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SYNTHESIS AND STUDY OF THE PROPERTIES OF SUPRAMOLECULAR COMPOUNDS OF Eu AND Tb (III) WITH TEREPHTHALIC ACID

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The article presents the results of studying newly synthesized europium and terbium (III) complexes with terephthalic acid using X-ray, elemental, IR spectroscopic and derivatographic analysis. The chemical formulas of the complexes, the coordination form of terephthalic acid, as well as the processes of thermal decomposition and formation of isostructural supramolecular coordination compounds are established. It is also established that, despite the same compositions and structures, the thermal decomposition of these compounds occurs differently, which is explained by the nature of the metals and the stereochemistry of the ligands.

Keywords: complexes, lanthanides, rare earth elements, terephthalic acid, isostructure, molecular compounds, polymeric porous structure

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INTRODUCTION

Rare earth element (REE) compounds are intensively studied due to their high practical significance – the possibility of creating promising materials on their basis that exhibit optical, magnetic, catalytic, and biologically active properties [1,9]. In recent years, particular attention has been attracted by metal-organic framework compounds containing REE ions – the basis of polyfunctional materials, sensors, white light sources, polymodal bioimaging compounds, drug delivery systems, etc. [7]. The development of methods for the targeted design of such compounds requires a comprehensive understanding of the influence of synthesis conditions on the mechanism of formation of metal-organic framework compound nuclei and the subsequent nucleation and crystallization processes of target compounds [2-4,6,8].

Systematic study of REE complexes with monocarboxylic acids, in particular with benzoic acid and its derivatives, with nitrogen-containing heterocyclic compounds, namely with 1,10-phenanthroline and $2,2^1$ -dipyridine, with a Schiff base began quite a long time ago [5,10]. However, there are few data on the structure of these compounds in the literature, which, in our opinion, is due to the difficulties of obtaining single crystals. There are data only for a few REE compounds with benzoic acid and its derivatives: neodymium and gadolinium with $2,2^1$ -dipyridine, neodymium and europium with 1,10-phenanthroline and $2,2^1$ -dipyridine [2,3, 6-8]. Based on these studies, it was concluded that the Nd and Eu complexes with 1,10-phenathroline and $2,2^1$ -dipyridine are isostructural.

Heterogeneous coordination compounds of lanthanides with 1,10-phenanthroline, $2,2^1$ -dipyridine and salicylic acid have also been studied; the structure shown in [10] has been proposed.

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To confirm the proposed structure of mixed-ligand complexes, a quantum-chemical calculation was performed for hypothetical complexes that were selected as model compounds:

$La(L^1)_2(NO_3)_3$ and $LaL^1HL^4(NO_3)_2$, where L^1 is 1,10 - phenanthroline; HL^4 is salicylic acid.

Based on quantum-chemical calculations, we obtained calculated data on interatomic distances and atomic charges for model compounds and the mixed-ligand complex $LaL^1HL^4(NO_3)_2$. We also previously synthesized complex compounds of samarium, neodymium, and gadolinium with o -phthalic acid with the chemical formula:

$Sm_2(C_6H_4(COO)_2)_3(H_2O)$, $Nd_2(C_6H_4(COO)_2)_3(H_2O)$, Gd_2 $C_6H_4(COO)_2)_3(H_2O)$ and clathrate compounds:

$[Sm_2(C_6H_4(COO)_2)_3(H_2O)_2(HCOOH)_3$, $[Gd_2$ $(C_6H_4(COO)_2)_3(H_2O)_5(CH_3COOH)_2$ [8,10].

Analysis of literary material shows that complexes of rare earth elements (III) with aromatic dibasic acids, in particular with o- and p - phthalic acids, are of particular interest.

The aim of this work is the synthesis and physicochemical study of new representatives of REE with organic ligands, in particular with terephthalic acid.

The following research methods were used in the work: elemental and X-ray phase analysis, IR spectroscopy and thermogravimetry methods.

EXPERIMENTAL

X-ray phase analysis was performed on a Commander device. Sample ID (CoupledTwoTheta) with copper cathode. IR absorption spectra were recorded on a Nicole 1810 spectrometer from Thermo Scientific, in the region of 400–4000 cm^{-1}. Samples were prepared as suspensions in vaseline oil at room temperature. Derivatograms were recorded on a derivatograph STA-449, F-3 (FRG). Elemental analysis for C, H was performed on a CHNSO «E» analyzer from CarloERBA. The metal content was calculated from the mass loss curve by the amount of oxides obtained after heating on a derivatograph to 900^0C.

