ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 2, pp. 284–288 © Pleiades Publishing, Ltd., 2013.
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Crystal and Molecular Structure and Luminescence Properties of Europium Trifluoroacetate Complex with Triphenylphosphine Oxide

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Received December 12, 2011

Abstract—Using XRD method, we determined the atomic structure of crystals of the compound [Eu(TFA)$_3$·2TPPO (H$_2$O)]$_2$, where TFA is a trifluoroacetate anion, TPPO is a triphenylphosphine oxide. The coordination polyhedra of two independent europium atoms with coordination number *CN* = 8 are isotypic and consist of a antiprism of [EuO$_8$] composition. The geometric and electronic structural features of the compound corresponding to the characteristics of its luminescent properties are discussed.

DOI: 10.1134/S1070363213020096

Coordination compounds of rare-earth elements possess unique optical, magnetic, and photochemical properties and are widely used in the development of multifunctional materials [1]. One promising class of lanthanides are complex compounds with carboxylic acids. A characteristic feature of this class of compounds is a high photo stability. An example of luminescent lanthanide carboxylates are coordination compounds of europium with trifluoroacetic acid.

Compounds of this type exhibit unique magnetic, optical, and photochemical properties and in contrast to respective acetates they have been poorly studied [2, 3]. It was shown in [3, 4] that the lanthanide trifluoroacetate crystallized as trihydrate, and the complex anion had dimeric structure. The XRD and IR data indicate that hydrates of praseodymium, neodymium, and europium compounds have a similar structure [3]. The information on the structure and properties of mixed-ligand trifluoroacetates with nitrogen–phosphorus-containing neutral ligands are very limited. The structure and luminescence properties of europium trifluoroacetate hydrate crystals and europium trifluoroacetate complexes with dipyridyl and hexamethylphodphoric amide were investigated in [5, 6]. Predetermined synthesis of new compounds with carboxylic acids, which are capable of efficient absorbtion of light in a given region of the spectrum and show intense luminescence requires a study of mutual influence of the coordination sphere composition, the nature of metal–ligand chemical bonding, geometric and electronic structure of complex compounds, and fluorescent and photochemical properties of the substances. Analysis of the literature reveals that such studies concerning in particular the relationship between luminescence characteristics of a Ln^{3+} compound and the parameters of its geometric and electronic structure are limited [5].

This paper is a continuation of the research of the relationships between the features of crystal structure and luminescent properties of the europium complex compounds with carboxylic acids and neutral ligands [4–7], and it concerns the determination of atomic structure of the crystals of complex compound [Eu(TFA)$_3$·2TPPO(H$_2$O)]$_2$, where TFA is a trifluoroacetate anion and TPPO is a triphenylphosphine oxide, and the study of dependence of the luminescent properties of the obtained substance on its geometric and electronic structure.

We performed determination of the atomic structure of crystals of europium trifluoroacetate complex with triphenylphosphine oxide at 298 and 243 K. No significant differences in the structure of the compound at these temperatures have been identified. The atomic structure of crystals **I** is composed of the

