UDC 546.650+547.1'13+541.64+543.426 doi: 10.33609/2708-129X.90.10.2024.69-87

COMPARATIVE CHARACTERISTICS OF SPECTRAL-LUMINESCENCE PROPERTIES OF Yb(III) COMPLEXES WITH UNSATURATED β-DIKETONES.

N.B. Ivakha[1,2]*, O.S. Berezhnytska[1,2]

1 *V.I.Vernadsky Institute of General and Inorganic Chemistry of the NAS of Ukraine, 32/34 Acad. Palladin Avenue, 03142 Kyiv, Ukraine;*
2 *National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», 37 Beresteiskyi Ave., 03056 Kyiv, Ukraine*
e-mail: ivakhanadiia@gmail.com

The study presents a comparative analysis of the spectral-luminescent properties of synthesized β-diketonate coordination complexes of ytterbium with the following ligands: 2,7-dimethyl-oct-1-en-3,5-dione, 2,6-dimethyl-hept-1-en-3,5-dione, 2-methyl-5-phenylpent-1-en-3,5-dione, 2-methyl-5-biphenylpent-1-en-3,5-dione. In addition, research was conducted on polymeric compounds based on these complexes and their phenanthroline mixed-ligand derivatives.

Using a range of physicochemical analysis methods, it was established that the structure of the elementary unit during polymerization, as well as the coordination sphere of the complexes during the formation of mixed-ligand compounds, does not undergo significant changes compared to the initial β-diketonate molecules. Thermal analysis revealed a significant increase in the decomposition onset temperature of mixed-ligand and metallopolymeric compounds compared to their monomeric counterparts. Luminescence spectroscopy demonstrated that the studied samples exhibit luminescence in the infrared (IR) range.

A comparative analysis of the integral luminescence intensities of ytterbium complexes identified key factors influencing the emission characteristics. Primarily, the synthesis of mixed-ligand complexes with phenanthroline mitigates the negative effects of one of the most well-known quenching factors: OH-oscillators of water molecules, which complement the coordination sphere of monomeric ytterbium complexes. Furthermore, the synthesis of polymeric compounds based on β-diketonate complexes positively affects the luminescence, potentially due to a reduction in concentration quenching, as in polymers, the emitting centers are uniformly distributed along the macromolecular chain. Besides directly enhancing luminescent properties, this approach aims to address the practical application of the synthesized compounds since polymers are significantly easier to process and can form film materials.

Based on the conducted research, the following luminescence intensity dependencies were established: dmod>dmhpd>mbphpd>mphpd, as well as monomer-polymer-MLC-MLC polymer. As seen from the presented data, the best emission characteristics are exhibited by ytterbium mixed-ligand mono- and polycomplexes with β-diketones containing alkyl substituents.

Keywords: ytterbium, complex, luminescence, β-diketones, polymers.

INTRODUCTION. The luminescence of ytterbium(III) coordination compounds is a subject of intensive research due to their unique spectroscopic properties and potential applications across various fields. A key feature of the Yb^{3+} ion is its ability to emit in the near-infrared (NIR) range [1], making it highly appealing for investigation. For example, Yb-containing compounds can be used as luminescent markers in immunofluorescence analysis [2–5], as well as in laser systems, electroluminescent devices, optoelectronics, and communication technologies [6, 7].

Ytterbium complexes with organic ligands, particularly β-diketones, are actively studied due to their ability to provide high luminescence efficiency and resistance to external influences. The ligand used for energy transfer determines the luminescence process's efficiency. β-Diketones, which have a high absorbance in the UV spectral range, serve as effective sensitizers for luminescence due to their ability to efficiently transfer absorbed energy to lanthanide ions [8, 9]. The luminescence intensity of lanthanide ions, including Yb^{3+}, in β-diketonate complexes is influenced by two primary factors: energy transfer from the triplet state of the ligand (T_1) to the resonant level of the Ln(III) ion and deactivation processes of the excited levels of the Ln(III) ion. The efficiency of energy transfer from the ligand to the metal is determined by the energy gap (ΔE) between the triplet and resonant levels, with the optimal ΔE value depending on the type of ligand and Ln(III) ion [9]. Experimentally, the T_1 energy levels of ligands are determined from molecular phosphorescence spectra of their complexes with rare-earth metals that have an empty (Y, La) or fully filled (Lu) 4f subshell or with gadolinium, as the resonant $6P_7/_2$ level of the Gd(III) ion lies above the triplet levels of most organic ligands [10].

The energy of triplet states in β-diketonates of Ln(III) depends on the nature of the radicals attached to the chelating [OCCCO] fragment of the ligand and generally decreases in the following substituent series: aliphatic > fluorinated > aromatic [11]. The energy of the triplet level also decreases with the elongation of the aliphatic chain of the fluorinated substituent. For instance, using fluorinated β-diketonates of Yb^{3+} can affect luminescence intensity, reducing it with the increasing chain length of fluorinated compounds [12, 13]. In β-diketonates containing aromatic substituents, a decrease in T_1 energy levels is observed with the increasing size of the conjugated radical system, e.g., phenyl > biphenyl > naphthyl ≈ phenanthryl > anthracenyl. Furthermore, the branching of the alkyl radical chain reduces the spectroscopic properties of the complexes due to increased steric hindrance during coordination.

Most β-diketones form hexacoordinated complexes [Ln(β-dik)$_3$] with lanthanide ions, where the coordination sphere of Ln(III) is completed by solvent molecules, particularly water. However, as shown in many studies, water is a primary quencher of luminescence due to the vibrational oscillations of O–H groups, which facilitate non-radiative energy transfer. Replacing water with organic ligands free of such quenchers (e.g., phenanthroline or its derivatives) significantly enhances the quantum yield of luminescence. The additional ligand may also participate in the energy transfer process to the Ln(III) ion, further increasing luminescence intensity [14-16]. The degree of luminescence quenching by water molecules is inversely proportional to the energy

gap ΔEg between the emitting and ground states. For Yb(III), this gap is relatively large (~10,000 cm^{-1}), enabling the synthesis of ytterbium compounds with sufficiently high quantum yields. Among β-diketonate lanthanide compounds emitting in the IR region, Yb(III) compounds exhibit higher quantum efficiency and longer luminescence lifetimes, with emission wavelengths of 980–1000 nm. This is particularly advantageous for applications in bio-objects, as they are transparent in this range [17–19].

Ytterbium(III) is a unique ion among lanthanides, as it has only one emission band corresponding to the $^2F_5/_2 \rightarrow {}^2F_7/_2$ transition. Optimizing Yb^{3+} luminescence requires selecting appropriate ligands that act as "antennas," absorbing light more efficiently than the lanthanide ion and transferring this energy to the excited state of Yb^{3+}, thereby enhancing luminescence intensity.

However, monomeric lanthanide complexes have several drawbacks, including insufficient thermal stability, a tendency to aggregate, and difficulties in obtaining film materials, limiting their use as precursors for luminescent materials. One approach to overcoming these challenges is incorporating polymer matrices such as polymethyl methacrylate (PMMA), polyvinylcarbazole (PVK), or polystyrene (PS) to create stable materials with high luminescence yields [20–22]. Lanthanide ion-based polymer compositions, prepared by dispersing lanthanide salts or β-diketonate complexes into polymer matrices, have been thoroughly studied. Ytterbium polymer complexes are typically formed by incorporating ytterbium coordination compounds into a polymer matrix, which acts as a stabilizing environment to enhance luminescence stability and efficiency. Polymers not only provide a protective coating but also influence the coordination environment of the ion, reducing the impact of luminescence-quenching factors such as water or ligand vibrations. However, these products often lack uniform metal distribution within the polymer matrix, resulting in unpredictable properties. Polymer compounds based on monomeric complexes are promising in terms of stability and enhanced luminescence intensity. Lanthanide complexes with unsaturated β-diketones containing a metal-chelating ring and a double bond represent a readily available and promising class of compounds for synthesizing polymeric metal complexes. These compounds enable one-stage synthesis of macromolecular metal chelates and uniform metal distribution throughout the polymer, which generally exhibits isotropic properties.

