

INVESTIGATION OF NEW POLYMER COMPLEXES BASED ON Yb(III) β -DIKETONATES

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The metal polymers based on mono- and heteroligand β -diketonate complexes of Yb(III) with 2,7-dimethyl-octen-1-dione-3,5, 2,6-dimethyl-heptene-1-dione-3, 5 and with phenanthroline was synthesized. It has been defined that the coordination environment of the central ion remains unchanged during radical polymerization. The shape and position of the bands in the electronic absorption spectra are similar to the corresponding monomeric β -diketonate metal complexes, and slight shifts indicate deformation of the elementary unit of the metal polymer during the formation of the polymer chain. It is shown that the polymerization process lead to an increasing in the thermal stability of polymer complexes in comparison with monomeric analogues. An increase in the emission of metal polymers in comparison with monomeric complexes was established by the method of luminescent spectroscopy, which is due to energy, steric, and structural-mechanical factors.

Keywords: unsaturated β -diketones, complexes, ytterbium, polymerization, luminescence.

INTRODUCTION. In the modern world, it is difficult to overestimate the role of polymeric materials in industrial production and it is almost impossible to find industries where they are not used. However, the requirements for the characteristics of such materials are constantly growing, so the efforts of many scientists are aimed at searching for

and developing polymer compounds with fundamentally new or improved physical and chemical properties (thermal, conductive, magnetic, luminescent, etc.).

In this regard, directions for obtaining composite, hybrid materials, as well as organometallic compounds with improved characteristics are developing at an ultrafast pace

[1–5]. Common to these areas is that due to the combination of components of different nature in the compounds (as a rule, organic and inorganic parts), there is a significant improvement in the final characteristics of the synthesized materials due to the synergistic effect. This makes it possible to obtain a large number of new compounds, varying both their qualitative and quantitative composition over a wide range, depending on the requirements for such products.

The synthesis of organometallic compounds has been the most important direction in coordination chemistry for several decades. If ligands with a double bond, which can enter into polymerization reactions, are used as initial components, then this is also one of the ways to obtain polymeric materials [6, 7]. It is important to note that with this method of synthesis, all units will be interconnected by strong covalent bonds (unlike supramolecular compounds), which will make it possible to evenly distribute the metal over the polymer matrix and expect an improvement in the performance of such a material.

Metal complexes acting as monomers during polymerization should have high thermal stability, solubility, and stability in organic solvents. In this regard, unsaturated β -diketonate complexes with metals of various nature (both 3d and 4f metals) are promising, on the basis of which both metal polymers and copolymers with predictable functional characteristics can be synthesized.

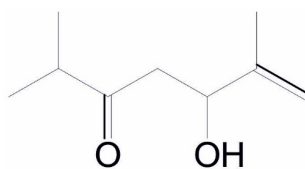
The most demanded today are materials with luminescent properties [8–10]. It is known that lanthanides often act as active centers in such compounds, which can emit both in the visible (Eu, Sm, Tb) and infrared (Nd, Er, Yb) regions. It is the last group that is

of the greatest interest, since it is the least studied, however, interest in such developments is constantly growing given their prospects in production (as components in optoelectronics, for the protection of securities, in the medical industry, etc.) [11–13].

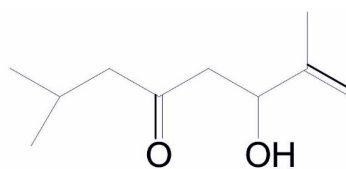
Since the use of monomeric luminescent materials is limited by a number of disadvantages (insufficient thermal stability, susceptibility to aggregation, difficulty in obtaining film materials), the synthesis and preparation of polymer compounds based on them seems even more reasonable, since it makes it possible to overcome them, and sometimes (for example, in the case of obtaining copolymers) also significantly reduce the cost of the process, without losing useful properties. In addition, an effective approach in the development of lanthanide-based luminescent compounds is the preparation of mixed-ligand β -diketonate systems, which becomes possible due to the high coordination capacity of the Ln(III) atom [14, 15].

