



Electronic structure and spectral properties of terbium(III) nitrate complex with hexamethylphosphoramide



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ABSTRACT

Spectral properties of terbium(III) nitrate complex with hexamethylphosphoramide have been studied by quantum-chemical methods within the density functional theory and methods of luminescent and X-ray photoelectron spectroscopy. Analysis of the luminescence excitation spectrum of the complex has indicated the absence of intramolecular transfer of electronic excitation energy from the ligand levels to the resonance levels of the rare earth central ion, so luminescence of the complex is associated with the electronic f-f-transitions of Tb³⁺ ion (transitions $^5D_4 \rightarrow ^7F_J$, $J = 3-6$). According to quantum-chemical modeling of the excited singlet and triplet levels of the complex, the excitation energy transfer from the ligands onto the central ion does not occur because of the significant difference of energies of their excited states.

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1. Introduction

Unique optical properties of lanthanide complexes make them promising for development of new functional materials for modern devices in fields of optoelectronics and biomedicine [1–7]. Research of excitation processes of electronic f-f-transitions in lanthanide complexes is of considerable interest in fundamental and applied aspects [8–10]. Luminescence intensity of rare earth complex compounds is determined by the efficiency of electronic excitation energy transfer from the levels of ligands onto the metal ion resonance levels, so a search for new ligands promoting the luminescence sensitization is an urgent task of photonics [11–14].

In chemistry and spectroscopy of coordination compounds, phosphorus compounds are especially attractive as ligands [15–20], which are also significant at development of promising optical materials based on phosphorus-containing glasses and ceramics [21,22]. In this regard, theoretical research on possible ways of electronic excitation energy dissipation in the complex compounds seems actual in order to control the optical properties of materials [23,24].

In this work, the electronic structure, spectral properties, and channels of electronic excitation energy relaxation of the phosphor

terbium(III) nitrate complex with hexamethylphosphoramide (HMPA) Tb(NO₃)₃HMPA₃ were studied by methods of the density functional theory (DFT) and by luminescent and X-ray photoelectron (XPS) spectroscopy (Fig. 1).

2. Computational and Experimental Details

Quantum-chemical calculations were carried out in a vacuum approximation by DFT methods with the functional PBE0 [25] using the program packages GAMESS-US (version 05.12.2014) [26] and FireFly v8.1.1 (b9295) [27]. For terbium atom it was used the 4f-in-core pseudopotential Stuttgart ECP54MWB and the corresponding basis set [28], for other atoms – the basis set 6-31G (d,p). The PBE0/6-31G(d,p)/ECP54MWB(Tb) level of calculations is rather adequate and validated for the description of the molecular geometry, electronic structure, thermodynamics characteristics, excitation processes, as well as optical properties of lanthanide complexes [29–35]. Dispersion corrections were calculated using the Grimme method DFT-D3 [36]. UV–visible absorption spectra were obtained using the time-dependent density functional theory (TDDFT) including 20 excited states. Since experimental structural data for the complex Tb(NO₃)₃HMPA₃ has not been published yet, so the experimental geometrical parameters of the europium complex of the similar composition [37] was used as an initial approximation at geometry optimization. The energy minimum

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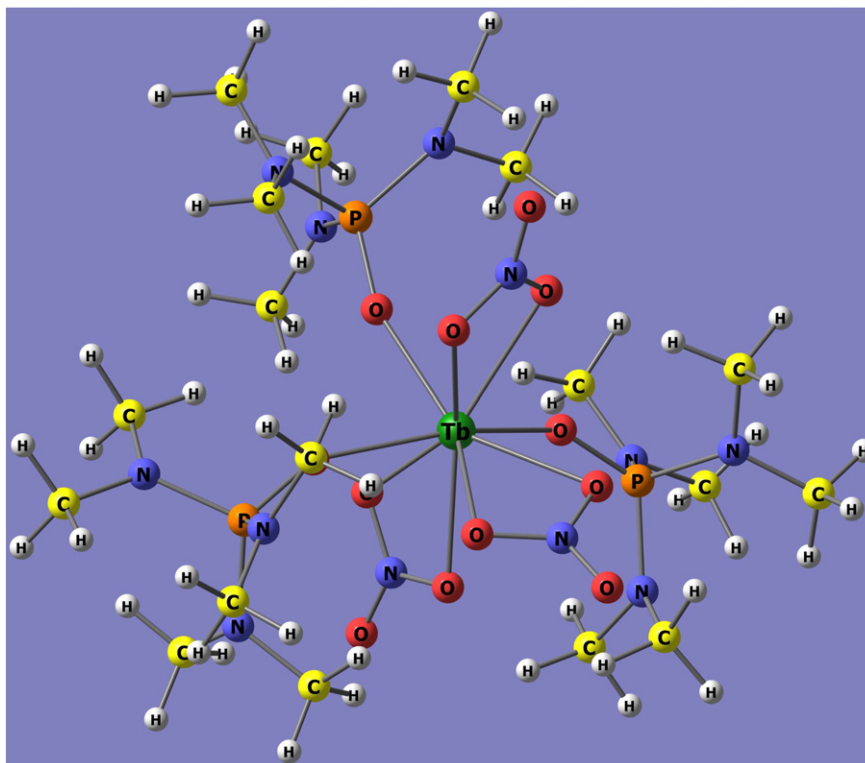


Fig. 1. Optimized molecular structure of the complex $\text{Tb}(\text{NO}_3)_3\text{HMPA}_3$.

was confirmed by Hessian. The calculated data were processed using the program Chemcraft 1.8 (b486) [38].