Despite the evident potential of such compounds as polymerization monomers, research on lanthanide β-diketonates with unsaturated substituents remains limited. Combining polymers with coordination complexes reduces the impact of external factors such as moisture or temperature on luminescent properties. This paves the way for stable materials for optical communication and biosensors operating under challenging conditions.

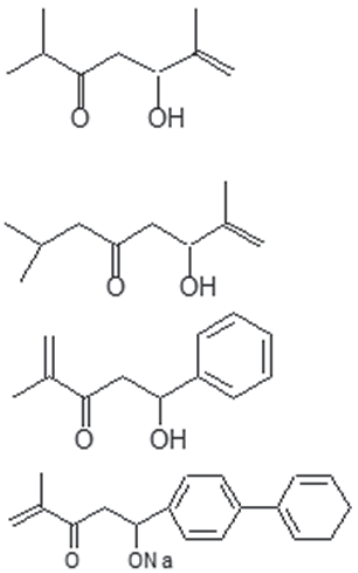
Since the 2010s, researchers at the Department of Heterophase Synthesis of Inorganic Compounds and Materials, Vernadsky Institute of General and Inorganic Chemistry, NAS of Ukraine, have investigated the polymerization of unsaturated diketonate lanthanide complexes [23–25]. Radical polymerization has been used to obtain metallopolymers based on mono- and mixed-ligand β-diketonate complexes of Ln(III) with 2,7-dimethyl-oct-1-en-3,5-dione, 2,6-dimethyl-hept-1-en-3,5-dione,

2-methyl-5-phenylpent-1-en-3,5-dione, 2-methyl-5-biphenylpent-1-en-3,5-dione, and their mixed-ligand derivatives with phenanthroline.

Currently, key challenges in this field include identifying optimal ligands to enhance luminescence efficiency and refining methodologies for controlling the coordination environment of ytterbium ions. Despite significant progress in understanding luminescence mechanisms, future research should focus on developing new ligand types that minimize quenching processes. Systematizing previously obtained data, including those by the authors of this article, is essential for these advancements.

This work summarizes the results of research on ytterbium metal complexes and their polymers with unsaturated β-diketones containing alkyl and aromatic substituents and compares the spectral-luminescent characteristics of the compounds depending on the nature of the substituents.

EXPERIMENT AND DISCUSSION OF RESULTS. The study focused on mono-, mixed-ligand, and polymer coordination compounds of ytterbium (III) with unsaturated β-diketones. The synthesis of the initial β-diketones was carried out via Claisen condensation according to the methodology described in [26–27] (Fig. 1).



2,6-Dimethyl-hept-1-en-3,5-dione (Hdmhpd)

2,7-Dimethyl-oct-1-en-3,5-dione (Hdmod)

2-Methyl-5-phenylpent-1-en-3,5-dione (Hmphpd)

2-Methyl-5-biphenylpent-1-en-3,5-dione (Hmbphpd)

Fig. 1 – Structural formulas of β-diketonate ligands.

The synthesis of Yb(III) complexes with β-diketones was conducted in aqueous-alcohol solutions by reacting ytterbium chloride ($YbCl_3 \cdot 6H_2O$) with the sodium salt of the respective ligand at a molar ratio of 1:3.5 (pH 8–8.5) at room temperature. The synthesis of mixed-ligand complexes, where phenanthroline was used as the second ligand, was performed in alcoholic solutions with a $Yb(\beta\text{-dik})_3 \cdot Phen$ ratio of 1:1 following the method described in [23].

Polymer β-Diketonates of Yb (III) were

obtained through the homopolymerization of the synthesized monomeric complexes via a radical mechanism [24]. The polymerization was carried out at 80 °C, with azobisisobutyronitrile (AIBN) chosen as the initiator for the radical polymerization, as the polymerization mechanism for β-diketonates of lanthanides is identical to that of vinylmonomers.

All synthesized compounds were investigated using IR spectroscopy, DRS, thermogravimetry, and luminescence analysis.

IR spectra were recorded using a Specord M80 spectrometer in the range of 400–4000 cm^{-1} in KBr pellets.

Diffuse reflectance spectra in the range of 300 – 1100 nm were registered using a UV-VIS-IR Shimadzu UV-3600 spectrophotometer.

The hydratecomposition of the synthesized compounds and their thermal stability were determined using DTA. Thermograms were recorded using a Q–1500°D derivatograph system from F. Paulik, J. Paulik, L. Erdey, in the temperature range of 20–500 °C at a heating rate of 5 °C/min in a platinum crucible with a carrier (anhydrous Al_2O_3) under a static air atmosphere.

The excitation and emission spectra of solid complexes were recorded using a Fluorolog FL 3-22 spectrofluorimeter, Horiba Jobin Yvon (Xe lamp 450 W), with a light filter OS 11, followed by corrections accounting for the emission distribution of the xenon lamp and the sensitivity of the photomultiplier tube (PMT). For the IR region, InGaAs photoresistors (DSS-IGA020L, Electro-Optical Systems, Inc, USA, cooled to liquid nitrogen temperatures) were used as radiation receivers.

The coordination mode of β-diketonates with the Yb(III) ion was determined by IR spectroscopy, which, in cases where direct X-ray structural analysis is not possible, allows the structural identification of β-diketonate complexes. Fig. 2 shows a typical IR spectrum of Yb(III) coordination compounds with β-diketonate ligands containing unsaturated substituents in the α-position, and Table 1 summarizes the main vibrational frequencies and their assignments for all studied ytterbium-containing β-diketonates.

The main characteristic vibration bands of complex β-diketonate compounds are located in the region of 1500–1700 cm^{-1}, which correspond to stretching vibrations of carbonyl groups and multiple CC bonds of the dicarbonyl fragment [28, 29].

Since there is a delocalization of electron density in the diketonate fragment, the stretching vibration bands occupy an intermediate position between the stretching vibrations of single C-O and C-C and double C=O and C=C bonds. Thus, the band with a higher frequency (~1580–1610 cm^{-1}) corresponds to the symmetric stretching vibration of the bond (C⁻⁻⁻O), and with a lower frequency (~1540–1580 cm^{-1}) to the asymmetric stretching vibration of the bond (C⁻⁻⁻C). It should be noted that for monomeric and polymeric complexes with mbphpd and Phen, the splitting of the ν_s(C⁻⁻⁻O) band into 2 components is observed, which may be due to the structural inequivalence of some chelate rings. For most polymeric compounds, the ν(C=C) band appears in the region of ~1650–1660 cm^{-1} as a shoulder, indicating the presence of terminal unsaturated groups, and in the case of the $[Yb(mphpd)_3Phen]_n$ complex, the average intensity of this band may indicate an incomplete polymerization process and the formation of a certain number of oligomeric products.

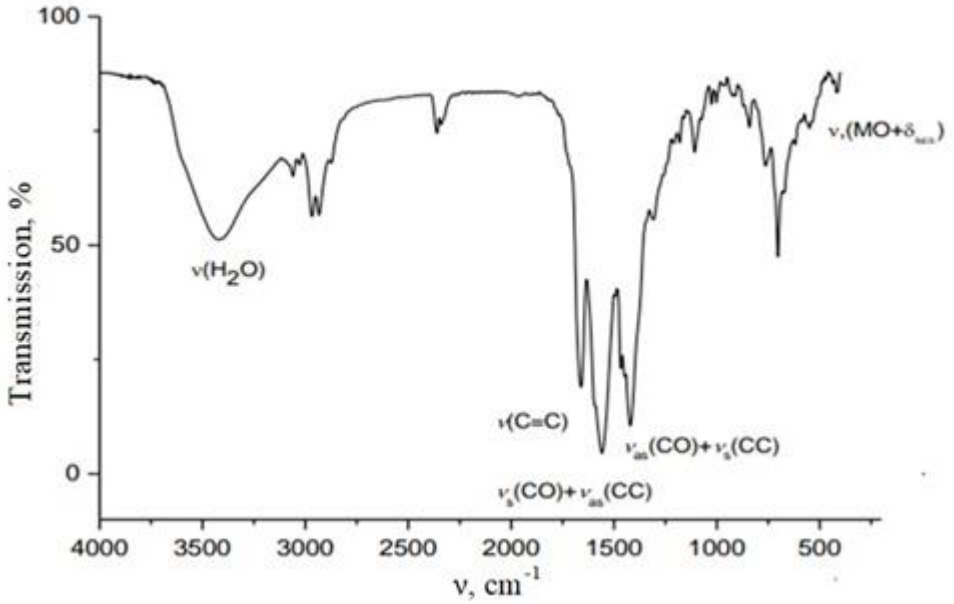


Fig. 2. – IR spectrum of the complex $Yb(mphpd)_3 \cdot 2H_2O$.