Therefore, the purpose of this work is to obtain and study the physicochemical characteristics of new polymer compounds based on monomeric ytterbium β -diketonate complexes ($\text{Yb}(\text{dmhpd})_3 \cdot 2\text{H}_2\text{O}$, $\text{Yb}(\text{dmhpd})_3 \cdot \text{Phen}$, $\text{Yb}(\text{dmod})_3 \cdot 2\text{H}_2\text{O}$, $\text{Yb}(\text{dmod})_3 \cdot \text{Phen}$) as precursors of efficient luminescent materials.

EXPERIMENT AND DISCUSSION OF THE RESULTS. In the work, homopolymerization of the synthesized Yb(III) β -diketonate complexes was carried out by a radical mechanism according to the method [16]. Mono- and mixed-ligand complexes of Yb(I–II) with 2,7-dimethyl-octene-1-dione-3,5 and 2,6-dimethyl-heptene-1-dione-3,5 were used as starting materials (Fig. 1). The synthesis of complexes is described in [17].



2,6-dimethyl-heptene-1-dione-3,5 (Hdmhpd)



2,7-dimethyl-octene-1-dione-3,5 (Hdmod)

Figure 1. – Structure formulas and names of β -diketonate ligands.

Since the polymerization of β -diketonates of lanthanides occurs according to the same mechanism as the polymerization of vinyl monomers, azobisisobutyronitrile (AIBN) was used as the initiator of radical polymerization, and the polymerization temperature was 80°C.

The synthesized compounds were investigated by IR spectroscopy, diffuse reflectance spectra (DRS), thermogravimetry and luminescence analysis.

IR spectra were recorded on a Specord M80 spectrometer in the region of 400–4000 cm^{-1} in KBr tablets.

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

The hydrate composition of the synthesized compounds and their thermal stability were determined by the DTA method. Thermograms were recorded on a Q-1500 °D derivative of the F. Paulik, J. Paulik, L. Erdey

system in the temperature range of 20–500 °C with a heating rate of 5°C/min in a platinum crucible in the presence of a carrier (anhydrous Al_2O_3). The excitation and luminescence spectra of solid complexes were recorded on a Fluorolog FL 3–22 spectrofluorimeter, Horiba Jobin Yvon (Xe-lamp 450 W) using an OS 11 filter, followed by their correction taking into account the radiation distribution of the xenon lamp and the sensitivity of the photomultiplier. An InGaAs photoresistor (DSS-IGA020L, Electro-Optical Systems, Inc, USA, (cooled to liquid nitrogen temperature) was used as a radiation detector for the IR region.

In order to determine the method of coordination of ligands to the metal ion during the polymerization of Yb(III) complexes, studies were carried out by the method of IR spectroscopy. The results of the study of IR spectra are presented in Table 1, where, taking into account the literature data, the vibration bands were assigned [18].

Table 1. – Assignment of oscillation frequencies in IR spectra.

compound	$\nu(\text{Ln-O}) + \delta_{\text{ch.ring}}$	$\nu(\text{Ln-N})$	$\nu_{\text{as}}(\text{C}=\text{C})$	$\nu_{\text{s}}(\text{C}=\text{C})$	$\nu(\text{C=O})$	$\nu(\text{C=C})$
$[\text{Yb}(\text{dmhpd})_3]_n$	419, 426, 484, 511	–	1537	1578	–	1659w
$[\text{Yb}(\text{dmhpd})_3 \cdot \text{Phen}]_n$	417, 429, 475, 515	468	1535	1577	–	1653w
$[\text{Yb}(\text{dmod})_3]_n$	421, 435, 481, 511	–	1542	1581	–	166w
$[\text{Yb}(\text{dmod})_3 \cdot \text{Phen}]_n$	419, 439, 474, 518	465	1544	1584	–	1663w