Synthesis of complex compounds:

To synthesize the complex compounds, $EuCl_3{\cdot}6H_2O$, $TbCl_3{\cdot}6H_2O$, $NaHCO_3$ "chemically pure" and terephthalic acid "chemically pure" were used. Two portions of terephthalic acid, 0.498 g (0.003 mol), were weighed and each was dissolved in 50 ml of distilled water with the addition of 0.504 g (0.006 mol) of $NaHCO_3$ to each. 0.732 g (0.002 mol) and 0.746 g (0.002 mol) of water-soluble salts $EuCl_3{\cdot}6H_2O$ and $TbCl_3{\cdot}6H_2O$, respectively, were gradually added to the resulting hot solutions.

The filtered precipitates were first washed several times with distilled warm water, then with benzene, and dried first in air and then in a drying cabinet at 50^0C. Polycrystalline powders have a yellowish color.

RESULTS AND DISCUSSION

Comparison of X-ray diffraction patterns of the synthesized compounds is shown in Fig. 1 a, b. Analysis of the X-ray diffraction patterns showed that the obtained compounds consist of one phase and are highly crystalline. The spread of peaks throughout the diffraction pattern means that the compounds have high symmetry and unit cell parameters of approximately 10.03; 9.70; 6.06Å and 10.11; 9.63; 6.03Å and are well identified under the indicated maxima. As can be seen from the indicated diffraction patterns and unit cell parameters, they are identical and, apparently, isostructural.

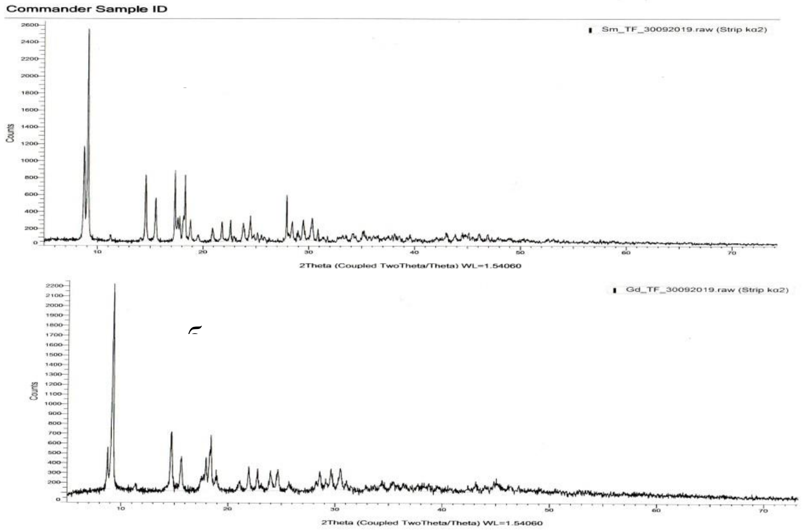

Fig.1. Diffraction pattern of a complex compound of europium (a) and terbium (b) with terephthalic acid

The elemental compositions of the synthesized samples of complex compounds are presented in the table. Based on the results of chemical elemental analysis, it was concluded that the compositions of the obtained compounds correspond to hexaaqua-triterephthalate-dieuropium and hexaaqua-triterephthalate-diterbium (III) and are in good agreement with the results of X-ray analyses.

The results of elemental analyses of samples of synthesized products are presented in the table 1

Table1. The results of elemental analyses of samples of synthesized products

$Eu_2(n\text{-}C_6H_4(COO)_2)_3(H_2O)_6$	$Eu_2C_{24}H_{24}O_{18}$	32.95/33.37	31.68/31.99	2.49/2.68
$Tb_2(n\text{-}C_6H_4(COO)_2)_3(H_2O)_6$	$Tb_2C_{24}H_{24}O_{18}$	33.96/34.37	31.22/31.51	2.39/2.64

IR spectroscopic studies of complex compounds show that in the IR spectra, respectively in the regions of 1585-1463, 1532-1377 and 1505-1308 cm^{-1} and 1586-1424, 1540-1311 and 1505-1311 cm^{-1}, clear bands appear that relate to asymmetric (δ_{as}) and symmetric (δ_s) absorption bands of the carboxyl groups of terephthalate dianions [7]. The differences between V_{as} and V_s, which are 122, 155 and 197 cm^{-1} and 162, 229 and 194 cm^{-1}, respectively, show that the carboxylate anions of terephthalate acids have a chelating function [6]. As can be seen from Fig. 2, a, b, the IR spectra contain broad bands in the regions of 3200-3600 cm^{-1} (max 3451 cm^{-1}) and 3200-3600 cm^{-1} (max 3461 cm^{-1}), respectively, related to water molecules.

