



Luminescent properties and structure of new CAPH-based lanthanide complexes [LnL₃Q], containing additional bis-heterocyclic aromatic ligand-antenna 2-(1,3,4-oxadiazole-2-yl) pyridine



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ABSTRACT

The new lanthanide coordination compounds of general formula [LnL₃Q], where Ln = Eu, Gd, Tb; L = dimethyl-N-trichloroacetylamidophosphate and Q = 2-(1,3,4-oxadiazole-2-yl)pyridine, have been synthesized and isolated in crystalline state with the purpose of finding new interesting optical materials. X-ray data reveal that complexes have molecular structure with numerous Van-der-Vaals contacts between molecules. All the ligands are coordinated in bidentate chelate manner, coordination polyhedron was interpreted as distorted square antiprism (CN 8). The obtained complexes were investigated by means of IR, absorption and luminescence spectroscopy as well and thermal gravimetric analysis. It was found that complex [TbL₃Q] is resistant to temperature of 200 °C. The Eu³⁺ and Tb³⁺ complexes exhibit bright metal-centered emission with decay time 1.65 and 1.74 ms respectively. Intrinsic quantum yield for [EuL₃Q] equals 85% that is one of the highest values, known to date for CAPH based europium complexes.

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1. Introduction

Lanthanides coordination compounds with powerful chelating ligands – “antennas” attract attention of many scientific groups, because of possessing a number of useful properties: from the creation of up-lighting to usage as biomedical sensors for biological objects imaging [1]. Despite the extremely interesting features of 4f-luminescence (large Stokes displacement, narrow emission bands, long luminescence decay time) a significant drawback is the inability of Ln³⁺ optical centers to absorb light efficiently (extinction coefficient of three-charged lanthanide cations is within $\epsilon \approx 1\text{--}10\text{ M}^{-1}\text{ cm}^{-1}$) [2]. Usage of organic chromophores as sensitizers of 4f-luminescence allows solving this problem. Therefore searching for good lanthanide luminescence sensitizers and design of efficiently luminescent complexes are still very relevant.

Among the most widely investigated groups of lanthanide complexes there are β -diketonates due to easy synthesis of these

ligands and unique luminescence properties of their complexes [3]. In particular, mixed ligand lanthanide complexes with general formula [LnL₃q], where L¹ is a β -diketonate anion and q is the Lewis base such as 2,2-bipyridine or 1,10-phenanthroline, are known to be studied as emitting layers in technology of light conversion molecular devices [4]. Recently, several similar mixed ligand lanthanide complexes with carbacylamidophosphates (CAPHs) and additional symmetric N-containing aromatic heterocycles have been reported [5]. Compared to β -diketonates the structure of CAPHs is organized to decrease the multiphonon quenching of lanthanide emission and to increase the ligand affinity to Ln³⁺ ion allowing to obtain thermo- and photostable Ln³⁺ coordination compounds with effective luminescence [6].

On the other hand, highly attractive compounds for the development of materials for organic electroluminescent (EL) devices are 1,3,4-oxadiazole derivatives since they possess high electron-accepting properties and display strong fluorescence with high quantum yield [7]. Compounds involving 1,3,4-oxadiazole rings have been used as electron transporting materials and emitters in organic EL devices [8] and for obtaining multifunctional (emitting

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and charge transporting) coordination compounds [9]. In this research we report synthesis, structure, thermal and the spectral properties of new CAPH-based lanthanide coordination compounds [LnL₃Q] containing the one of the simplest CAPH type ligand – dimethyl-N-trichloroacetylamidophosphate (HL) – and asymmetric bis-heterocyclic aromatic compound 2-(1,3,4-oxadiazole-2-yl)pyridine (Q) as an additional neutral ligand - antenna.

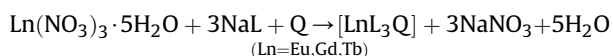
2. Experimental

2.1. Methods

IR measurements were performed on a Perkin–Elmer Spectrum BX spectrometer on samples in form of KBr pellets. The thermal properties of [TbL₃Q] complex were investigated by means of synchronous TG/DTA analyzer Shimadzu DTG-60H. The samples were heated in air to 800 °C in alundum crucibles with a rate of heating equal 10 °C/min. The crystalline powder of Al₂O₃ (alpha modification) was used as a standard material for comparison. Absorption spectra of NaL, Q and [GdL₃Q] complex were recorded in UV region at room temperature in methanol solution on a KSVU-23 “LOMO” spectrometer using a 3 cm³ stoppered quartz cell of 1 cm path length. Emission and excitation spectra of the Eu³⁺ and Tb³⁺ complexes were measured on a «Fluorolog FL 3-22» spectrofluorimeter at 298 K. The energy of the lowest ligands triplet state in complexes was determined from phosphorescence spectrum of [GdL₃Q] complex acetonitrile solution at 77 K.

2.2. Synthesis

Dimethyl-N-trichloroacetylamidophosphate (HL) and its sodium salt NaL were synthesized and identified according to reported earlier methods [6,10]. The synthesis of 2-(1,3,4-oxadiazole-2-yl)pyridine was carried out by the analogy of synthesis, described in Ref. [11]. The synthesis of complexes [LnL₃Q] was conducted in 2-propanol according to the scheme:



Ln(NO₃)₃·5H₂O (1 mmol) was dissolved with heating in 20 ml of 2-propanol in the presence of HC(OEt)₃ as a dehydrating agent. The obtained solution was added to the solution of NaL (3 mmol) in 30 ml of 2-propanol and heated until precipitation of sodium nitrate was observed. Then, solid Q (1.25 mmol) was added and mixture was heated again to the boiling point and then cooled down to room temperature. Precipitated NaNO₃ was filtered off and the filtrate was allowed to stand in a desiccator for crystallization. After 5–7 days, well-faced crystals of the complexes were filtered off, washed with isopropanol and dried in air. The average yield: ~70%. The obtained complexes are stable on air, soluble in acetone, methanol, less soluble in 2-propanol and insoluble in nonpolar solvents, diethyl ether and water.