Table 1.

Assignment of vibration bands in the IR spectra of Yb(III) β-diketonate (cm^{-1})

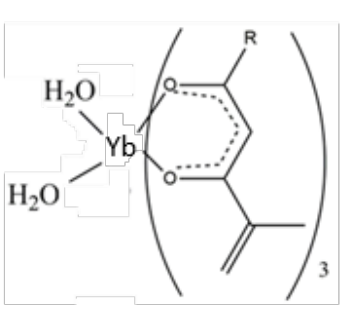
Complex	$\nu(Yb–O)+\delta_{hel.\ ring}$	ν (Yb-N)	$\nu_{as}(C{=}{-}{=}C)$	$\nu_s(C{=}{-}{=}O)$	$\nu_s(C{=}C)$
$Yb(mphpd)_3 \cdot 3H_2O$	421, 453, 490, 505, 545	-	1580	1596	1655
$Yb(mphpd)_3 \cdot Phen$	405, 464, 487, 504, 545	467	1582	1601	1655
$Yb(mbphpd)_3 \cdot 2H_2O$	411, 429, 450	-	1560	1586	1653
$Yb(mbphpd)_3 \cdot Phen$	410, 428, 451	474	1558	1575, 1607	1653
$Yb(dmhpd)_3 \cdot 2H_2O$	408,430, 478, 501, 526	-	1555	1555	1640, 1660
$Yb(dmhpd)_3 \cdot Phen$	420, 435, 481, 495, 507	477	1552	1590	1630
$Yb(dmod)_3 \cdot 2H_2O$	456, 470, 489, 520	-	1542, 1560	1590	1680
$Yb(dmod)_3 \cdot Phen$	450, 468, 470, 515	480	1547	1592	1650
$[Yb(mphpd)_3]_n$	421, 453, 490, 505, 545	-	1560	1590	1651sh.
$[Yb(mphpd)_3 \cdot Phen]_n$	410, 420, 435, 495, 507	481	1565	1585	1650
$[Yb(mbphpd)_3]_n$	406, 427, 455	-	1559	1581, 1599	1652sh.
$[Yb(mbphpd)_3 \cdot Phen]_n$	409, 432, 461	481	1561	1580, 1607	1651sh.
$[Yb(dmhpd)_3]_n$	419, 426, 484, 511	-	1537	1578	1659sh.
$[Yb(dmhpd)_3 \cdot Phen]_n$	417, 429, 475, 515	468	1535	1577	1653sh.
$[Yb(dmod)_3]_n$	421, 435, 481, 511	-	1542	1581	1661sh.
$[Yb(dmod)_3 \cdot Phen]_n$	419, 439, 474, 518	465	1544	1584	1663sh.

In the low-frequency region of the spectra (400–600 cm^{-1}) a set of bands appears, which corresponds to a combination of stretching vibrations of the Yb-O bond and deformation vibrations of the chelate ring. At the same time, the frequencies of the δ_{ring} and ν(Yb–O) differ slightly for different complexes, since the structure of the [OCCCO] fragment of the ligands practically does not depend on the type of substituents in them, which may indicate a close coordination environment of Yb(III) in all the studied compounds. For complexes with phenanthroline in the IR spectra in the range of 465–480 cm^{-1}, bands corresponding to the stretching vibration of Yb-N are additionally observed. Their presence confirms the formation of mixed-ligand complexes. The position of the ν vibration of the Yb-O bonds in the IR spectra of polymer and monomer complexes is almost the same, and the slight shift of the band data to the low-frequency region (up to 20 cm^{-1}) for polymer complexes is probably due to the deformation of the coordination site. That is, during polymerization, the immediate environment of the lanthanide ion practically does not change in comparison with metal complexes.

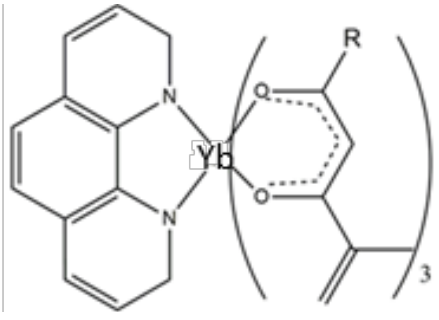
In the region of 3200–3600 cm^{-1} for all monomer complexes, there is a broad vibration band of the O-H groups, which is associated with the addition of water molecules to the coordination sphere of ytterbium(III) complexes. In the case of phenanthroline complexes, this band is not observed in the IR spectra, which indicates the displacement of water molecules from the inner coordination sphere due to the coordination of the Phen molecule to the central ion. In the case of polymer complexes, the ν(O–H) band has a low intensity in the given spectral range. This can be explained by the presence of a small amount of occluded water in the structure of metal polymers.

The similarity of the IR spectra of metal chelate monomers, mixed ligand and polycomplexes suggests the proximity of the ligand environment of metal ions in these compounds.

Based on the analysis of the IR spectra, it can be unequivocally stated that in the complexes $Yb(\beta\text{-dik})_3 \cdot 2H_2O$ the metal ion coordinates the β-diketonate ligands bidentately-cyclically with a delocalized system of π-bonds in the chelate ring. In this case, six-membered metallocycles are formed (Fig. 3).



a



b

Fig. 3 – Schematic structure of Yb(III) complexes: $Yb(\beta\text{-dik})_3$ (a), $Yb(\beta\text{-dik})_3$Phen (b).

From the point of view of the possible practical application of the synthesized coordination compounds of ytterbium (III), an important stage of the study is the thermal analysis, in particular the determination of the thermal stability of the synthesized compounds. The thermal stability of Yb(III) complexes with unsaturated β-diketonesis analyzed in sufficient detail in [23, 24]. The generalization of the results of thermal studies of Yb(III) β-diketonates shows that the thermal decomposition of all compounds proceeds in the same way:

- dehydration of monomeric complexes $Yb(\beta\text{-dik})_3$, regardless of the β-diketone, occurs in the temperature range of 120–127 °C and is accompanied by endoeffects, which corresponds to the elimination of two coordinated water molecules;
- for mixed-ligand compounds, the absence of this thermal effect indicates the replacement of water molecules by a phenanthroline molecule. The elimination of a phenanthroline molecule begins at about 170 °C;
- in the case of polymer complexes at a temperature of ~ 130 °C, a slight endoeffect is observed, which may indicate the elimination of water remaining in the voids of the polymer matrix during polymerization of the monomer;
- at a temperature of > 180 °C, polymerization of complexes occurs without an initiator;
- in the temperature range of 250–450 °C, oxidative thermal destruction of all complexes is accompanied by a number of exoeffects, which is due to the decomposition of organic fragments of the molecule, and the final decomposition products are non-stoichiometric ytterbium(III) oxides;
- the thermal stability of the studied compounds increases in the following order: monocomplexes>mixed-ligand complexes>metalpolymers>mixed-ligand metalpolymers.

The temperature at the onset of degradation varies from 250 °C (for monomers) to 375 °C (for polymers). This effect may be due to the denser, ordered packing of polycomplexes with a complex, possibly branched, system of bonds.

