect an efficient energy transfer along the $T_1 \rightarrow {}^5D_4$ pathway in complex **I**. However, the measured quantum yield of luminescence is relatively high, so is the excited state lifetime. This prompts that complex **I** has a more complex energy transfer pathway than a mere transfer from the triplet level of the ligand to the resonance level of the terbium ion, probably involving singlet excited (S_1 or higher) levels of the ligand with sufficient energy. These anomalous energy transfer pathways were con-

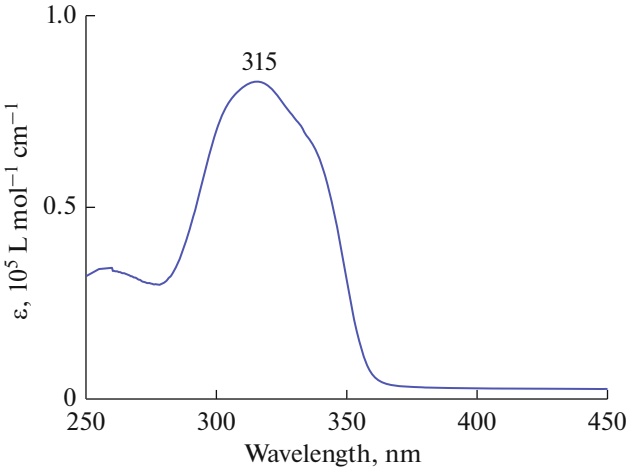


Fig. 3. Absorption spectrum of a 5×10^{-5} M solution of $[Tb(L)_3(MeOH)_2]$ in acetonitrile.

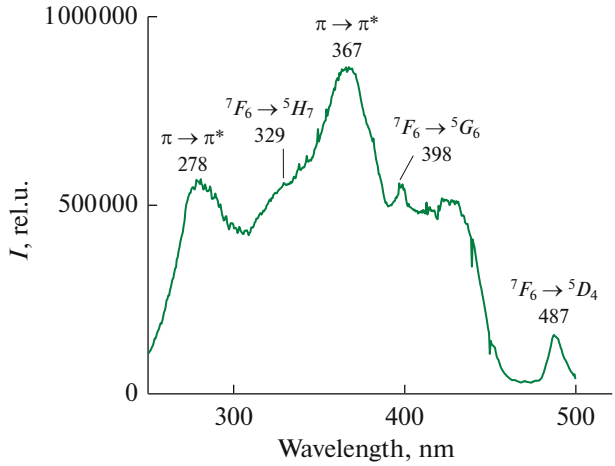


Fig. 4. Excitation spectrum of crystalline complex **I** at 300 K (λ_{em} = 545 nm).

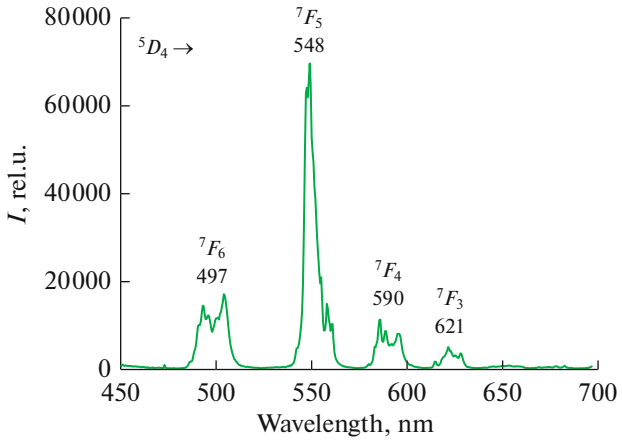


Fig. 5. Emission spectrum of crystalline complex **I** at 300 K (λ_{excit} 365 nm).

sidered back in the classical paper of Sato [15]; however, additional photophysical measurements are required to confirm this assumption.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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