The IR spectra of the investigated polymer compounds showed that the shape and position of the characteristic vibration bands are similar to those of the corresponding monomer complexes, i.e. they do not depend on the length of the hydrocarbon radical. The intensity of the bands is significantly lower, which is due to the increase in molecular weight and indirectly indicates the formation of a polymer structure. The C-O and C-C vibration bands undergo only a slight shift to the low-frequency region, but their position clearly indicates the bidentate-cyclic coordination of β -diketonate ligands to ytterbium [19]. It should be noted that the vibration band corresponding to the C=C double bond almost completely disappears in the case of polymer samples, which also indicates the polymerization of complexes. The presence of insignificant shoulders in this range indicates the remains of terminal double bonds in polymer molecules. Oscillation bands observed for the studied samples in the region of 400–600 cm⁻¹ indicate the presence of a metal-oxygen bond. Thus, confirming the invariance of the structure of the elementary links of the polymer molecule. It is difficult to draw conclusions about changes in the Yb-O bond based on the IR spectra, since in this range the sum of fluctuations of both the M-O bond and deformational vibrations of the chelate ring is observed [18]. However, it should

be noted that these bands are more ordered in the case of polymer monoligand complexes compared to their monomer counterparts, which may be due to a more strong structure of the polymer chain.

For polymers obtained on the basis of mixed ligand complexes, in addition to the above-mentioned vibration bands, we also observe a band corresponding to the Yb-N bond (465, 468 cm⁻¹). Its presence confirms that the hetero-ligand complexes (HLC) molecule is part of the elementary link of the polymer chain without undergoing changes in its structure.

In the region of 3200–3600 cm⁻¹ in the IR spectra of all synthesized ytterbium metallopolymers, there is a weak wide band of oscillations, which may indicate the presence of water in the samples. Presumably, this may be due to both the moisture content of the sample and the presence of water molecules in the voids of the metal polymer.

In order to identify the hydrate composition and thermal stability of the investigated compounds, analysis by DTA was carried out. The study of thermal destruction of metal-polymer samples is carried out not only for the purpose of obtaining new heat-resistant materials, but also to determine correlations between their structure and properties. The results of their study are given in table. 2.

Table 2. – Results of thermogravimetric analysis.

Compound	dehydration process		t _{start of decomposition} , °C
	t, °C / thermal effect	Δm , %	
[Yb(dmhpd) ₃] _n	124/ endo	2,1	325
[Yb(dmhpd) ₃ ·Phen] _n	131/ endo	1,6	371
[Yb(dmod) ₃] _n	135/ endo	1,8	343
[Yb(dmod) ₃ ·Phen] _n	134/ endo	1,5	358

Comparing the thermograms of polymer compounds with the corresponding thermograms of metal complexes, some differences can be noted. For all studied polymer samples in the temperature range of 110–150 °C, as well as for monomer complexes, we observe a loss of mass, but in the case of polymers, its value is insignificant ($\Delta m = 1.5\text{--}2.1\%$). This may indicate that water molecules are not included in the structure of the macromolecule. However, taking into account the rather high values of the dehydration temperature, we can conclude about the presence of occluded water, that is, water distributed in the cavities of the polymer molecule. Such a structure is caused by the polymerization process at low temperatures. Another feature of the thermal decomposition of metallopolymers is that the temperature of the start of destruction increases by 10–15 °C in the studied monoligand samples compared to their monomer counterparts [20]. For heteroligand polymers, the temperature of the beginning of the destruction of the structure of macromolecules is 358–371 °C, which indicates the greatest thermal stability among the studied systems. This can be explained by a decrease in the mobility of bonds in the polymer molecule with the formation of mesh structures. With increasing temperature, a wide exoeffect is observed on the thermograms of monoligand samples, which can be attributed to the destruction of the polymer chain. For mixed-ligand polymer compounds above 350 °C, a number of minor thermal effects are noted, which can be associated with both the rearrangement in the structure of the metallopolymer and the destruction of their macromolecules.

The process of thermal decomposition of Yb(III) metal polymers is similar for different

ligands, but comparing the thermograms of mono- and heteroligand samples, one should note an increase in the thermal stability of the latter.

