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Spectroscopy and structure of [LnL_3bipy] and [LnL_3phen] complexes with CAPh type ligand dimethylbenzoylamidophosphate

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ABSTRACT

Coordination compounds with general formulas [LnL_3bipy] (**Ln1**) and [LnL_3phen] (**Ln2**), where Ln=La–Nd, Sm–Yb, L^-–phosphoro-azo β-diketone analog anion: $[C_6H_5CONPO(OCH_3)_2]^-$, phen=1,10-phenanthroline, bipy=2,2′-bipyridine, were synthesized and characterized by means of IR, ^{1}H NMR and high resolution UV–vis absorption and luminescence spectroscopy (emission, excitation spectra and emission decay times) at 300, 77 and 4.2 K. The thermal behavior and stability of Eu^{III} and Tb^{III} complexes were studied by thermogravimetric and differential thermal analyses. Single-crystal X-ray diffraction data showed that **Pr1**, **Yb1** and **La2**, **Eu2**, **Gd2**, **Yb2** crystalize in the monoclinic and triclinic systems, respectively with eight-coordinated lanthanide ions. The relation between the crystal structure and spectroscopic properties of the complexes are discussed. The Eu^{III} and Tb^{III} complexes exhibited a strong metal-centered emission with decay time 1.5–1.8 ms. Intrinsic quantum yields (Q_{Ln}^{Ln}) equal 57 (**Eu1**) and 55% (**Eu2**). The Tb^{III} complexes revealed a very efficient ligand-to-metal energy transfer at room and low temperatures.

1. Introduction

A keen interest to lanthanide coordination compounds results from their potential applications [1,2]. The mixed ligand lanthanide complexes with general formula [LnL_3Q], where L^- is a β-diketonate anion and Q is a 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 [2,3]. Since subtle changes in the molecular structures of the complexes could acutely tune the photoluminescence and electroluminescent (EL) properties, the development of new lanthanide β-diketonate mixed ligand complexes for the light-emitting layers of the EL device is a prevalent research activity. The research efforts include design of new β-diketones and analogs as well as neutral second ligands. This combination of ligands completes all coordination positions of the metal ion providing a stable complex with rigid metal ion environments. Thus, most of the published work covers these basic ligands and differ in the choice of their derivatives. Chemical modification of the neutral ligand or β-diketone and analogs is dictated by three major principles: (1) the complex lowest triplet level must match the metal emitting state, being, ideally-slightly, above it; (2) for EL applications it is considered advantageous to enrich the ligand(s) with electron and hole-transporting chemical groups in order to facilitate charge carrier injection and exciton trapping in the complex; (3) the complex must be thin-film forming upon vacuum deposition without aggregation or crystallization problems. It also must be miscible with other species (if necessary) as well as thermally stable [4]. Recently, the structural characteristics and photophysical studies of several mixed ligand carbacylamidophosphate (CAPh) based lanthanide compounds were reported [5]. All these compounds are stable, have monomeric structure and demonstrate bright luminescence. Compared with β-diketones in the CAPhs C=O vibrations (~1600 cm^{-1}) are reduced by replacing one of C=O group with P=O having lower energetic vibrations (~1250 cm^{-1}) and C–H vibrations in chelating ring are eliminated by replacement of carbon atom with nitrogen. This allows expecting the decrease of multiphonon quenching of the lanthanide emission in Ln (III) CAPh based complexes.

In this paper we report synthesis, crystal structure and photophysical data for two rows of mixed ligand lanthanide complexes ([LnL_3bipy] (**Ln1**) and [LnL_3phen] (**Ln2**)) with carbacylamidophosphate

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(CAPh) ligand dimethylbenzoylamidophosphate. Of special interest in this work is the relative contribution of the radiative and nonradiative paths to excited-state deactivation. These will be discussed along with implications concerning future initiatives to design efficient UV–vis energy converters.

2. Results and discussion

2.1. Description of structures

The **Pr1** and **Yb1** complexes are isostructural (Table S1, Fig. 1). According to criteria proposed in [6] the coordination polyhedra for Pr^{III} and Yb^{III} ions are established as intermediate between bicapped trigonal prism and square antiprism (Table S2, Fig. 3).

The compound **La2** and earlier reported **Nd2** complex [7] differ by the position of the methoxy groups in one of the CAPh ligands, also lanthanide ions have slightly different geometries of their surroundings (Table S2). The coordination polyhedra of La^{III} ions are slightly distorted Hoard's dodecahedrons (Table S2, Fig. 3). Compounds **Eu2**, **Gd2** and **Yb2** are not isostructural to lanthanum and neodymium analogs, but are isostructural with each other. The coordination polyhedra of Eu^{III}, Gd^{III} and Yb^{III}, like for central ions in complexes with 2,2′-bipyridine, are established as intermediate between bicapped trigonal prism and square antiprism (Table S2). The molecular structure of the europium complex with 1,10-phenantroline is shown on Fig. 2.