The IR spectra also revealed bands at 1608.23 and 1608.57 cm^{-1}, respectively, corresponding to deformation vibrations of water molecules (HOH), which confirms the presence of crystallization water.

To determine the amount of water, temperature and nature of dehydration, thermal destruction, a thermographic analysis of complex compounds was carried out in the temperature range of 20-100^{0}0 C (heating rate 10^0/min, standard Al_2O_3).

From those presented in figure 3 a and b the derivatogram of the complex compounds shows that, despite the isostructurality and identical chemical composition, the thermal destruction of the complexes occurs differently. Thus, on the DTA curve of the europium complex compound, two endothermic effects are observed with maxima at 108.2^0 C and 248.1^{0}C, at which 4.9% and 7.9% of the mass are removed, respectively. These masses correspond to 2 and 4 H_2O molecules. This means that water molecules are removed from the crystal lattice in two stages.

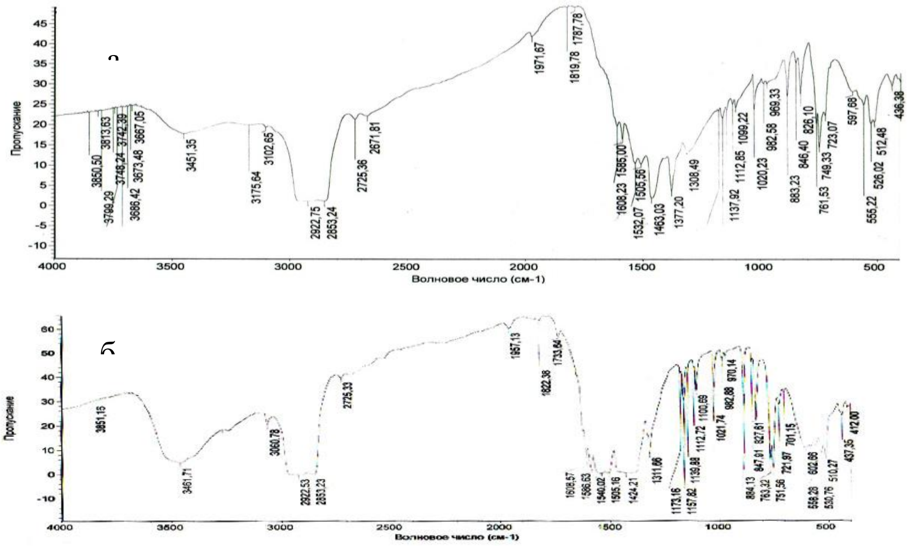

Fig. 2. IR spectra of the complex compound europium (a) and terbium (b) with terephthalic acid

In the case of the terbium complex, the same amount of water from the crystal lattice is removed in one step with a maximum of a clear endothermic effect at 181^{0}C. This is apparently due to the nature of the metal and their crystallographic position in the structure. Anhydrous products of complex compounds are stable up to temperatures of 280 and 50^0 0 C, after which the decomposition of anhydrous products of complex compounds begins temperature ranges of 280–776^{0}C and 500–898^{0}C, respectively.