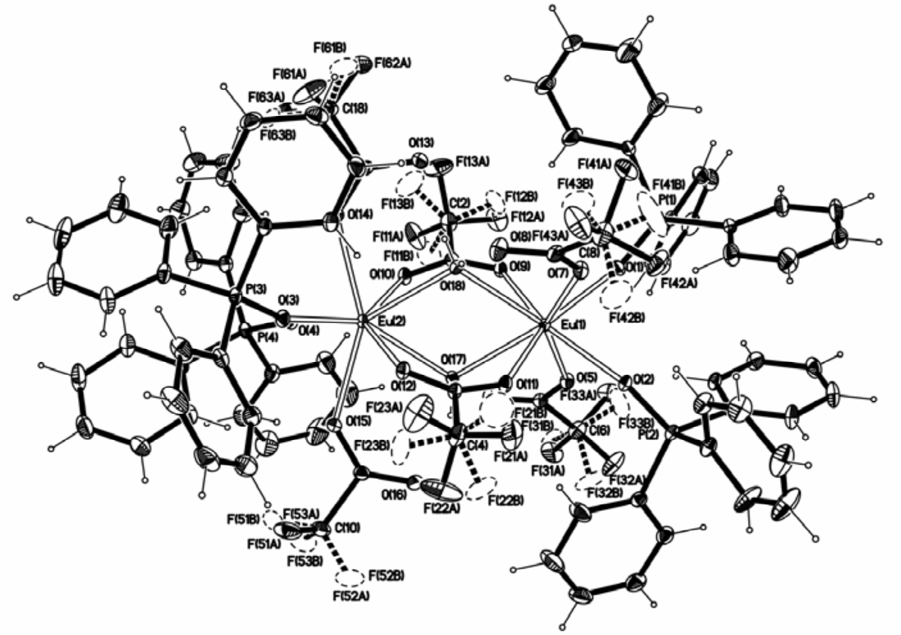

Fig. 1. Elementary cell of crystal structure **I**.

island dual-core complexes of the compound $[Eu(TPA)_3 \cdot 2TPPO(H_2O)]_2$, which, through van der Waals interaction are combined into a three-dimensional framework. In the dual-core complex of compound **I** the four trifluoroacetate ions coordinated by the europium atoms perform different functions: two are monodentate and two other perform a bridging function (Fig. 1). Each of the two crystallographically independent europium ions are coordinated by eight oxygen atoms: two oxygen atoms of the monodentante and two oxygen atoms of two bridging carboxylate ions, two oxygen atoms of two molecules of triphenylphosphine oxide and two oxygen atoms of water molecules. Thus, the oxygen atoms around both Eu build coordination polyhedra of the $[EuO_8]$ composition, which can be represented as a slightly distorted square antiprism, characteristic of many coordination compounds of rare earth elements. Figure 1 shows the general form of the molecule $[Eu(TPA)_3 \cdot 2TPPO(H_2O)]_2$. The hydrogen atoms of water molecules coordinated by europium through the formation of hydrogen bonds of the O–H···O type are connected to the second uncoordinated oxygen atoms of the monodentate trifluoroacetate ions and thus are involved in intramolecular interactions.

In the luminescence spectra of europium complexes with trifluoroacetic acid the most intense bands belong to the electric dipole $^5D_0$–$^7F_2$ transition (612 nm), which is typical of most luminescent europium compounds (Fig. 2). In the series of mixed-ligand europium trifluoroacetates, the compound **I**, unlike the europium trifluoroacetates with nitrogen-containing neutral ligands, at 77 K has the highest intensity of luminescence (Table 1) [8].

The method of X-ray photoelectron spectroscopy revealed that in a series of mixed-ligand europium trifluoroacetate complexes, in compound **I** the lowest charge on the europium atom (E_b = 136.7 eV) is

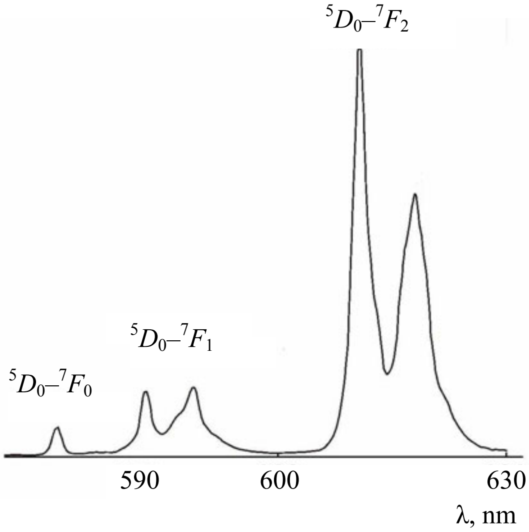

Fig. 2. The luminescence spectrum of $[Eu(TFA)_3 \cdot 2TPPO \cdot (H_2O)]_2$ (77 K).