Since the remains of the samples after thermolysis up to 500 °C are 48–54%, this may indicate the incomplete destruction of polymer molecules at a given temperature due to the progress of structuring reactions in parallel with the thermal decomposition reactions, and, consequently, the high thermal stability of the presented samples.

To determine the structure of the elementary unit of the metal polymer molecule, the synthesized compounds were studied by diffuse reflection spectroscopy. On the figure 2 have shown the diffusive reflectance spectra of dimethyloctenedione polymer complexes in comparison with their monomeric counterparts. In the near ultraviolet (200–400 nm) region (Fig. 2a), there are bands associated with $\pi \rightarrow \pi^*$ transitions. In this range, for the monomeric monoligand complex, an extended band ($\lambda_{\max} = 288\text{ nm}$) is observed, corresponding to electronic $\pi \rightarrow \pi^*$ transitions from the ground (S_0) to the excited state (S_1) of the ligand molecule.

For the polymer analogue of the Yb(III) complex, this band broadens and splits into two components ($\lambda_{\max} = 268\text{ and }290\text{ nm}$), which can be a confirmation of polymerization. As for the heteroligand compounds of ytterbium dimethyloctenedionate, this band is broadened, split and significantly shifted to the region of high energies ($\lambda_{\max} = 257\text{ and }347\text{ nm}$ for $[\text{Yb}(\text{dmokd})_3 \cdot \text{Phen}]_n$), which may be due to the overlap of the bands $\pi \rightarrow \pi^*$ transition and charge transfer bands from the ligand to the metal. The shape and position of this band for metal-polymer compounds also

confirms the formation of a polymer structure.

As is known, the electronic spectra of ytterbium compounds (Fig. 2b) are characterized

by one transition ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ of the Yb(III) ion from the ground state.

The maxima of these transitions for the studied metallopolymer are shown in Table 3.

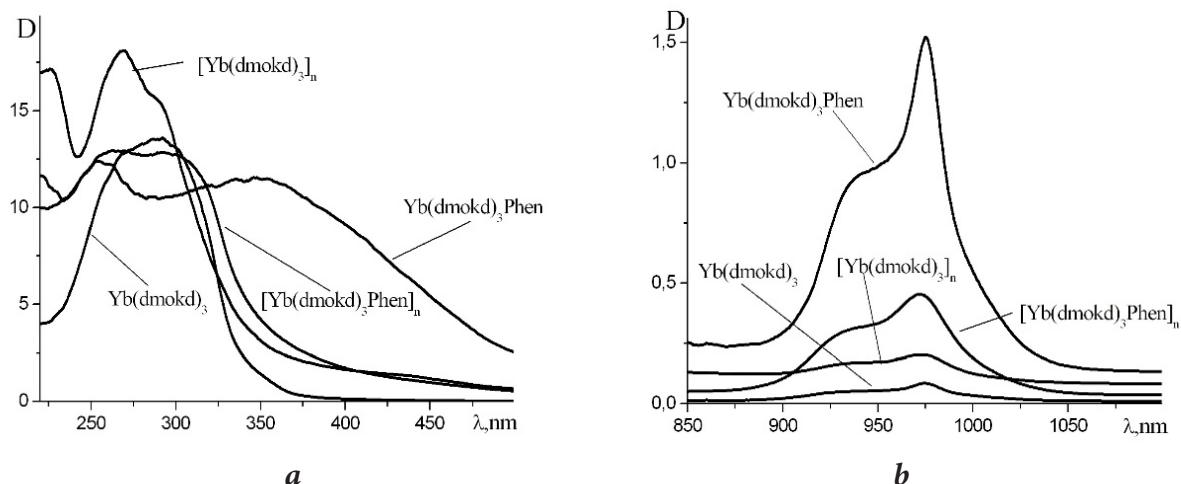


Figure 2. – DRS of mono- and polymer compounds of ytterbium(III).

Table 3. – Positions of transition maxima in the DRS of Yb(III) metallopolymer.