The geometry evaluation, coordination number, and determination of the symmetry of the nearest coordination environment around the Yb(III) ion were carried out based on the analysis of the position and intensity of the f-f transition bands in the diffuse reflectance (DR) spectra of the studied compounds.

In Fig. 4, as an example, the DR spectra of Yb(III) complexes with 2,7-dimethyl-octen-1-dione-3,5 are shown, while Table 2 lists the characteristics of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition for all synthesized complexes. In the DR spectra of all complexes, one $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition characteristic of the Yb(III) ion is observed, with a maximum in the range of 970–980 nm. At the same time, the overall appearance of the spectra for both monomeric and polymeric complexes is similar, indicating that polymerization does not affect the geometry and structure of the coordination polyhedron of the lanthanide. The slight difference in λ_{max} values is due to the geometric structure of the substituents in the β-diketonate ligands, which have different λ_{max} values for allowed π–π^* transitions in the near ultraviolet region (200–400 nm). For example, replacing a biphenyl substituent with an alkyl substituent causes a significant shift in the absorption maximum and broadening of spectral lines, which is due to different energy characteristics of the of the ligands being studied [10, 24].

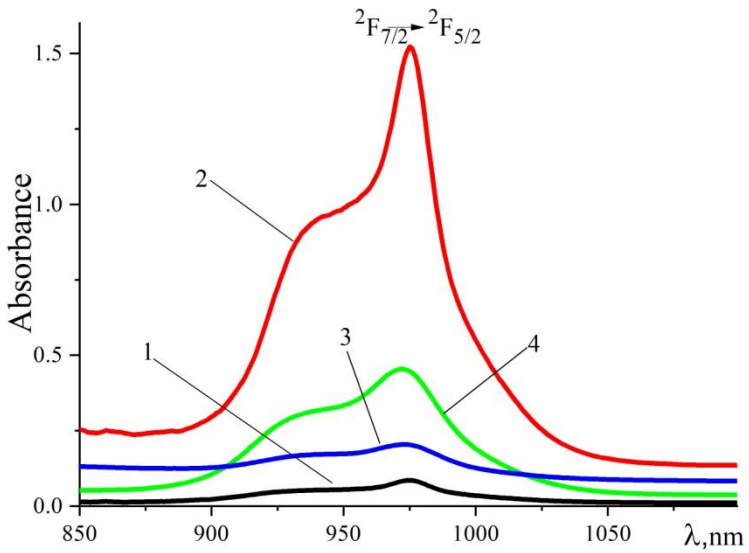


Fig. 4 – Diffuse reflection spectra of complexes$Yb(dmod)_3 \cdot 2H_2O$ (1), $Yb(dmod)_3 \cdot Phen$ (2), $[Yb(dmod)_3]_n$ (3), $[Yb(dmod)_3 \cdot Phen]_n$ (4) [24].

Table 2

Position of the maxima of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transitions in the DRS of Yb(III) complexes with unsaturated β-diketones

Complex	λ_{max}, nm	β	δ	$b^{1/2}$
$Yb(mphpd)_3 \cdot 3H_2O$	975	0,9945	0,5530	0,05244
$Yb(mphpd)_3 \cdot Phen$	978	0,9968	0,3210	0,04000
$Yb(mbphpd)_3 \cdot 2H_2O$	974	0,9957	0,4319	0,04637
$Yb(mbphpd)_3 \cdot Phen$	976	0,9941	0,5935	0,05431
$Yb(dmhpd)_3 \cdot 2H_2O$	973	0,998	0,2004	0,03162
$Yb(dmhpd)_3 \cdot Phen$	974	0,998	0,2004	0,03162
$Yb(dmod)_3 \cdot 2H_2O$	975	0,9951	0,4924	0,04950
$Yb(dmod)_3 \cdot Phen$	975.5	0,9969	0,3110	0,03937
$[Yb(mphpd)_3]_n$	971	0,9978	0,2205	0,03317
$[Yb(mphpd)_3 \cdot Phen]_n$	973	0,9962	0,3814	0,04359
$[Yb(dmhpd)_3]_n$	972	0,998	0,2004	0,03162
$[Yb(dmhpd)_3 \cdot Phen]_n$	973.5	0,997	0,3009	0,03873
$[Yb(dmod)_3]_n$	973	0,9978	0,2205	0,03317
$[Yb(dmod)_3 \cdot Phen]_n$	972	0,9947	0,5328	0,05148

It should be noted that for mixed-ligand phenanthroline complexes, regardless of the ligand, there is a slight (~30 cm^{-1}) bathochromic shift of the band maximum and a significant increase in absorption intensity. Probably, the N,N-donor ligand makes the structure of the complexes more rigid due to the axial distortion of the f-metal coordination site during the coordination of the Phen molecule with two nitrogen heteroatoms, providing effective shielding of the Yb^{3+} nucleus from external quenching compared to the original complexes without Phen.

However, in general, the shape and position of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition band for all ytterbium compounds are almost the same, which indicates a similar coordination environment of Yb(III) in all synthesized samples. At the same time, the absorption maxima for monocomplexes are close to λ_{max} of the aquated Yb_{aq3+} ion (973 nm), which indicates a close symmetry of the nearest coordination environment of the ytterbium ion in complexes and inorganic salts [30]. Thus, it can be assumed that the synthesized Yb(III) β-diketonates are characterized by C_{4v} symmetry, the lanthanide coordination number = 8, to which the coordination polyhedron corresponds is a deformed square antiprism.

For all synthesized compounds, the covalent bond parameters were calculated: the nepheloxetic parameter (β), the covalent parameter ($b_{1/2}$) and the Sinha parameter (δ) (Table 2). As can be seen from the data in Table 2, for all complexes the values of β are close to 1, which may indicate a high ionicity of the Yb–O bond [31]. The parameters $b_{1/2}$ and δ characterize the degree of covalent bond of the lanthanide with the donor ligand molecules. The largest values of $b_{1/2}$ are found in monomeric complexes, which also correspond to the largest values of δ, which indicates a smaller contribution of the covalent component to the Yb–O bond. During polymerization of the complexes, the values of $b_{1/2}$ decrease by almost 1.5 times, which indicates an increase in the covalent bond when transitioning from mononuclear to polymeric complexes. This is also confirmed by the values of the parameter δ: $\delta_{[Yb(\beta\text{-dik})3]n} < \delta_{Yb(\beta\text{-dik})3}$. The lowest values of covalence parameters are found in ligands with alkyl substituents (2,7-dimethyl-oct-1-en-3,5-dione, 2,6-dimethyl-hept-1-en-3,5-dione), which are structurally less bulky than β-diketones with phenyl substituents (2-methyl-5-phenylpent-1-en-3,5-dione, 2-methyl-5-biphenylpent-1-en-3,5-dione). Therefore, dmhpd/dmod easily "fit" to the central atom, while bulky mphpd/mbphpd molecules do not create additional shielding of the emitting centers and can form a more ionic bond with the central atom. Thus, a decrease in the parameter $b_{1/2}$ in the order mphpd> mbphpd>dmod>dmhpd indicates a decrease in the covalent contribution to the metal-ligand bond. It is clear that in the case of polymers, the contribution of the covalent componentis greater, which is due to the insignificant deformation of the coordination site due to the polymerization processes, while the structure and symmetry of the complexes do not under go major changes. Due to the weakening of the ionicity of the bond with increasing covalency, the intensity of the radiation can increase due to the decrease in the shielding of the emitting ion. However, this is not the only factor affecting the intensity of luminescence.

For all obtained Yb(III) complexes, a characteristic 4f-luminescence is observed in the near-IR region of the spectrum ($\lambda_{lum.}$ = 980–1015 nm, transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$).

