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Electronic structure and optical properties of Eu(III) tris-β-diketonate adducts with 1,10-phenanthroline

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ABSTRACT

Adducts of tris-β-diketonates of the rare earth metal Eu(III) with 1,10-phenanthroline are studied by photoelectron spectroscopy and quantum chemistry methods. The electronic structure, peculiarities of the nature of chemical bonds, and the geometric structure of the adducts are determined. The interpretation of UV photoelectron spectra of vapors and X-ray photoelectron spectra of solid is carried out with the chosen technique. DFT/TDDFT methods make it possible to study the 1,10-phenanthroline molecule influence on the adduct electronic structure and to analyze the electronic effects of substitution of methyl groups by trifluoromethyl groups in the ligands. At transition from the tris-β-diketonate complexes to the adducts, it is observed an increase of the absorption region and a decrease in the energy gap that contributes to the efficiency growth in electronic excitation energy transfer in the ligand-metal. Moreover, phenanthroline displaces water groups, that are luminescence quenchers, from the first coordination sphere, closes coordination in the adduct, and blocks their further attachment. Both factors contribute to an increase in the luminescence intensity.

1. Introduction

Among the known classes of complex compounds of transition metals with organic ligands, β-diketonates have been most widely used, that has been shown in a series of the published thematic Proceedings [1–4]. Numerous β-diketonate complexes of metals with n = 1–4 as well as their mono- and diheterosubstituted derivatives have been widely applied in various fields of science and in the high-tech. From the theoretical and practical points of view, these complexes are of interest due to the following properties: 1) More than 70% of elements of the periodic system from lithium to actinides can be a complexing agent; 2) Substitutions of R_β and R_γ groups and heteroatoms in the ligands can modify consumer properties of the complexes; 3) Due to high stability of the metal cycles, a considerable part of the complexes, including the adducts, transit to the gas phase without appreciable decomposition. Tris-β-diketonates of lanthanides are of interest primarily as light-transforming and luminescent materials [5–8]. They are used as luminescent thermotropic liquid crystals, ionogels, nanocapsules, and long-life phosphors [10]. Lanthanide complexes are used for treatment of bone tissue density disorders [11] and for research of bimolecular interactions of fluorescent proteins [12].

The coordination unsaturation of lanthanide tris-β-diketonates causes a wide use of their adducts (of the general formula $Ln(OC_\beta(R_1)C_\gamma HC_\beta(R_2)O)_3 \cdot L$) with neutral ligands (L: 1,10-phenanthroline (Phen), 2,2′-dipyridyl (Dipy), triphenylphosphine oxide (TPPO), and hexamethylphosphoramide (HMPA)) in promising technological spheres to develop phosphors, bio-markers, antioxidants, etc. [23–28].

The fundamental problem of chemistry and photochemistry of lanthanide complexes of the island and polymer structure is a revealing of the mechanism of influence of the chemical bond nature on their fluorescent and photochemical properties. The quantum yield of luminescence in the visible and near IR regions depends to a large extent on the ligand nature and can vary by 2–3 orders of magnitude depending on the efficiency of nonradiative transitions from the ligands to metal. The energy transfer processes depend on the energy interval between the lower triplet state of the ligands and the excited state of *f*-electrons as well as on the excitation localization upon functional groups of the ligands.

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Synthesis of complexes with sufficient resistance to photodegradation remains an important problem [9]. Determination of relationship of the spectral-luminescent and photochemical properties of the complexes with their electronic structure and the orbital nature of chemical bonds makes it possible to plan synthesis of new compounds with necessary optical properties.

Photoelectron spectroscopy (PES) is an informative method to study the electronic structure of complex compounds. The recording of ultraviolet (UV) photoelectron spectra of vapors (UPS) of $Ln(\beta)_3$ tris-β-diketonates and other coordination-unsaturated complexes with diketonate ligands is complicated by the possibility of their transition to the gas phase, but when transition is possible, the method makes it possible to obtain the most detailed data on the electronic structure of valence electrons.

Photoelectron HeI spectra and absorption spectra in the vacuum UV of vapors of twelve complexes $Ln(Fot)_3$ ($R^1 = C_3F_7$, $R^2 = C(CH_3)_3$) are published in Ref. [13]. Results of studying the photoelectron spectra of scandium and lutetium tris-acetylacetonates obtained by evaporation of preliminary synthesized compounds are presented in Ref. [14].

Based on the density functional theory (DFT) method calculations, the features of the geometric structure of complexes $Ln(C_3H_5)Cp(OMe)$ ($Ln = La$–Lu, $Cp = C_5H_5$) as well as the ionic nature of the chemical bond « metal-ligand» were found [15]. The electronic structure of La, Nd, Gd, Er, Yb, and Lu tris-dipivaloylmethanates was studied by the gas electron diffraction and DFT methods [16].

The nature of molecular orbitals (MOs) was analyzed on base of the HeI and HeII spectra of the complexes $M(Dpm)_3$ (M = Y, Gd, Yb) in Ref. [17]. The analysis results for the HeI spectra of the complexes $Ln(Acac)_3$ (Ln = Pr, Nd, Tm) and fluorine-containing $Nd(Tfac)_3$ are shown in Ref. [18].

The rare-earth complexes $M(Dbm)_3$ (M = Sc, Y, La) were studied by X-ray photoelectron spectroscopy (XPS) and DFT [19]. The structure modeling of tris-Dpm complexes for a series of lanthanides La–Lu was published in Ref. [20]. The published review [21] on the photoelectron spectra and electronic structure of rare-earth β-diketonate complexes and their adducts exhibits the gas-phase PES data as high-informative.