Compound	$\lambda_{\max}$, nm	Compound	$\lambda_{\max}$, nm
Yb(dmhpd) ₃ ·2H ₂ O	10270	Yb(dmokd) ₃ ·2H ₂ O	10255
[Yb(dmhpd) ₃ ·2H ₂ O] _n	10290	[Yb(dmokd) ₃ ·2H ₂ O] _n	10280
Yb(dmhpd) ₃ ·Phen	10265	Yb(dmokd) ₃ ·Phen	10250
[Yb(dmhpd) ₃ ·Phen] _n	10275	[Yb(dmokd) ₃ ·Phen] _n	10288

For all Yb(III) compounds, a slight shift of the band ($\sim 20\text{--}40\text{ cm}^{-1}$) to the short wavelength region is observed in comparison with monomeric metal complexes, which has a slight deformation of the polyhedron during polymerization and, probably, indicates an increase in the bond metal with a ligand. It should be noted that the shape and position of the bands in the DRS of ytterbium polymers practically do not differ from their monomeric counterparts, which indicates the same structure of the

molecule of the complex and the corresponding elementary units of the polymer chain. That is, the geometry and structure of the coordination polyhedron of the structural units of the macromolecule does not change during the polymerization of the complexes (Fig. 3). Thus, based on the results of the study and drawing an analogy with the previously studied metal complexes [20, 21], we can conclude that the coordination polyhedron of the polymer unit is a square antiprism:

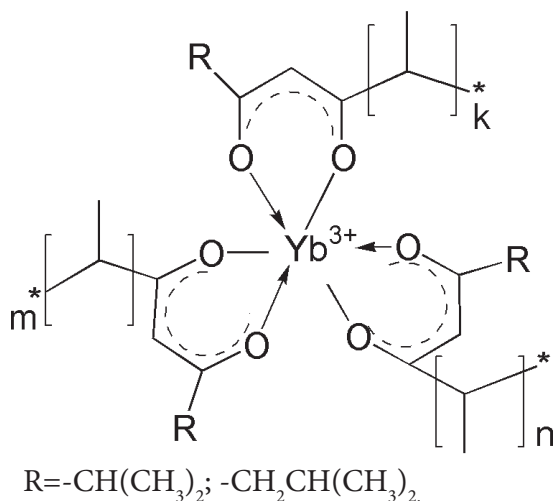


Figure 3. – Scheme of structure of Yb (III) poly-complexes.

Thus, according to the totality of the analyzes performed, it was found that the composition of the polymers corresponds to the formulas $[Yb(\beta\text{-dik})_3]_n$ and $[Yb(\beta\text{-dik})_3 \cdot \text{Phen}]_n$ ($\beta\text{-dik} = \text{dmhpd}, \text{dmod}$).

As is known, ytterbium complexes are capable of exhibiting 4-f luminescence in the near IR range. Regarding the information on the emission characteristics of polymers containing compounds Yb(III) in their composition, they usually concern materials obtained by metal intercalation into the polymer matrix of industrial monomers [22]. The number of works on the study of the luminescent properties of polymers, in which each metal ion is associated with the organic component by chemical bonds and is uniformly distributed in the macromolecule, is still limited. Of particular interest are the emission properties of the synthesized polymer compounds. In order to select metal complexes, precursors of luminescent materials, a comparative analysis of the luminescent characteristics of Yb(III)

monomeric and metal-polymer β -diketonate complexes was carried out.

To record the luminescence spectra of the synthesized compounds in the solid state, the excitation spectra of $[Yb(\text{dmhpd})_3]_n$ and $[Yb(\text{dmhpd})_3 \cdot \text{Phen}]_n$ were recorded. One band with a maximum at $\lambda_{\text{max}} = 365 \text{ nm}$ and 361 nm , respectively, is identified in the excitation spectra of the compounds under study. Excitation to the maxima of these $[Yb(\text{dmhpd})_3]_n$ and $[Yb(\text{dmhpd})_3 \cdot \text{Phen}]_n$ bands causes emission due to the transition of an electron from the triplet level of the ligand to the singlet level of the lanthanide ion.