Table 1. The values of the luminescence intensity (I_{rel}) and the binding energy of inner electrons (eV) at 77 K for the mixed-ligand europium trifluoroacetate complexes

Compound	I (77 K)	Eu $4d_{5/2}$	References
$[Eu(TFA)_3{\cdot}3H_2O]_2$	16.7	137.5	[5]
$Eu(TFA)_3{\cdot}2DMF{\cdot}H_2O$	43.3	137.0	[5]
$[Eu(TFA)_3{\cdot}dipy{\cdot}3H_2O]dipy$	74.1	136.3	[5]
$[Eu(TFA)_3{\cdot}2TPPO{\cdot}H_2O]_2$	100.0	136.7	[5]

observed compared to the europium trifluoroacetate hydrate (E_b = 137.5 eV), which indicates an increase in the strength of europium(III)–neutral ligand (triphenylphosphine oxide) bond.

Thus, high donor properties of triphenylphosphine oxide molecule contribute to the increase in the electron density at the europium(III) and to the luminescence intensity.

EXPERIMENTAL

For the synthesis of compound $[Eu(TFA)_3{\cdot}2TPPO{\cdot}(H_2O)]_2$ (**I**) the following reagents of "pure" grade were used: europium nitrate hexahydrate, trifluoroacetic acid, and triphenylphosphine oxide. Europium trifluoroacetate trihydrate was prepared according to [2]. Complex of europium trifluoroacetate with triphenylphosphine was synthesized by dissolving europium trifluoroacetate in water with adding an ethanol solution of triphenylphosphine oxide. The resulting water–ethanol solution was left standing till the formation of crystals of the required size. Compound **I** is a colorless crystalline substance, stable to moisture and soluble in most polar solvents, mp 270°C.

X-ray diffraction analysis was carried out using a colorless single crystal of natural isometric cut. A set of experimental data was obtained on a Bruker SMART CCD-1000 device with MoK_α radiation. Collection of experimental data was carried out in three groups of 906 frames each at the values of the angle φ 0°, 90°, and 180°, respectively, at ω-scanning with a step 0.2° and exposure 20 s on each frame. Data processing and editing, and refinement of the unit cell parameters were carried out with the software in [9]. The structure was determined by the direct method and refined by root mean squares (RMS) method with accounting for the anisotropy of thermal vibrations of atoms in the harmonic approximation, anomalous scattering, and isotropic extinction using the software of the complex [10]. The positions of hydrogen atoms of the complex (except for the hydrogen of water molecules) "appeared" well in the syntheses of electron density, but the principal novelty was not

Table 2. Crystallographic data, characteristics of X-ray diffraction experiment, and structure refinement details of compound $C_{84}H_{64}Eu_2F_{18}O_{18}P_4$

Parameter	Value
Formula	$C_{84}H_{64}Eu_2F_{18}O_{18}P_4$
Molecular weight	2131.15(2)
Temperature	293(2) K
The wavelength	MoK_α (0.71073 Å)
Space group	$P2(1)$
a, Å	12.516(1)
b, Å	16.725(2)
c, Å	21.193(2)
β	91.945(2)°
Z	2
d_{calc}, g cm^{-3}	1.596
μ, mm^{-1}	1.577
F(000)	2120
Crystal size, mm	0.35×0.28×0.22
Region of the data collection on θ	1.92–30.02°
Intervals of reflection indices	$-17 \le h$ 17, $-23 \le k$ 23, $-29 \le l \le 29$
Measured reflections	64849
Independent reflections	25794 (R_{int} 0.0383)
Completeness on 29.02°	99.9%
Reflections with $I > 2\sigma(I)$	22858
Extinction	According to cutting
Refinement method	Full-matrix on RMS on F^2
Number of variables to refine	1314
S	1.020
R-Factors for $I > 2\sigma(I)$	R_1 0.0318, wR_2 0.0645
R-Factors for all reflections	R_1 0.0404, wR_2 0.0683
Extinction coefficient	0.00001(2)
Residual electron density, (min/max), e Å^{-3}	–0.380/0.942

Table 3. The main bond lengths and angles in the structure of $C_{84}H_{64}Eu_2F_{18}O_{18}P_4$

Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Eu^1–O^1	2.287(2)	O^{1}Eu^{1}O^2	81.99(5)	O^{4}Eu^{2}O^3	83.11(6)
Eu^1–O^2	2.304(1)	O^{1}Eu^{1}O^5	81.69(6)	O^{4}Eu^{2}O^{10}	76.00(6)
Eu^1–O^5	2.401(1)	O^{2}Eu^{1}O^5	76.79(5)	O^{4}Eu^{2}O^{15}	76.74(6)
Eu^1–O^{11}	2.408(2)	O^{2}Eu^{1}O^{11}	75.44(5)	O^{3}Eu^{2}O^{15}	81.72(6)
Eu^1–O^7	2.438(2)	O^{1}Eu^{1}O^7	77.62(6)	O^{3}Eu^{2}O^{12}	75.42(6)
Eu^1–O^9	2.445(1)	O^{2}Eu^{1}O^7	77.34(6)	O^{15}Eu^{2}O^{12}	73.67(5)
Eu^1–O^{18}	2.508(2)	O^{11}Eu^{1}O^7	75.32(6)	O^{4}Eu^{2}O^{14}	83.01(6)
Eu^1–O^{17}	2.525(1)	O^{1}Eu^{1}O^9	74.86(5)	O^{3}Eu^{2}O^{14}	75.11(6)
Eu^2–O^4	2.274(2)	O^{5}Eu^{1}O^9	77.65(6)	O^{10}Eu^{2}O^{14}	74.70(6)
Eu^2–O^3	2.287(2)	O^{11}Eu^{1}O^{18}	73.50(5)	O^{10}Eu^{2}O^{17}	69.79(5)
Eu^2–O^{10}	2.409(2)	O^{7}Eu^{1}O^{18}	72.91(5)	O^{15}Eu^{2}O^{17}	72.93(5)
Eu^2–O^{15}	2.421(2)	O^{9}Eu^{1}O^{18}	70.34(5)	O^{12}Eu^{2}O^{17}	74.73(5)
Eu^2–O^{12}	2.436(2)	O^{5}Eu^{1}O^{17}	72.81(5)	O^{10}Eu^{2}O^{18}	73.67(5)
Eu^2–O^{14}	2.447(2)	O^{11}Eu^{1}O^{17}	69.73(5)	O^{12}Eu^{2}O^{18}	69.03(5)
Eu^2–O^{17}	2.534(1)	O^{9}Eu^{1}O^{17}	72.74(5)	O^{14}Eu^{2}O^{18}	73.31(5)
Eu^2–O^{18}	2.537(2)	O^{18}Eu^{1}O^{17}	71.84(5)	O^{17}Eu^{2}O^{18}	71.22(5)

revealed, and therefore for the further work were used the values calculated geometrically and refined within the "rider" model. The positions of the hydrogen atoms of water molecules were found in the electron density syntheses and refined by RMS in the usual way.

Final constructions of the syntheses of electron density and subsequent RMS refinement showed that in the vicinity of all CF_3 groups the fluorine atoms occupy the A and B positions with the population factor equal to 0.5. An attempt to refine the population factor of fluorine atoms at a temperature of 243 K revealed no tendency to redistribution of the population of the positions of the fluorine atoms of CF_3 groups between the A and B positions. Thus, taking into account the above stated it can be assumed that the observed statistical distribution of CF_3 groups between the A and B positions, apparently, should not be considered a consequence of their rotation, but only the influence of the packing factor for translations along the main crystallographic directions of the cell. The main crystallographic parameters of compound **I**, characteristics of the X-ray diffraction experiment, and refinement details of the model of atomic structure by the least squares method are given in Table 2. Coordinates of basis atoms of the complex and their thermal parameters can be found in the CIF file, and the main bond lengths and angles, in Table 3 of this paper. The structure of molecule **I** is shown in Fig. 1.

The CIF file containing full information on the investigated structure is deposited in CCDC under the number 853541 and can be obtained on request at the following website: www.ccdc.cam.ac.uk/data_request/cif.

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