Using the UPS spectra of vapors, XPS spectra of solid, and DFT modeling of a series of Eu (III) and Lu (III) tris-β-diketonates, it was shown the effect of substitution of ligands and metal on the electronic structure of the complexes [22].

The first research results of adducts of europium β-diketonate complexes by XPS, including the spectra of valence and internal electrons of the compounds $Eu(Acac)_3\cdot Phen$, $Eu(Hfac)_3\cdot Phen$, $Eu(Hfac)_3\cdot TPPO$ и $EuCl_3\cdot 6H_2O$, were published in Ref. [29]. In Ref. [30], the spectra of eight β-diketonates of Eu^{3+} and Tb^{3+} as well as the europium nitrate adduct with 1,10-phenanthroline ($Eu(NO_3)_3\cdot Phen$) were studied by XPS. The adducts $Eu(Hfac)_3$, $Eu(Hfac)_3\cdot L$(L = Phen, 2TPPO, 2HMPA) and tetrakis-β-diketonates $K^+[Eu(Hfac)_4]^-$ and $Cs^+[Eu(Hfac)_4]^-$ were studied by PES in the gas phase [31]. In Ref. [32], the IR, NMR, Mass spectra, X-ray diffraction data for the adducts $Lu(Acac)_3\cdot Phen$ and $Lu(Acac)_3\cdot Dipy$ were obtained and the adduct structure of $Ln(Acac)_3Q$ (Ln = La, Gd, Lu; Q = Phem, Dipy) was modeled in the DFT approximation.

Development of modern computers and quantum chemistry methods makes it possible to carry out theoretical studies of adducts of lanthanide β-diketonate complexes. The combination of experimental methods of photoelectron spectroscopy and theoretical methods of quantum chemistry is a powerful and reliable way to analyze the electronic structure of chemical compounds.

In the present work, the photoelectron spectroscopy and DFT methods were used to study the electronic structure of the adducts $Eu(OC_\beta(R^1)C_\gamma HC_\beta(R^2)O)_3\cdot Phen$, where $R^1 = R^2 = CH_3$ (Acac), CF_3 (Hfac); Phen = 1,10-phenanthroline $C_{12}H_8N_2$ (Fig. 1). The following notation was introduced for convinience: I = $Eu(Acac)_3Phen$, Ia = $Eu(Acac)_3$, II = $Eu(Hfac)_3Phen$, IIa = $Eu(Hfac)_3$.

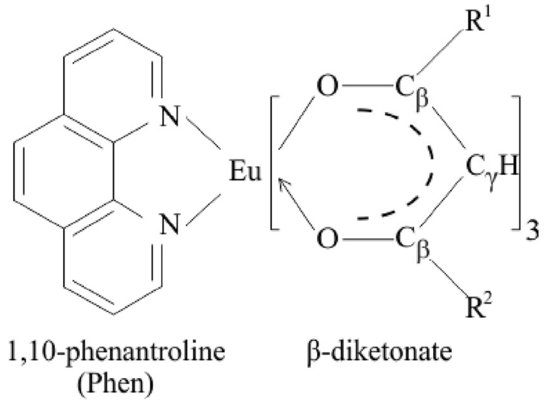

Fig. 1. Scheme of structure of the adducts $Eu(OC_\beta(R^1)C_\gamma HC_\beta(R^2)O)_3\cdot Phen$.

The UPS spectra of the Eu adducts with 1,10-phenanthroline (R = CH_3, CF_3) were obtained in vapors with HeI emission, XPS spectra of the valence region and core levels were obtained in the condensed phase with MgKα emission.

In order to study the features of adduct formation, the results of theoretical calculations and UPS of the Eu (I_a, II_a) complexes and the molecule of 1,10-phenanthroline are presented in this paper.

2. Experimental and theoretical methods

The UPS spectra of vapors were obtained on a spectrometer ES-3201 with a direct sample introduction system with a hemispherical electrostatic analyzer and a monochromatic HeI radiation source (21.2 eV). The sample temperature in the evaporator-ampoule was varied to 200 °C. The working pressure in the chamber of the spectrometer energy-analyzer was 10^{-6} mbar, the sample vapor pressure in the ionization cuvette reached values of 10^{-1}–10^{-2} mbar. The spectrometer energy scale was calibrated by the internal-standard lines (the Krypton lines $^2P_{3/2}$ and $^2P_{1/2}$ with energies of 14.00 and 14.67 eV); the instrument resolution was ±0.08 eV; the reproducibility of the center of a band was ±0.03 eV [29].

The XPS spectra were obtained on an ultrahigh-vacuum photoelectron spectrometer (Omicron, Germany) with a hemispherical electrostatic analyzer (a curvature radius of 125 mm) and MgKα radiation source (1253.6 eV). The spectra were processed with the CASA XPS program [33]. The calibration of the electron binding energy scale was done using the internal standard technique for which was chosen the C1s level (285.0 eV). The chemical state of atoms were determined by decomposition of spectral bands into components with contours compiled by a combination of the Gaussian and Lorentz types.

Quantum-chemical calculations were carried out in the approximation of the density functional theory (DFT/TDDFT) using the FireFly 8.1.0 program [34]. The hybrid exchange-correlation functional B3LYP was used in the calculations. For Eu atom effective core potential (ECP), developed by the Stuttgart/Cologne group [35], is chosen and which includes 52 inner electronic shells. For the outer shells of Eu atom was chosen the (7s6p5d)/[5s4p3d] valence basis sets. The full-electron basis set 6-311G* was used for other atoms. The choice of the functional and the basis sets was proved by previously successfully performed calculations which results are shown in Refs. [13,14,19,20,36,37]. To model the absorption spectra, 50 singlet and triplet states were calculated for all complexes, adducts, and 1,10-phenanthroline.