In fig. 4 shows the luminescence spectra of polymer compounds of ytterbium with dimethylheptendione.

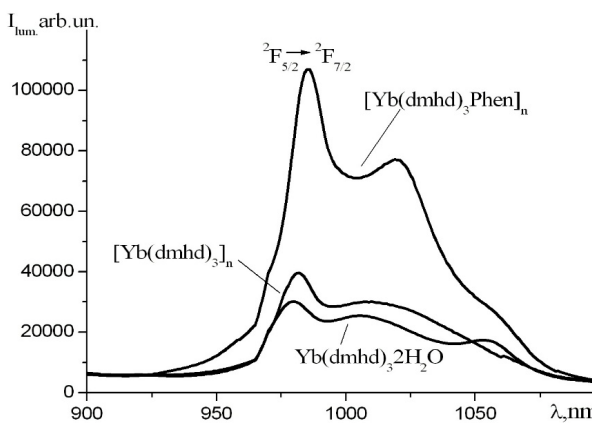


Figure 4. – Luminescence spectra of ytterbium polydimethylheptendionates.

It is known that the Yb(III) ion has one transition from the excited level $^2F_{5/2} \rightarrow ^2F_{7/2}$ ($\lambda_{\text{max}} = 981 \text{ nm}$ and 985 nm , respectively). The shape and position of the presented bands do not differ significantly. As can be seen from the figure, the relative emission intensity of $[Yb(\text{dmhpd})_3]_n$ is 1.5 times higher than the relative intensity of the monomer analogue

$\text{Yb}(\text{dmhpd})_3$. This is due to a decrease in concentration quenching and, as a result, non-radiative losses.

The emission intensity of mixed ligand complexes $[\text{Yb}(\text{dmhpd})_3 \cdot \text{Phen}]_n$ is 3–3.5 times higher than that of monoligand analogs $\text{Yb}(\text{dmhpd})_3 \cdot \text{Phen}$. This is due to the replacement of water molecules in the nearest coordination environment and the additional antenna effect of the phenanthroline molecule.

On fig. 5 shows the photoluminescence spectra of polymeric derivatives of dimethyloctenedione complexes ytterbium. The excitation of these samples $\lambda_{\text{exc}} = 361 \text{ nm}$ leads to intense 4-f radiation. The shape and position of the band maxima are similar to dimethylheptenedionates. As can be seen from the figure, the band is split into 2 components, and the maxima are observed at 984 and 985 nm for $[\text{Yb}(\text{dmod})_3]_n$ and $[\text{Yb}(\text{dmod})_3 \cdot \text{Phen}]_n$, respectively.

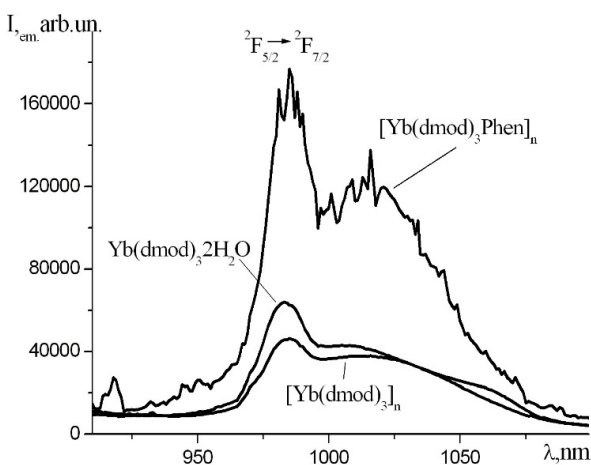


Figure 5. – Luminescence spectra of ytterbium polydimethyloctenedionates.

