

STUDY OF HETEROMETALLIC β -DIKETONATE COMPLEXES BASED ON ZINC AND LANTHANIDES(III)

Ivakha N.^{1,2}, Berezhnytska O.^{1,2}

¹ V.I.Vernadsky Institute of General and Inorganic Chemistry of NAS of Ukraine,
Kyiv, Ukraine

² National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute»,
Kyiv, Ukraine
ivakhanadiia@gmail.com

Heterometallic complex formation is a new and modern direction in coordination chemistry, as it allows expanding the spectrum of polyfunctional compounds with predicted properties and achieving the formation of new crystalline forms and structures. Undoubtedly, one of the important goals of the synthesis of heterometallic complexes (HMC) is the possibility of intensifying the emission of lanthanide complexes upon the addition of a second metal ion. The majority of works concerning bimetallic complexes are based on the doping of coordination compounds with salts or oxides of other metals, which allows to expand the spectrum of monochromatic emission, and in some cases to change its color. However, this approach has its disadvantages, since it is difficult to control the uniformity of the distribution of the second metal in this case. At the same time, some 3d-metal ion in heterometallic compounds can shield the lanthanide ion, causing the quenching of luminescence. In the synthesis of 3d-4f-HMC, zinc was chosen as the 3d metal, since its ability to sensitize the luminescence of lanthanides in coordination compounds is known from the literature. Among the lanthanides, the greatest attention of researchers is usually paid to ions emitting in the visible region of the spectrum. Such compounds are quite widely studied. In contrast, the study of the ways of synthesis of heterometallic composites based on lanthanides emitting in the IR region and the investigation of their luminescent characteristics are still limited. That's why Nd and Yb were chosen as the objects of the study

In the work, Zn-Nd and Zn-Yb HMC based on the unsaturated β -diketonate ligand 2,6-dimethyl-heptene-1-dione-3,5 (dmhpd) were synthesized and its physicochemical properties were investigated in comparison with monometallic prototypes.

The compounds were investigated by IR spectroscopy. No significant changes were observed in the position and shape of vibration bands, characteristic of β -diketonate complexes of metals, compared to monometallic analogues (in the region of 1500-1650 cm^{-1} there are bands that indicate bidentate-cyclic coordination of ligands to metal ions, in the range of 400-600 cm^{-1} - vibration bands of the M-O bond). This fact allows us to assume the invariability of the coordination environment of the central atoms during the synthesis of HMC. However, the given characteristic bands undergo a certain splitting, which can indirectly confirm the formation of heteronuclear compounds.

Thermal studies of HMC showed an increase in the temperature of the beginning of destruction of such samples by an average of 20°C compared to monometallic prototypes. On the thermograms, the processes of melting, polymerization, rearrangement, and splitting of structural units of heterometallic systems are superimposed, so it is rather difficult to make a clear classification of all processes.

The formation of heterometallic complexes, and not their mixtures, can be evidenced by changes in the intensity and positions of the transition bands in the diffuse reflection spectra (DRS) of solid samples. On the DRS of complexes with dmhpd (Fig. 1) in the region of 250-350 nm, we observe broad bands that can be attributed to electronic π - π^* -transitions from the ground (S_0) to the excited state (S_1) of the ligand molecules. At the same time, it

should be noted that in the case of heterometallic complexes there is a significant shift (by 800-1600 cm^{-1}) and a narrowing of this band, which may indicate heterocoordination.