As it can be seen from Figs. 1 and 2 the phosphoryl ligands are coordinated to the lanthanide ions in a deprotonated form in a bidentate chelating manner via the oxygen atoms of the phosphoryl and carbonyl groups with formation of six-membered metallocycles. In most of complexes under study Ln–O distances for oxygen atoms belonging to phosphoryl groups are shorter than those for carbonyl groups, but for compound **Pr1** and **La2** we observed a reverse trend (Table S3). In the complexes, in comparison to free ligand [8], the average P–O and C–O bond lengths increase and P–N and C–N bond lengths decrease that is typical for CAPh based complexes and may be explained by change of bond order in C(O)NP(O) fragment. For all compounds chelate 6-membered metal-cycles formed by CAPh ligands are almost planar and are characterized by deviations from mean-square planes of the metal-cycles, which do not exceed 0.42 Å ((N8) for **La2**, molecule 2). Maximal deviations of the Ln atoms from the mean planes defined by the other chelate cycle five atoms for the complexes are in the range 0.35–0.71 Å.

Additional chelating ligands bipy or phen complete the coordination sphere of Ln^{III} ions to coordination number 8 not leaving place for molecules of solvent. These ligands are bidentate coordinated forming five-membered chelate cycles, which are almost planar. The deviations from the plane plotted through atoms of chelate cycle do not exceed 0.08 Å for bipy and 0.16 Å for phen.

In crystal structure for all complexes numerous intermolecular contacts were found. The contacts exist between aromatic rings of both CAPh and nitrogen-donor ligands, methoxy groups of dimethylbenzoylamidophosphate and N, C, O atoms of chelating rings as well.

2.2. Thermal behavior investigations

Whereas complexes possible practical use in electroluminescent devices the thermal stabilities of Eu^{III} and Tb^{III} complexes were studied (Fig. S1). The thermal analyses exhibits an absence of any effects untill the melting points of the complexes, when on the DTA curves endothermic peaks appear. Melting points are equal 190, 200, 180 and 200 °C for **Eu1**, **Eu2**, **Tb1** and **Tb2** respectively. Main weight loss is observed in region of 230–300 °C for complexes with bipy and in region 240–310 °C for complexes with phen. In these regions for all complexes the DTA curves display distinct exothermic peaks at 250 °C and 260 °C for **Ln1** and **Ln2** complexes respectively and then endothermic peaks at the end of this temperature region. After heating till 800 °C total weight loss for complexes is 56.3–67.5%. According to accounted metal content in the residues and their IR spectra they were found to be mixtures of phosphates. Hereby the TGA data show high thermal stability of the compounds and confirm the absence of solvents in the composition of the complexes.

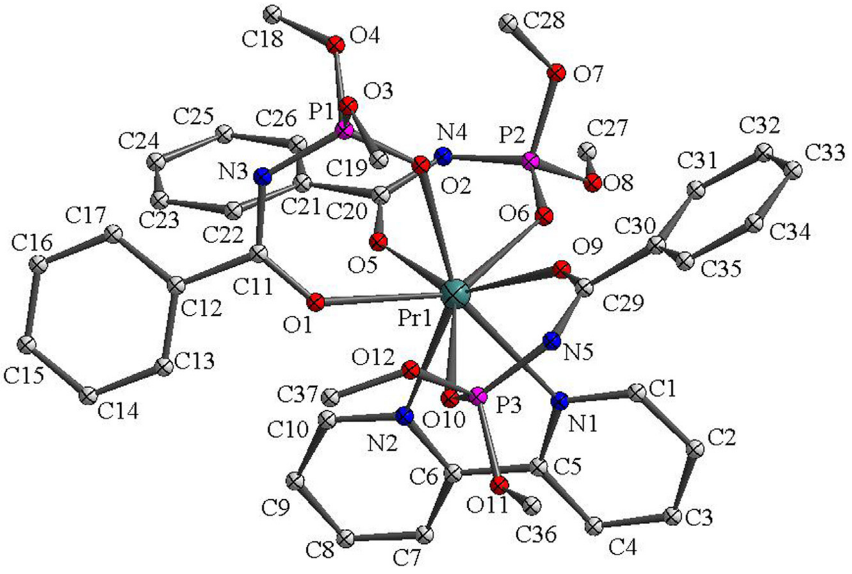

Fig. 1. Molecular structure of **Pr1**. The hydrogen atoms are omitted for clarity.