However, there is some difference in the properties of the complexes based on the given ligands of these systems. Thus, the rela-

tive emission intensity of the metallopolymer $[\text{Yb}(\text{dmod})_3]_n$ is 1.5 times less than that of the monomer. A comparative analysis of monomeric and metallopolymer complexes of ytterbium with different ligands indicates higher emission properties of compounds based on dimethyloctenedione, which is due to the longer length of the hydrocarbon radical and the increase in the covalency of the bond [20]. In addition, this may be due to the low degree of polymerization of dmhpd-based compounds due to rapid chain breakage, and, as a result, the formation of several oligomeric forms that will cause concentration quenching. This fact is confirmed by the half-width and splitting of the emission band.

It is known that the spectral lines have a certain width - the larger, the wider the gap. All spectra were recorded at the same slit width, except for $[\text{Yb}(\text{dmod})_3 \cdot \text{Phen}]_n$. It was possible to register a qualitative spectrum only with an increase in the width of the slit, which resulted in the expansion of the emission band and its significant splitting. In this case, the radiation intensity of $[\text{Yb}(\text{dmod})_3 \cdot \text{Phen}]_n$ is 3 times higher than the radiation intensity of $\text{Yb}(\text{dmod})_3 \cdot 2\text{H}_2\text{O}$. A significant antenna effect of the phenanthroline molecule due to additional energy transfer, luminescence sensitization, and the formation of a more strong structure of such compounds contribute to an increase in emission characteristics. It should also be noted that the addition of phenanthroline, which replaces H_2O molecules in the nearest coordination environment of the lanthanide ion, neutralizes the additional quenching effect of water molecules.

The studies performed have shown that the nature of the substituents in the ligand molecules and the length of the hydrocarbon ra-

dical have a significant effect on the emission properties of metal complexes.

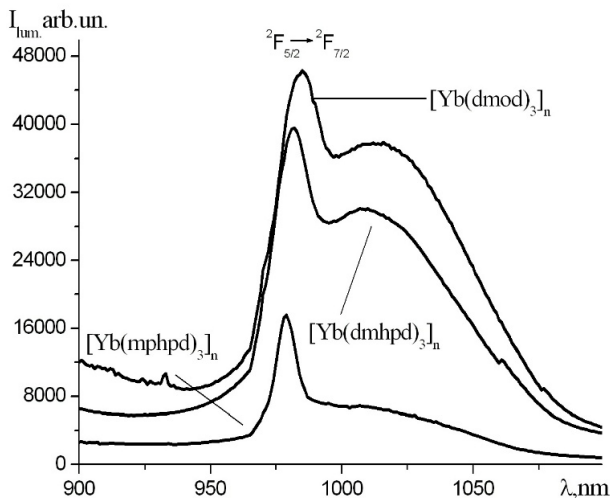


Figure 6. – Luminescence spectra of ytterbium metalopolymers.

Figure 6 shows the luminescence spectra of Yb(III) metal polymers with aromatic (mphpd) and aliphatic substituents. The maximum emission intensity is characteristic of the ytterbium metal polymer with dimethyloctenedione. The relative emission intensity of $[Yb(dmD)_3]_n$ is 2.2 and 2.7 times higher than the emission intensity of $[Yb(dmhpD)_3]_n$ and $[Yb(mphpd)_3]_n$, respectively. The large difference in the energy of the triplet level of the ligand and the resonance level of the lanthanide, the steric factor, and the shielding of the emitting ion by bulky ligand molecules cause the low emission of complexes with aromatic substituents.

For heteroligand metal polymers with phenantroline (Fig. 7), this dependence is more noticeable. In this case, a similar dependence is observed: the relative intensity of the luminescence of the HLC increases in the series: $[Yb(mphpd)_3 \cdot Phen]_n < [Yb(dmhpD)_3 \cdot Phen]_n < [Yb(dmD)_3 \cdot Phen]_n$.