An important condition for observing intense luminescence is the optimal energy gap between the triplet level of the ligand (E_T) and the resonance level of the lanthanide. To experimentally determine the energy of the triplet levels of β-diketones, the fluorescence spectra of Gd(III) complexes were studied, which were synthesized by a similar method as the Yb(III) complexes (Fig. 5, Table 3) [10].

Table 3.

Calculated energies of the triplet levels of the ligands.

Ligand	E_T (cm^{-1})	$\Delta E_T - E_{Yd(2F5/2),}$($cm^{-1}$)
dmhpd	19570	9370
$[dmhpd]_n$	19230	9030
dmod	19350	9150
$[dmod]_n$	18900	8700
mphpd	19490	9290
$[mphpd]_n$	20600	10400
mbhppd	21000	10800
$[mbhppd]_n$	20750	10550

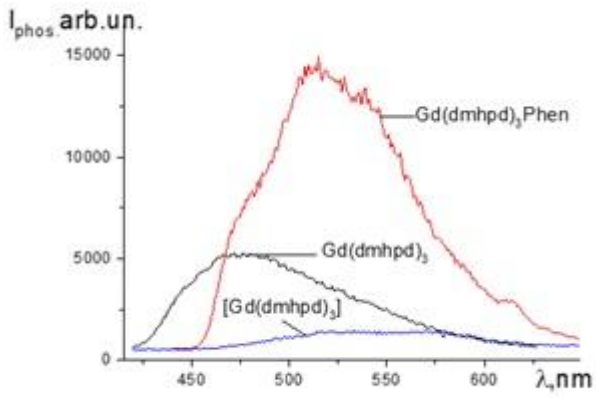


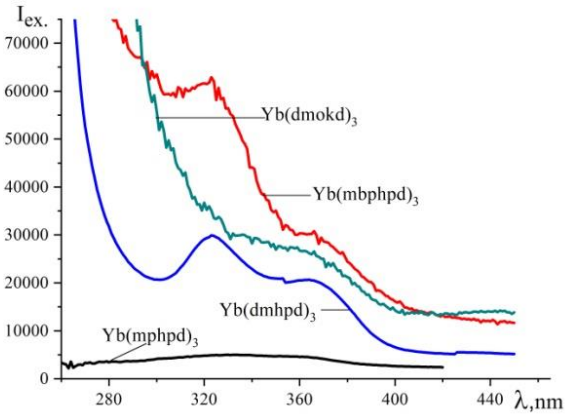
Fig. 5 – Phosphorescence spectra of some gadolinium complexes, T=77 K.

The calculated values of the triplet energy levels of the ligands and the width of the energy gap between the E_T of the ligands and the resonance $^2F_{5/2}$ level of Yb(III) (10330 cm^{-1}) show that in all cases, intramolecular energy transfer to the metal ion is fundamentally possible, which indicates the ability of the complexes to exhibit effective 4f-luminescence.

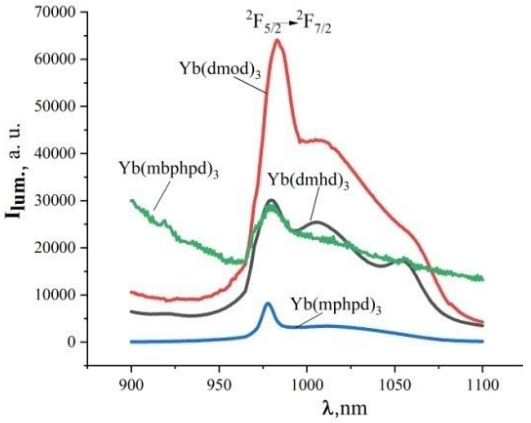
Fig. 6 (a, b, c) presents the excitation and luminescence spectra of ytterbium compounds with the studied β-diketones. The excitation spectra of the complexes (Fig. 6, a) are similar for all compounds regardless of the ligands and represent broad structured bands in the region of 230–410 nm, corresponding to the π-π* transitions of the β-diketonate fragment. The partial overlap of the ligand absorption spectra and the excitation spectra of the complexes indicates the sensitization of 4f-luminescence due to intramolecular energy transfer from the β-diketonate fragment to the ytterbium ion. Compared with the absorption of the organic ligand, the bands of the f-f transitions of Yb(III) are quite weak, which confirms the predominant sensitization due to the excitation of the ligand compared to the direct excitation of the lanthanide ion.

In the luminescence spectra of Yb(III) β-diketonates, the most intense is one band, which corresponds to the transition from the excited level $^2F_{5/2} \rightarrow {}^2F_{7/2}$ in the region λ_{max}= 978–985 nm. Table 5 shows the position of this band for all synthesized ytterbium complexes, and also the calculated integral intensities of luminescence of the samples. In addition to the narrow peak, a broad band at λ≈1000nm is observed in the spectra, which corresponds to optical transitions of an electron between the Stark sublevels of the ion and depends on the symmetry of the crystal field of the ligand. The difference in the shape of the spectral lines and the integrated intensity for different ligands can be due to both the different

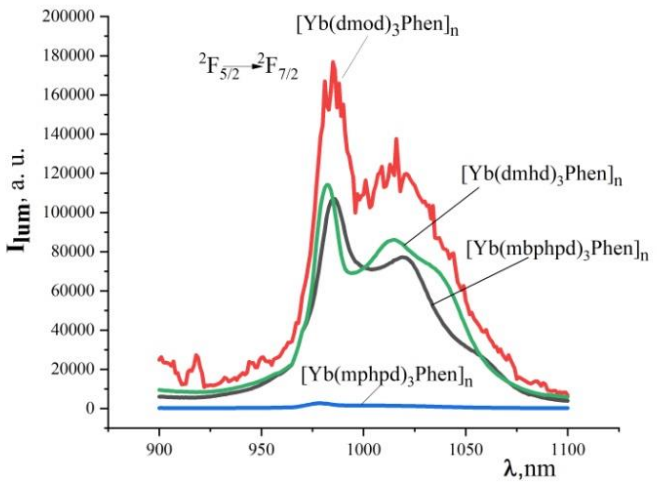
structure of the ligands and the screening of the emitting centers by phenyl substituents of aromatic β-diketones or phenanthroline. Thus, the maximum relative emission intensity is observed for complexes with dmod, which is up to ≈ 6 (for monomers) and ≈ 1.5 (for polymers) times higher than the relative intensity for complexes with other β-diketones, which can be explained by the positive effect of the additional methylene group of the hydrocarbon radical in dmod, which in a certain way weakens the bond of the Yb(III) ion with the ligand due to there distribution of the electron density in the molecule, and, presumably, contributes to a more efficient transfer of energy from the ligand to the metal.



a



b



c

Fig. 6 – Excitation (a) and luminescence (b, c) spectra of Yb(III) β-diketonates (λ_{em}.=365 nm, T=293K).

The minimum value of I_{lum} is exhibited by complexes based on methacroylacetophenone (Table 4), which maybe due to the structural features of the methacroylacetophenone molecule, namely, the screening of the emitting centers of the ytterbium ion by the aromatic-ring. The higher integral intensity of complexes based on mbphpd compared to mphpd could be explained by an antenna effect or stacking-stacking interactions in the biphenyl substituent.

Table 4.

Characteristics of luminescence spectra of complexes with unsaturated diketones.