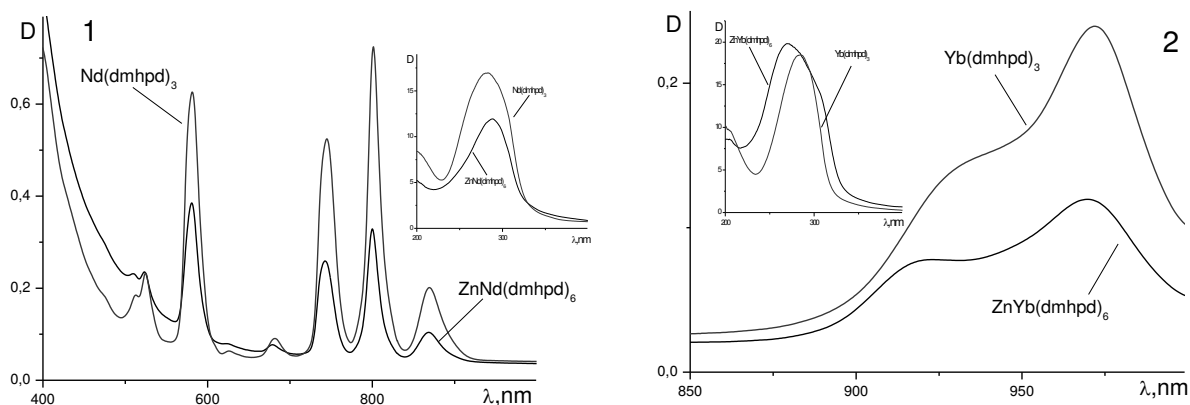


Figure 1. – DRS of mono- and HMC of neodymium (1) and ytterbium (2).

In the region of 400-1000 nm for neodymium complexes and ≈ 1000 nm - for ytterbium ones, there are bands on the spectra that correspond to f-f transitions of lanthanide ions. In the case of a heterometallic complex, these bands undergo slight shifts up to 150 cm^{-1} , their shapes remain unchanged, but their intensity decreases significantly. Unfortunately, all synthesized mono- and heterometallic complexes are X-ray amorphous compounds, so it is impossible to establish the structure and symmetry of coordination polyhedra by direct X-ray diffraction.

To study the influence of the heteroatom on the luminescent properties of the compounds, the excitation and luminescence spectra of the complexes were recorded. Figure 2 shows luminescent spectra of mono- and heterocomplexes.

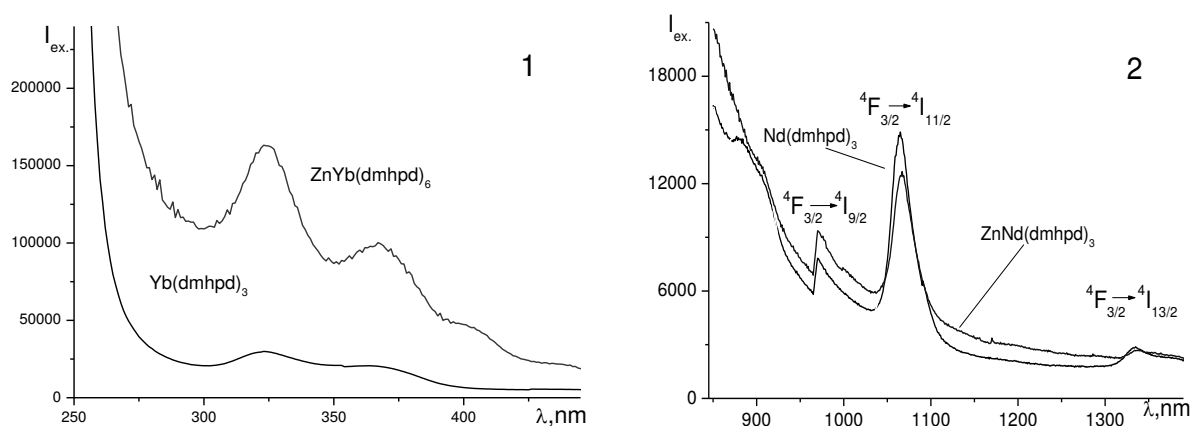


Figure 2. Luminescence spectra mono- and HMC of Yb (1) and Nd(2)

The change in luminescence intensity of heterometallic compounds compared to monometallic complexes indirectly indicates the formation of heterostructures. A comparative analysis of HMC spectra showed that in the case of the ytterbium complex, the presence of the Zn^{2+} ion in its composition increases the luminescence efficiency by ~ 5.5 times when excited at a wave length of 323 nm, which indicates its sensitizing effect. For complexes with neodymium(III), the relative emission intensity slightly decreased ($\lambda_{\text{excitation}} = 365$ nm).

Such a difference in the emission intensity depending on the lanthanide ion can primarily be related to the realization in the zinc-ytterbium HMC of the optimal gap between the triplet level of the ligand and the emitting level of the ytterbium ion, as a result non-radiative losses are reduced. Besides, probably, in the case of zinc-neodymium HMC, the neodymium ion acts as an energy donor.