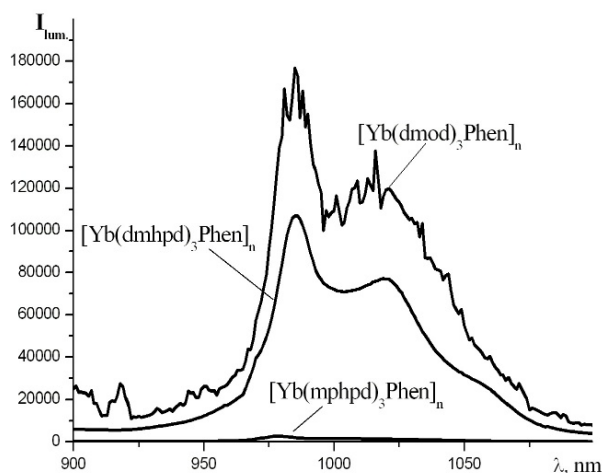


Figure 7. – Luminescence spectra of heteroligand ytterbium metal polymers.

Based on the data of luminescent analysis, it can be concluded that heteroligand polymer complexes based on β -diketones with aliphatic substituents can be the most effective precursors of luminescent materials emitted in the NIR region. The use of their analogs with aromatic components is less reasonable, since bulky structural units shield the emitting centers, thus reducing the emission characteristics of the compounds.

CONCLUSIONS. In this work, for the first time, metalopolymer samples based on ytterbium (III) dimethylheptenedionate and dimethyloctenedionate, and polymer compounds of their heteroligand derivatives, were obtained by radical polymerization. Their structure, thermal and luminescent properties have been studied. It has been determined by DRS and IR spectroscopy that the structure of the elementary unit of the polymer chain of the obtained polycomplexes does not undergo significant changes during polymerization. The ligands are coordinated to the metal in a bidentate-cyclic manner, and the shape of the coordination

polyhedron corresponds to a square anti-prism. Thermogravimetric studies have shown a significant increase in the thermal stability of the studied compounds compared to their monomeric counterparts, which is associated with the formation of a more stable polymer structure with a system of branched bonds. At the same time, heteroligand metal polymers demonstrated the highest thermal stability. An analysis of the luminescent properties showed that all polymers exhibit effective IR luminescence, while its relative intensity varies in the series $[\text{Yb}(\text{dmhpd})_3]_n < [\text{Yb}(\text{dmod})_3]_n < [\text{Yb}(\text{dmhpd})_3 \cdot \text{Phen}]_n < [\text{Yb}(\text{dmod})_3 \cdot \text{Phen}]_n$. Comparison of the emission characteristics of the studied compounds with metal polymers based on methacrylacetophenoates and terbium showed that the use of aliphatic β -diketones with a linear structure as initial ligands in order to obtain mixed-ligand systems and polymeric materials on their basis seems to be the most promising. A high relative emission intensity is characteristic of heteroligand complexes; therefore, they can be proposed as precursors of luminescent materials.



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ДОСЛІДЖЕННЯ НОВИХ ПОЛІМЕРНИХ КОМПЛЕКСІВ НА ОСНОВІ β -ДИКЕТОНАТІВ Yb(III)

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Методом радикальної полімеризації одержано металополімери на основі моно- та змішанолігандних β -дикетонатних комплексів Yb(III) з 2,7-диметил-октен-1-діоном-3,5 та 2,6-диметил-гептен-1-діоном-3,5 та фенантроліном. За допомогою комплексу фізико-хімічних методів аналізу встановлено, що будова елементарної ланки не зазнає суттєвих змін порівняно з вихідними молекулами β -дикетонатів. Термічний аналіз показав значне підвищення температури початку розкладання металополімерних сполук відносно їхніх мономерних аналогів. Методом люмінесцентної спектроскопії встановлено, що досліджувані зразки проявляють інтенсивну ІЧ-люмінесценцію. Зростання емісійних властивостей металополімерів зумовлено зменшенням обмінних взаємодій за рахунок утворення впорядкованої структури, а у випадку змі-

шанолігандних сполук – унаслідок додаткового переносу енергії та сенсibilізації люмінесценції.

Ключові слова: ненасичені β -дикетони, комплекси, ітербій, полімеризація, люмінесценція.

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