Complex	λ_{lum}, nm	$I_{lum.}$ 10^{-4},a.u.	Complex	λ_{lum}, nm	$I_{lum.}$ 10^{-4},a.u.
$Yb(mphpd)_3 \cdot 3H_2O$	978	309580.54	$Yb(dmhpd)_3 \cdot 2H_2O$	980, 1005, 2054	1758376.24
$Yb(mphpd)_3 \cdot Phen$	978	1758712.35	$Yb(dmhpd)_3 \cdot Phen$	984	5416980.82
$[Yb(mphpd)_3]_n$	978	477261.68	$[Yb(dmhpd)_3]_n$	982	2076017.15
$[Yb(mphpd)_3 \cdot Phen]_n$	979, 1001, 1037	114618.03	$[Yb(dmhpd)_3 \cdot Phen]_n$	985,1020	5927269.72
$Yb(mbphpd)_3 \cdot 2H_2O$	980	514338.36	$Yb(dmod)_3 \cdot 2H_2O$	983	3348353.14
$Yb(mbphpd)_3 \cdot Phen$	982	5446747.50	$Yb(dmod)_3 \cdot Phen$	982	6284268.62
$[Yb(mbphpd)_3]_n$	981	529824.78	$[Yb(dmod)_3]_n$	985	2693542.02
$[Yb(mbphpd)_3 \cdot Phen]_n$	982, 1014, 1038	6367072.55	$[Yb(dmod)_3 \cdot Phen]_n$	981, 985, 987, 990	9429427.30

For the all studied complexes, the integral luminescence intensity of metallo polymers exceeds the luminescence of their monomeric analogues, which is due to the presence of a larger number of emitting centers in $[Yb(\beta\text{-}dik)_3]_n$ (Fig. 5, b, c). In addition, the higher luminescence intensity of polymeric metal complexes enhanced with monomeric ones may be due to an increase in the molecular weight of the metallopolymer, which, in turn, contributes to a decrease in exchange interactions between lanthanide ions, and, consequently, to a decrease in energy loss, and also contributes to a more efficient transfer of energy from the molecular levels of the polymer to the resonance level of Yb(III).

The highest luminescence intensity is observed in the mixed ligand complexes, regardless of the β-diketonate ligand. Thus, for monomeric dimethyloctene and dimethylheptene complexes I_{lum}. increases by 2 and 3 times, respectively, and for complexes with mphpd and mbphpd $I_{lum.}$ increases by 6 and 10 times, respectively. The tendency to increase the intensity of luminescence is also preserved for polymeric mixed-ligand compounds, with this value of $I_{lum.}$ individual monoligand polymers increases by up to 1.5 times. The exception is the complex with methacroylacetophenone, the luminescence of which decreases upon formation of a mixed-ligand polymer complex. The obtained data can be explained by two reasons, one of which is possibly due to the removal of OH oscillators from the inner sphere of the complexes, which quench the luminescence of the compounds [32]. On the

other hand, due to the additional coordination of the REE ion of the neutral phenanthroline ligand, intramolecular energy transfer occurs from Phen to β-dik, after E_T(β-dic)<E_T(Phen) (E_T(Phen) = 21480 cm^{-1}), which only leads to an additional antenna effect.

As can be seen from Fig. 5c, for the homopolymer $[Yb(dmod)_3 \cdot Phen]_n$, a broadening and splitting of the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition line into 4 components at 981, 985, 987, and 990 nm is observed. Such splitting indicates the presence of several emitting centers. This may be due to the formation of complexes with different degrees of polymerization. It is known that compounds with long alkyl substituents polymerize with a low degree of conversion, which is due to the transfer of the chain to the monomer, therefore, during polymerization, several polymer compounds of different molecular weights and, accordingly, different optical properties can be formed.

Summarizing the data of the luminescent properties of Yb(III) complexes with unsaturated β-diketones, we can draw the following conclusions (Fig. 7):

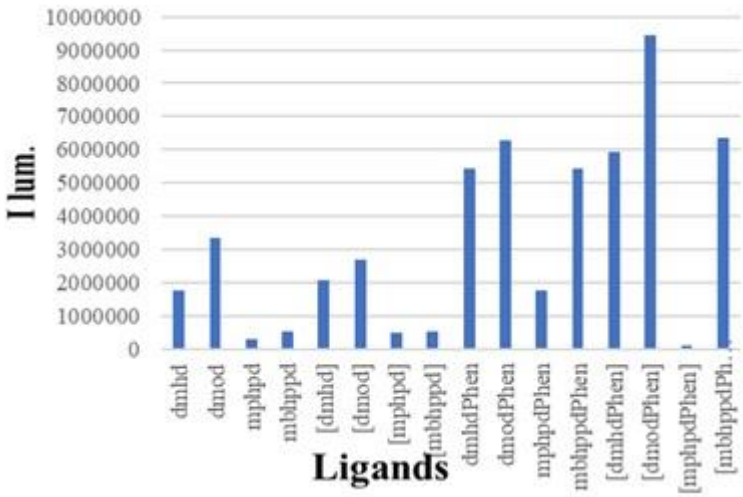


Fig. 7 – Diagram of the change of integral intensity of luminescence inYb(III) β-diketonates depending on the nature of the substituents in the ligands molecules.

• the intensity and efficiency of luminescence directly depend of the nature of the substituents in the ligand molecules (aliphatic substituents in the α-position contribute to more efficient emission in the near-IR range than aryl ones) and increase in the order dmod> dmhpd>mbphpd>mphpd;

• the luminescence intensity of Yb(III) complexes with phenanthroline for all synthesized compounds is higher than for monoligand complexes, which is due to the leveling of the gassing action of water molecules and additional energy transfer and luminescence sensitization;

• the luminescence intensity of metallopolymers is higher than that of monomeric complexes. Not a very significant difference in the integral intensity of luminescence between monomeric and polymeric samples maybe due to the complex structure of ytterbium (III)

β-diketonate complexes, which prevents the production of polymers with high molecular weight;

• the change in the luminescent properties of Yb(III) β-diketonates occurs in the following series: $Yb(\beta\text{-dik})_3 \cdot 2H_2O < [Yb(\beta\text{-dik})_3]_n < Yb(\beta\text{-dik})_3 \cdot Phen < [Yb(\beta\text{-dik})_3 \cdot Phen]_n$, β-dik: mphpd<mbphpd<dmhpd<dmod.

According to the obtained data for the studied Yb(III) complexes with unsaturated β-diketones, the following excitation and energy transfer scheme can be proposed (Fig. 8)

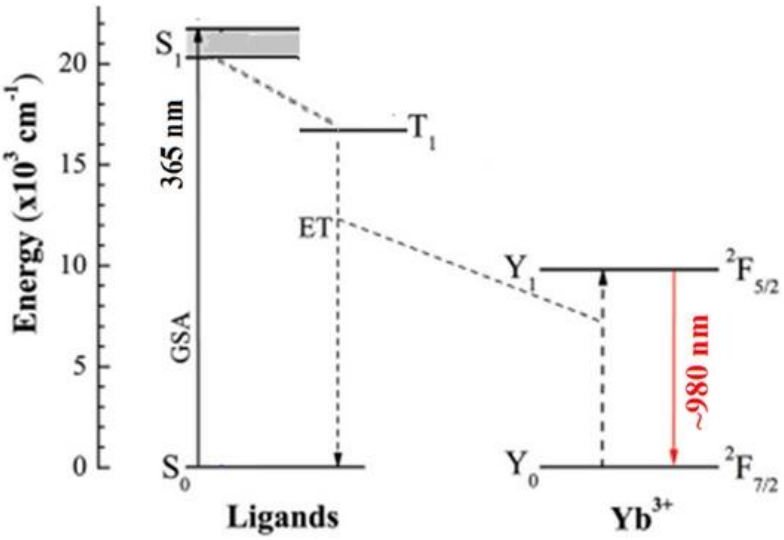


Fig. 8 – Scheme of energy transfer from an organic ligand to the Yb(III) (GSA – ground state absorption).

As calculated above, there is a significant energy gap between the triplet state of the ligand and the excited state of the ytterbium (III) ion. In addition, for Yb^{3+} ions, the $^2F_{5/2}$ fluorescence level lies ~10,000 cm^{-1} above the $^2F_{7/2}$ ground state, which in this case allows us to speak about vibronic interaction or the mechanism of internal electrontransfer from the ligand to the metal [33]. We propose that the energy transfer from the ligand triplet state to the excited level of Yb^{3+}, facilitated by vibronic coupling, accounts for the population of the Yb^{3+} excited state, which can then relax radiatively to the ground state by emitting photons at approximately 980 nm. This indicates an effective antenna effect, since the excitation energy photogenerated inorganic ligands is quickly transferred to the Yb^{3+} nucleus. The type of β-diketone mainly affects the intensity of absorption and emission.

