

COORDINATION COMPOUNDS OF LANTHANIDE WITH 3-METHYL-1-PHENYL-4-FORMYLPYRAZOLE-5-ONE

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The article is devoted to the synthesis and study of the structure and luminescence properties of coordination compounds of lanthanide with 3-methyl-1-phenyl-4-formylpyrazole-5-one. It has been established that the ligand belonging to aldehydoketones, when complexed, exhibits the basic properties inherent in β -diketones and 4-acylpyrazolones, introducing new features in the coordination-chemical behavior of ligands of this class. Neutral and multiligand complexes of lanthanides with phenanthroline, as well as anionic tetrakis complexes, were investigated. The composition and structure of the complexes are determined from the data of elemental and thermogravimetric analysis, IR and luminescence spectroscopy, thermogravimetry, X-ray phase and X-ray diffraction analysis.

As a result of undertaken studies it was established that 3-methyl-1-phenyl-4-formylpyrazole-5-one forms stable coordination compounds with lanthanides in deprotonated enol form. Relieving of steric strains in coordination polyhedron due to small size of hydrogen atom of formyl group allows for realization in coordination compounds of 3-methyl-1-phenyl-4-formylpyrazole-5-one with cations of lanthanum(III), cerium(III), praezodim(III) and neodimium(III) of rare for this class dimeric structure with bridging pyrazolone anions. It is shown that the formation of binuclear complexes in which metal cations are bound by three oxygen bridges is rather characteristic for lanthanides. However, only one binuclear structure with three oxygen bridges is registered for lanthanide β -diketonates.

The study of complexes' luminescence spectrum showed that displacement of OH-oscillators from coordination sphere by means of appending of phenantroline in complexes and of four chelated ligands in tetrakis-complexes significantly increases the intensity of luminescence of cations of europium(III) and terbium(III), but almost not affects the intensity of luminescence of other lanthanides.

A feature of the tris complexes is the coordination unsaturation of the lanthanide cation, which is compensated for by the addition of solvent molecules (water, methanol, ethanol). When attempts are made to excite ion luminescence in complexes with low-molecular-weight additional ligands, a considerable part of the excitation energy is transferred to vibrational levels of OH bonds, which effectively extinguishes the radiation processes. Anomalously high intensity of luminescence was detected for molecular and

anionic complexes of samarium (III) with 3-methyl-1-phenyl-4-formylpyrazole-5-one compared to similar complexes of europium (III). The singularity of the samarium (III) complexes is the transfer of energy from the resonant level to the highly located sublevels of the ground state. This process is realized due to nonradiative transitions and leads to dissipation of excitation energy and a decrease in the quantum yield of luminescence. As for the europium (III) cation this process is suppressed due to the absence of high-lying sublevels of the ground state, the luminescence intensity of its complexes is 1-2 orders of magnitude higher than the luminescence intensity of similar samarium (III) complexes.

Among the ways of practical application of the complexes studied the most promising is their use as materials for the creation of highly efficient electroluminescent devices.

Keywords: 3-methyl-1-phenyl-4-formylpyrazole-5-one, lanthanide, complexes, luminescence.

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