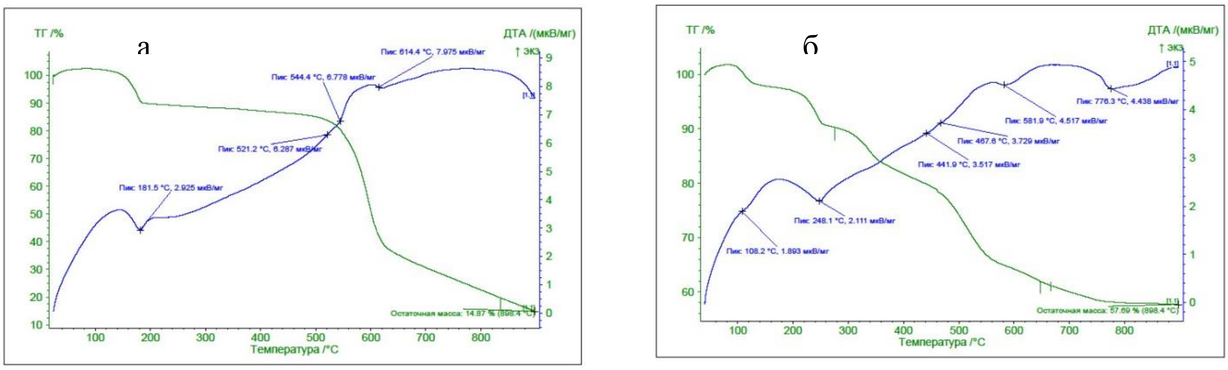

Fig. 3. Derivatogram of the complex compound of europium (a) and terbium (b with terephthalic acid

As can be seen from the DTA curve, the decomposition of anhydrous products and the burning of organic residues also occurs in a peculiar way. The decomposition of the anhydrous product of the samarium complex occurs without any endothermic effect - the burning of the organic part of the complex begins immediately, and this process is accompanied by a wide exothermic effect in the temperature range of 280–898 0 C, and the decomposition of the anhydrous product of the complex compound Europium I is accompanied by a vague endothermic effect with a maximum of 540^0 C. Too high a temperature does not allow it to form completely and is overlapped by an exothermic effect, which appears due to the combustion of the organic residue. In this case, the combustion of the organic residue is much faster compared to the complex compound of terbium. In this case, the mass loss is 49.16% (calc. 49.27%) and 48.77% (48.55%), respectively. The final products of thermolysis are Eu_2O_3 and Tb_2O_3, respectively.

Thus, complex physical and chemical studies have revealed that the coordination number of each central atom is 9, and this is explained by the participation of f- orbitals in the formation of bonds. And the coordination polyhedron is a nine-vertex polyhedron. It has also been established that the obtained complex compounds have, respectively, the chemical formulas: $Eu_2(n\text{-}C_6H_4(COO)_2)_3(H_2O)_6$and $Tb_2(n\text{-}C_6H_4(COO)_2)_3(H_2O)_6$and are isostructural.

The coordination environment of metals includes six oxygen atoms of three carboxylate groups of the dianion, three oxygen atoms and three water molecules.

Based on the obtained results, a hypothetical schematic structure of the complex compounds is given (Fig. 4), it is polymer-layered. The structure forms columns that have the shape of a regular hexagon with a diameter of approximately 20 Å. We assume that the coordinately bound water molecules participate in the formation of an intra- and interlayer network of hydrogen bonds and thus the 2D structure is transformed into a 3D structure and a supramolecule.

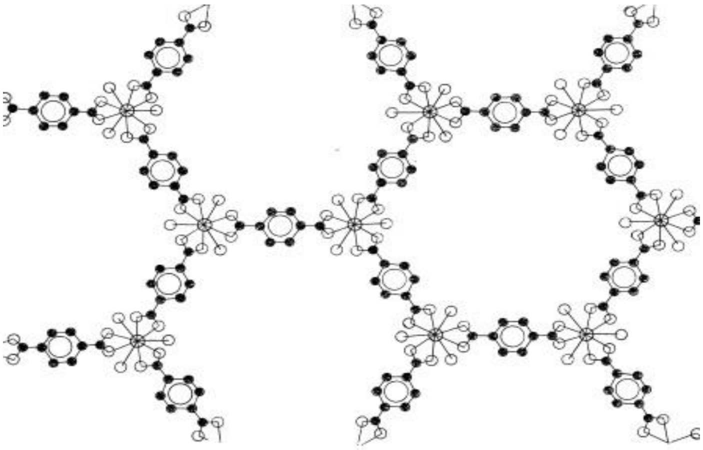

Fig. 4. Supposed schematic structure of the complex compound of europium and terbium with terephthalic acid

CONCLUSION

Europium and terbium complexes with terephthalic acid were synthesized for the first time and it was established that, unlike phthalic acid, they form isostructural complexes. A series of physicochemical studies established their composition and chemical formula. A hypothetical schematic structure of the synthesized complex compounds was proposed.

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