Luminescence spectra were recorded using a spectrofluorometer Shimadzu RF-5301. XPS spectra were obtained on an ultra-high-vacuum spectrometer SPECS with a hemispherical electrostatic energy analyzer PHOIBOS-150 and an X-ray source with the line Al K_{α} (1486.6 eV). An error in the binding energy did not exceed 0.1 eV, an error in the relative intensity was not more than 5%. The spectra were obtained at 300 K.

3. Results and Discussion

Analysis of the luminescence spectra has showed that the studied complex $\text{Tb}(\text{NO}_3)_3\text{HMPA}_3$ possesses an intense luminescence (the

bands at wavelengths of 489, 544, 586, and 620 nm, Fig. 2) which corresponds to the electronic transitions of Tb^{3+} ion $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4,$ and $3,$ respectively) [39].

According to analysis of the luminescence excitation spectrum of the complex, the luminescence excitation is caused by the f-f-transitions of Tb^{3+} ion and it is associated with an energy absorption by the ion (the transitions $^5\text{D}_J \leftarrow ^7\text{F}_6$ ($J = 2-4$) and $^5\text{G}_J \leftarrow ^7\text{F}_6$ ($J = 3, 5, 6$)).

Thus, the feature of the studied complex is the absence of an intramolecular transfer of the electronic excitation energy from levels of the ligands (NO_3 , HMPA) to resonance levels of the luminescent center that is due to a localization of the ligand absorption in the shortwave UV region.

At that, a reasonable question arises: what are ways for dissipation of the electronic excitation energy in this complex? In order to study in

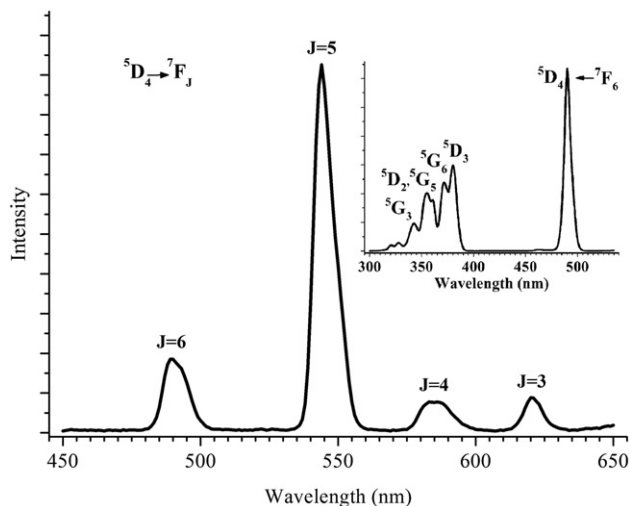


Fig. 2. Luminescence spectrum of the complex $\text{Tb}(\text{NO}_3)_3\text{HMPA}_3$ ($\lambda_{\text{ex.}} = 490$ nm). Inset: Luminescence excitation spectrum of $\text{Tb}(\text{NO}_3)_3\text{HMPA}_3$ ($\lambda_{\text{lum}} = 545$ nm).

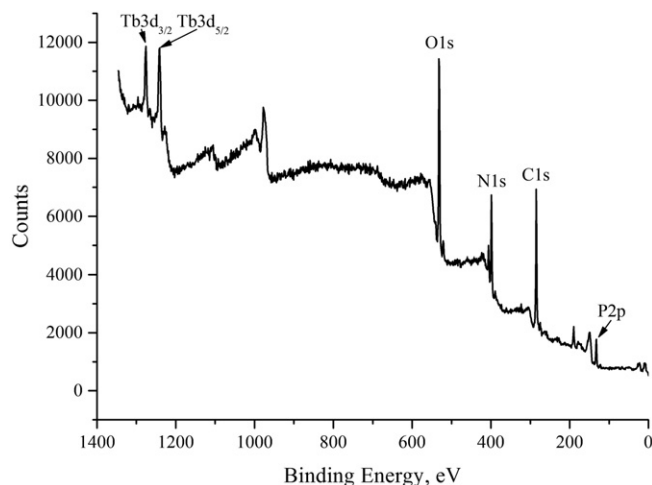


Fig. 3. XPS spectrum of $\text{Tb}(\text{NO}_3)_3\text{HMPA}_3$.

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