CONCLUSIONS. Monomeric, mixed-ligand and polymeric complexes of ytterbium (III) with β-diketonate ligands with alkyl and aryl substituents were synthesized and studied. It was established that the Yb(III) ion forms triscomplexes with β-diketonate ligands of the general formula $Yb(\beta\text{-dik})_3 \cdot 2H_2O$, the coordination sphere in monoligand complexes is supplemented by 2 water molecules, the coordination number of the lanthanide = 8,

the coordination polyhedron is a square antiprism. Yb(III) β-diketonates easily attach a donor ligand (phenanthroline), which displaces H_2O molecules (OH-oscillators) due to the formation of stronger bonds with the central ion. Replacing water molecules with a phenanthroline molecule does not affect the structure of the coordination polyhedron, but causes only its slight deformation, which is reflected in the covalence parameters (increasing the covalence of the bond). The polymerization process also does not significantly affect the structure of the elementary unit, there is only a slight distortion of the coordination polyhedron. The thermal stability of the synthesized complexes increases from monoligand monomeric compounds to mixed-ligand polymers, which can be explained by the formation of compounds with a more rigid structure and a system of branched chemical bonds.

The study of luminescent characteristics showed that the integral intensity of luminescence varies in the series: dmod>dmhpd>mbphpd>mphpd and monomer-polymer-MLC-MLC polymer. The best luminescent characteristics are possessed by the ytterbium complex based on dmod. A significant increase in the luminescent properties of the synthesized complexes occurs when obtaining mixed ligand complexes with phenanthroline, which is primarily associated with solving the problem of the quenching effect of water molecules. Also, a noticeable increase in I_{lum} occurs when synthesizing MLC polymers. The preparation of such compounds is of practical importance, since it is easy to obtain film materials from polymer samples. Thus, the conducted studies of Yb(III) β-diketonate complexes may hold promise for practical applications as precursors of luminescent materials.

The work was financially supported by the National Academy of Sciences of Ukraine within the framework of the state budget topic 322E «Creation of new hybrid, composite and polymeric materials doped with coordination compounds of 3d- and 4f-metals based on β-diketonate and carboxylate acyclic ligands» (state registration number 0122U001299).

ПОРІВНЯЛЬНА ХАРАКТЕРИСТИКА СПЕКТРАЛЬНО-ЛЮМІНЕСЦЕНТНИХ ВЛАСТИВОСТЕЙ КОМПЛЕКСІВ Yb(III) З НЕНАСИЧЕНИМИ β-ДИКЕТОНАМИ

Н. Б. Іваха[1,2]*, О. С. Бережницька[1,2]

[1]Інститут загальної та неорганічної хімії ім. В. І. Вернадського НАН України, просп. Академіка Палладіна, 32/34, Київ 03142, Україна;
[2]Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського», просп. Берестейський, 37, Київ 03056, Україна
e-mail: ivakhanadiia@gmail.com

У роботі проведено порівняльний аналіз спектрально-люмінесцентних властивостей синтезованих координаційних β-дикетонатних комплексів ітербію з такими лігандами: 2,7-диметил-октен-1-діоном-3,5, 2,6-диметил-гептен-1-діоном-3,5, 2-метил-5-фенілпентен-1-3,5-діоном, 2-метил-5-бі-фенілпентен-1-3,5-діоном. Крім цього проведено дослідження полімерних сполук на основі представлених комплексів та їхніх

фенантролінових змішанолігандних похідних.

За допомогою низки фізико-хімічних методів аналізу встановлено, що будова елементарної ланки при полімеризації, а також координаційна сфера комплексів при утворенні змішанолігандних сполук не зазнає суттєвих змін порівняно з вихідними молекулами β-дикетонатів. Термічний аналіз показав значне підвищення температури початку розкладання змішанолігандних і металополімерних сполук відносно їхніх мономерних аналогів. Методом люмінесцентної спектроскопії встановлено, що досліджувані зразки проявляють люмінесценцію в ІЧ-діапазоні.

Порівняльний аналіз інтегральних інтенсивностей люмінесценції ітербієвих комплексів дозволив виявити ключові фактори впливу на емісійні характеристики. Насамперед це одержання змішанолігандних комплексів із фенантроліном, що дозволяє нівелювати негативний вплив одного з найбільш відомих чинників гасійної дії: ОН-осциляторів молекул води, яка доповнює координаційну сферу мономерних ітербієвих комплексів. Крім цього позитивно позначається на I_{lum}синтез полімерних сполук на основі β-дикетонатних комплексів, що може бути зумовлено зменшенням впливу концентраційного гасіння, оскільки у полімерах випромінювальні центри рівномірно розподілені по ланцюгу макромолекули.Такий підхід, окрім прямого позитивного впливу на люмінесцентні властивості, має на меті вирішення питання прикладного застосування синтезованих сполук, оскільки полімери значно легше піддаються переробленню та можуть утворювати плівкові матеріали.

Загалом на основі проведених досліджень можна сформувати такі залежності інтенсивності люмінесценції: dmod> dmhpd>mbphpd>mphpd та мономер-полімер-ЗЛК-ЗЛК-полімер. Як видно з цих даних, найкращими емісійними характеристиками володіють ітербієві змішанолігандні моно- та полікомплекси з β-дикетонами з алкільними замісниками.

Ключові слова: ітербій, комплекс, люмінесценція, β-дикетони, полімери.

REFERENCES

1. Nehra K., Dalal A., Hooda A., Bhagwan S., Saini R. K., Mari B., Kumar S., Singh D. Lanthanides β-diketonate complexes as energy-efficient emissive materials: A review. *Journal of Molecular Structure*. 2022. **1249:** 131531. https://doi.org/10.1016/j.molstruc.2021.131531.
2. Ning Y., Zhu M., Zhang J.-L. Near-infrared (NIR) lanthanide molecular probes for bioimaging and biosensing. *Coord. Chem. Rev.* 2019. **399**. https://doi.org/10.1016/j.ccr.2019.213028.
3. Cao J., Zhang R., Chen L., Wang D., Wang W., Tan E., Meng X., Xiu H., Wang L., Yang X., Yang Z., Yang Q., Zhao L. Design strategies and applications of responsive metal-based luminescence probes in the bioanalysis. *TrAC Trends in Analytical Chemistry*. 2023. **168**: 117338. https://doi.org/10.1016/j.trac.2023.117338.
4. Cheng P. Chapter 8 - Lanthanides in biosensing. In: Cheng P., editor. *Lanthanides*. Elsevier. 2023. 409–540. https://doi.org/10.1016/B978-0-12-822250-8.00008-4.
5. Cheng P. Chapter 9 - Lanthanides in bioimaging. In: Cheng P., editor. *Lanthanides*. Elsevier. 2023. 541–647. https://doi.org/10.1016/B978-0-12-822250-8.00009-6.