[EuL₃Q] IR: ν_{max} = 3006w, 2953w, 2851w, 1605vs ($\nu(\text{C}=\text{O})$), 1511 m, 1373s ($\nu(\text{C}-\text{N})_{(\text{amide}-2)}$), 1236w, 1192 m, 1153s ($\nu(\text{P}=\text{O})$), 1042vs ($\delta(\text{POC})$), 887s, 850 m, 819s, 794 m, 725 m, 677 m ($\nu(\text{C}-\text{Cl})$), 649w, 549 m cm⁻¹. Anal. Calc. (Found): Eu, 13.7 (13.6). [GdL₃Q] IR: ν_{max} = 3009w, 2953w, 2852w, 1608vs ($\nu(\text{C}=\text{O})$), 1512 m, 1372s ($\nu(\text{C}-\text{N})_{(\text{amide}-2)}$), 1236w, 1192 m, 1152s ($\nu(\text{P}=\text{O})$), 1044vs ($\delta(\text{POC})$), 886s, 849 m, 821s, 794 m, 725 m, 680 m ($\nu(\text{C}-\text{Cl})$), 645w, 548 m cm⁻¹. Anal. Calc. (Found): Gd, 14.2 (14.0). [TbL₃Q] IR: ν_{max} = 3008w, 2954w, 2852w, 1607vs ($\nu(\text{C}=\text{O})$), 1510w, 1376vs ($\nu(\text{C}-\text{N})_{(\text{amide}-2)}$), 1262w, 1190 m, 1151 ($\nu(\text{P}=\text{O})$), 1043vs ($\delta(\text{POC})$), 887s, 850 m ($\nu(\text{P}-\text{N})$), 822 m, 794w, 727w,

681 m ($\nu(\text{C}-\text{Cl})$), 647w, 552w cm⁻¹. Anal. Calc. (Found): Tb, 14.3 (14.4).

2.3. X-ray structure determination and refinement

Crystal Structure Analysis. Preliminary examination and intensity data collections were carried out on a KM4 diffractometer with CCD Sapphire and MoK α . All data were corrected for Lorentz, polarization and absorption effects [12]. The structures were solved by direct methods and refined by the full-matrix least-squares method on all F² data using the SHELX program [13]. The crystal data and structure refinement are given in Table 1.

3. Results and discussion

3.1. Description of the structure

The molecular structure of the complex [TbL₃Q] and Tb³⁺ coordination polyhedron are shown on Figs. 1 and 2, respectively. Some geometrical characteristics are given in Table 2. In the crystal there are numerous Van-der-Vaals interactions between molecules with participation of both CAPH and Q ligands. The three deprotonated CAPH ligands are coordinated to lanthanide ion in bidentate manner via oxygen atoms of P=O and C=O groups with formation of six-membered chelate cycles. The Tb–O bond lengths lay in range 2.324(5) – 2.361(5) Å that is typical for CAPH based terbium complexes [5g]. It is known that for lanthanide complexes with carbacylamidophosphates the Ln–O(P) bond lengths are usually shorter compared to Ln–O(C) bonds because of greater affinity of phosphoryl group oxygen to lanthanide ions [5]. In our case such ratio was also observed for two CAPH ligands (Table 2), however for the third one the mentioned ratio was reverse, that can be explained by presence of short contact between O(9) phosphoryl oxygen and H(13) hydrogen of Q ligand oxadiazole fragment. The O(9) ... H(13) contact length is equal 2.492 Å and is significantly shorter than O(5) ... H(13) contact (2.685 Å). The average values of C–O and P–O bond lengths in the [TbL₃Q] complex increased as compared with the free ligand ($d(\text{C}-\text{O})_{\text{ligand}} = 1.202(2)$ Å, $d(\text{P}-\text{O})_{\text{ligand}} = 1.466(2)$ Å [10,14]) and respectively equal 1.235(9) –

Table 1
Crystal data and structure refinement for [TbL₃Q].

Empirical formula	C ₁₉ H ₂₃ Cl ₉ N ₆ O ₁₃ P ₃ Tb
Formula weight	1114.31
Crystal system	Monoclinic
Space group	P21/n
Temperature (K)	293(2)
a, (Å)	9.1001(6)
b, (Å)	34.265(2)
c, (Å)	12.7118(9)
α , (°)	90.00
β , (°)	97.842(7)
γ , (°)	90.00
V, (Å ³)	3926.7(4)
Z	4
D, (g cm ⁻³)	1.885
μ , (mm ⁻¹)	2.598
F(0 0 0)	2184
2 θ range for data collection, (°)	4.9–50
Reflections collected	6872
Independent reflections	5669
Data/restraints/parameters	6872/0/466
Goodness of fit on F ²	1.055
Final R indices [I > 2 σ (I)]	R ₁ = 0.0598, wR ₁ = 0.1610 R ₂ = 0.0719, wR ₂ = 0.1701
CCDC reference number	1565707

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