6. Dalal A., Nehra K., Hooda A., Singh D., Kumar P., Kumar S., Malik R. S., Rathi B. Luminous lanthanide diketonates: Review on synthesis and optoelectronic characterizations. *Inorganica Chimica Acta*. 2023. **550:**121406. https://doi.org/10.1016/j.ica.2023.121406.
7. Sun Z., Sun L. Chapter 337 – Rare-earth upconversion luminescence and its applications: from molecular to nano and micro scales. In: Bünzli J.-C. G., Kauzlarich S. M., editors. *Handbook on the Physics and Chemistry of Rare Earths*. 2024. **65**. 1–33. https://doi.org/10.1016/bs.hpcre.2024.03.001.
8. Balmus D. Novel stable ytterbium acetylacetonate–quinaldinate complexes as single-molecule magnets and surprisingly efficient luminophores. *Dalton Transactions***.** 2023. https://doi.org/10.1039/D3DT03253A
9. Fan, W.; Wang, H.; Huang, X.; Shi, T.; Du, J.; Xu, H. B. Energy transfer process, luminescence optimizing and various applications of lanthanide complexes. *Chem. Synth.* 2024, **4**, 12. http://dx.doi.org/10.20517/cs.2023.35
10. Berezhnytska O., Horbenko A., Savchenko I., Rohovtsov O., Rusakova N., Trunova O. Investigation of coordination compounds of Gadolinium (III) with β-diketones. *Chem. Chem. Technol.* 2023. **17**(4): 748–757. https://doi.org/10.23939/chcht17.04.748
11. Su L., Liu X., Niua Q., Li G. Photoresponsive lanthanide luminescent materials *J. Mater. Chem. C***.** 2024. **12**: 10759–10774. https://doi.org/10.1039/D4TC01353K
12. Ahmed Z., Mahiya K., Iftikhar K. Synthesis, crystal structure, NMR and near infra-red luminescence studies of nine-coordinate Nd and Yb complexes based on fluorinated β-diketone and a tridentate antenna chromophore, 2, 4, 6-Tris-(2-pyridyl)-s-triazine. *Inorganica Chimica Acta*. 2022. 541: 121086. https://doi.org/10.1016/j.ica.2022.121086.
13. Bhat, S. A., Hasan, N., Zargar, R. A., Wankar, S., Rawat, J. Evidencingthe NIR luminescence and longer lifetime from ytterbium complex constructed from perfluorinated β-diketone and heteroatom based ancillary ligand. *Journal of Molecular Structure*. 2024. **1299**: 137016. https://doi.org/10.1016/j.molstruc.2023.137016
14. Hasegawa M., Ohmagari H., Tanaka H., Machid K. Luminescence of lanthanide complexes: From fundamental to prospective approaches related to water- and molecular-stimuli. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. 2022. **50:** (100484). doi.org/10.1016/j.jphotochemrev.2022.100484
15. Brito-Santos G., Gil-Hernández B., Martín I. R., Guerrero-Lemus R., Sanchiz J. Visible and NIR emitting Yb (III) and Er (III) complexes sensitized by β-diketonates and phenanthroline derivatives. *RSC advances*. 2020. **10**(46): 27815–27823. https://doi.org/10.1039/D0RA05539E
16. Santos H. P., Gomes E. S., dos Santos M. V., D'Oliveira K. A., Cuin A., Martins J. S., Quirino W. G., Marques L. F. Synthesis, structures and spectroscopy of three new lanthanide β-diketonate complexes with 4,4′-dimethyl-2,2′-bipyridine. Near-infrared electroluminescence of ytterbium(III) complex in OLED. *Inorganica Chimica Acta*. 2019. **484**: 60–68. https://doi.org/10.1016/j.ica.2018.09.030.
17. Ning Y., Tang J., Liu Y., Jing J., Sun Y., Zhang J. Highly luminescent, biocompatible ytterbium(III) complexes as near-infrared fluorophores for living cell imaging. *Chem. Sci***.** 2018. **9:** 3742–3753. https://doi.org/10.1039/C8SC00259B
18. Staszak K., Wieszczycka K., Marturano V., Tylkowski B. Lanthanides complexes – Chiral sensing of biomolecules. *Coordination Chemistry Reviews*. 2019. **397:** 76–90. https://doi.org/10.1016/j.ccr.2019.06.017.
19. Dasari S., Singh S., Kumar P., Sivakumar S., Patra A. K. (). Near-infrared excited cooperative up conversion in luminescent Ytterbium (III) bioprobes as light-responsive the ranosticagents. *European Journal of Medicinal Chemistry*. 2019. **163**: 546–559.

https://doi.org/10.1016/j.ejmech.2018.12.010,
20. Fan S., Yao X., Li J., Li W., Li G. Near-infrared luminescent materials: From β-diketonate ytterbium complexes to β-diketonate-ytterbium-complex@PMMA thin film. *Journal of Luminescence*. 2018. **203**. 473–480. https://doi.org/10.1016/j.jlumin.2018.07.003.
21. Yang D., Li H., Li H. Recent advances in the luminescent polymers containing lanthanide complexes. *Coord. Chem. Rev*. 2024. **514:** 215875. https://doi.org/10.1016/j.ccr.2024.215875
22. Zhang Z., Yu C., Liu L., Li H., He Y., Lü X., ... & Jones R.A. Efficient near-infrared (NIR) luminescent PMMA-supported hybrid materials doped with tris-β-diketonate Ln^{3+} complex (Ln= Nd or Yb). *Journal of Photochemistry and Photobiology A: Chemistry*. **2016**. 314: 104–113. https://doi.org/10.1016/j.jphotochem.2015.08.022
23. Ivakha N., Berezhnytska O., Rohovtsov O., Rusakova N., Trunova O. Mono- andmixed-ligand complexes of Yb(III) with new β-diketones. *Ukrainian Chemistry Journal*. 2021. **87**(2): 65–76. https://doi.org/10.33609/2708-129X.87.02.2021.65-76
24. Ivakha N., Berezhnytska O., Rohovtsov O., Trunova O., Smola S. Investigation of new polymer complexes based on Yb (III) β-diketonates. *Ukrainian Chemistry Journal*. 2022. **88**(5): 3–14. https://doi.org/10.33609/2708-129X.88.05.2022.3-14
25. Berezhnytska O., Savchenko I., Ivakha N., Trunova O., Rusakova N., Smola S., Rogovtsov O. Synthesis, characterization, and luminescent properties of polymer complexes of Nd (III) with β-dicarbonyl ligands. *Nanoscale Research Letters*. 2017. **12**: 1–8. https://doi.org/10.1186/s11671-017-2074-0
26. Savchenko I., Berezhnytska O., Fedorov Ya., Smola S., Trunova O. Luminescent properties of new polymer metal complexes based β-diketones and REE. *Molecular Crystals and Liquid Crystals,* 2018. **673**(1): 48–60. https://doi.org/10.1080/15421406.2019.1578493
27. Ivakha N.B., Berezhnytska O.S., Rohovtsov O.O., Trunova O.K. Complexes of Nd(III) and Er(III) with novel unsutaratedβ-diketones. *Ukr. Chem. J*. 2019. **85** (6): 87–96. [in Ukrainian] https://doi.org/10.33609/0041-6045.85.6.2019.87-96
28. Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 2009, Sixth Edition, Part B, Wiley, Hoboken, New Jersey.
29. Larkin P. *Infrared and Raman spectroscopy: principles and spectral interpretation*. 2017 Elsevier. Amsterdam.
30. Kofod N., Nawrocki P., Platas-Iglesias C., &Sørensen T. J. Electronic structure of ytterbium (III) solvates – a combined spectroscopic and theoretical study. *Inorganic chemistry*. 2021. **60**(10): 7453–7464. https://doi.org/10.1021/acs.inorgchem.1c00743
31. Yatsimirskii K.B., Davidenko N.K. Absorption spectra and structure of lanthanide coordination compounds in solution. *Coordination Chemistry Reviews*. 1979. **27**(3): 223–273. https://doi.org/10.1016/S0010-8545(00)82068-8
32. daSilva P.S.P., Martín-Ramos P., Silva M.R., Lavín V., Chamorro-Posada P., Martín-Gil J. X-ray analysis, molecular modeling and NIR-luminescence of erbium (III) 2, 4-octanedionate complexes with N,N-donors. *Polyhedron*. 2014. **81**: 485–492. https://doi.org/10.1016/j.poly.2014.07.006
33. Martín-Ramos P., da Silva P. S. P., Lavín V., Martín I. R., Lahoz F., Chamorro-Posada P., ... & Martin-Gil J. Structure and NIR-luminescence of ytterbium (III) beta-diketonate complexes with 5-nitro-1, 10-phenanthroline ancillary ligand: assessment of chain length and fluorination impact. *Dalton Transactions*. 2013. **42**(37): 13516–13526. https://doi.org/10.1039/C3DT51376A

Стаття надійшла 27.05.2024.